

SYMPOSIUM F

Nano- and Microcrystalline Semiconductor Materials and Structures

November 27 – 30, 2000

Chairs

Philippe M. Fauchet

Dept of E&CE
Univ of Rochester
Computer Studies Bldg
Rochester, NY 14627-0231
716-275-4066

Jillian Buriak

Dept of Chemistry
Purdue Univ
1393 Brown Laboratories
West Lafayette, IN 47907-1393
765-494-5302

Leigh T. Canham

Nanotechnology Dept
DERA-Malvern
Worcestershire, WR14 3PS UNITED KINGDOM
44-1684-895007

Nobuyoshi Koshida

Div of Elec & Information Tech
Tokyo Univ of Agriculture & Tech
Faculty of Tech
Koganei Tokyo, 184-8588 JAPAN
81-42-388-7128

Bruce E. White

Digital DNA Laboratories
Motorola Inc
MD K20
Austin, TX 78721
512-933-2621

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* Invited paper

SESSION F1: SILICON QUANTUM DOT DEVICES I

Chair: Bruce E. White
Monday Morning, November 27, 2000
Constitution A (Sheraton)

NOTE EARLY START

8:15 AM INTRODUCTION

8:30 AM *F1.1

THE CMOS ROADMAP AND THE NEED FOR ALTERNATIVE SILICON-BASED DEVICES. James Hutchby and Victor Zhirnov, Semiconductor Research Corporation, Research Triangle Park, NC.

Silicon CMOS technology, the engine of the microelectronics industry for the past 30 years, is encountering fundamental physical and material barriers that will limit its continued voracious scaling within the next two decades. The 1999 International Technology Roadmap for Semiconductors (ITRS) recognized technical barriers having no known solutions that are on the five-to-ten year implementation horizon. Following a brief outline of these barriers and current approaches to their solution, this discussion will briefly consider alternative silicon-based approaches to sustaining the scaling of silicon technology for 2-3 additional generations. The discussion will conclude with an overview of candidate replacement technologies, with a focus on the potential role of nanocrystalline semiconductor materials and structures. In particular, research requirements in the basic physical sciences needed to sustain the progress in nanoelectronics will be addressed. Examples will include physics and chemistry of interfaces, conductivity at low dimensions, deterministic doping effects etc. to fine tune the electrical, optical, mechanical, and sensing properties of nanomaterials by precise compositional and size control.

9:00 AM F1.2

LAYERED TUNNEL BARRIERS FOR NANOCRYSTAL MEMORY APPLICATIONS. Julie D. Casperson, Harry A. Atwater, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA; L. Douglas Bell, Jet Propulsion Laboratory, Pasadena, CA.

Nonvolatile memories using silicon nanocrystal arrays as floating gates have potential performance advantages (e.g., retention time, gate stack thickness, scalability) over conventional flash memory devices. One of the main limitations of all floating gate devices are the long program ($\sim \mu s$) and erase times (~ 1 ms) achievable with a Fowler-Nordheim tunneling mechanism for charging the floating gate. An interesting alternative to homogeneous dielectric tunnel barriers is a silicon compatible "layered" tunnel barrier heterostructure, which enables a large decrease in the barrier height with applied voltage and thus holds potential for simultaneously achieving short write/erase times and long retention times. We have performed tunneling probability simulations for a layered tunnel barrier structure consisting of a 6 nm Si_3N_4 /6 nm Al_2O_3 /6 nm Si_3N_4 dielectric heterostructure with assumed conduction band offsets with respect to the Si conduction band of 2.0 eV and 3.4 eV for Si_3N_4 and Al_2O_3 respectively. For this structure, the tunneling probability varies much more rapidly with applied bias than for a homogeneous Al_2O_3 or SiO_2 barrier whose transport is dominated by Fowler-Nordheim tunneling. For example, with the new structure a change in bias from 2 V to 6 V yields a change in tunneling probability by 20 orders of magnitude. We have fabricated Al gate layered tunnel barrier MOS structures consisting of 6 nm Si_3N_4 /6 nm Al_2O_3 /6 nm Si_3N_4 , as well as homogeneous 6 nm Al_2O_3 barrier structures by reactive ion beam sputter deposition. A comparison of the current-voltage and capacitance-voltage properties of these structures with conventional SiO_2 tunnel dielectrics will be discussed.

9:15 AM F1.3

SILICON SINGLE ELECTRON TRANSISTORS WITH SINGLE AND MULTI DOT CHARACTERISTICS. A. Savin, A. Manninen, J. Kauranen, J. Pekola, Dept of Physics, Univ of Jyväskylä, Jyväskylä, FINLAND; M. Kamp, M. Emmerling, A. Forchel, Technische Physik, Univ Würzburg, Würzburg, GERMANY; M. Prunnila, J. Ahopelto, VTT Microelectronics Centre, Espoo, FINLAND.

Silicon single electron transistors (SET) with side gate have been fabricated on a silicon-on-insulator (SOI) substrate. The fabrication process utilized standard CMOS process steps, only the barrier constructions have been defined by e-beam lithography. The final dimensions of the devices were achieved by thermal oxidation. Samples prepared on one substrate and in one processing demonstrate two types of the characteristics: some of them demonstrate multi dot array behaviour and one demonstrates single island behaviour in a wide temperature range. I-V characteristics of all devices have Coulomb blockade region. SETs demonstrate oscillations of drain-source current and blockade voltage with change of gate voltage at least up to 100K. With increase of positive gate voltage the

maximum conductivity of the device increases and the value of blockade voltage decreases. Dynamic response of the SETs on a fast change of gate voltage has been investigated. At temperatures below 25K long-term oscillations (relaxation) of source-drain current after switching of gate voltage has been observed in both multi dot and single dot samples. Characteristic time of the process is about 10-30 min at 4.2K. With increase of the temperature the rate of the process increases (characteristic time decreases) and at $T > 25-30K$ there is no noticeable relaxation of the drain-source current after switching of the gate voltage. Telegraph noise has been observed in the definite range of source-drain and gate voltage: near to the edge of Coulomb blockade region and in the vicinity of the step on the current-voltage characteristic. Current switches between two states at fixed drain-source and gate voltage. The amplitude of the current oscillation is about 1.5pA. The drain-source voltage range within which noise is observed shifts with the change of the gate voltage.

9:30 AM *F1.4

LOCALIZATION, TUNNELING AND RESONANT PHENOMENA IN NANOCRYSTALLINE SILICON/SILICON DIOXIDE SUPERLATTICES. L. Tsybeskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY.

Vertical carrier transport in layered structures comprised of Si nanocrystals separated in the growth direction by angstrom-thick, tunnel transparent SiO_2 layers exhibits at low temperature conductivity fluctuations. Analysis of the fluctuation spectra shows a featureless, $1/f$ noise component coexisting with entirely unexpected, well-defined resonances. Performing measurements under resonant conditions, we observe giant self-oscillations in the conductivity and unique signatures of phase coherent carrier transport, including low ($\sim 10^{-3}$ T) magnetic field induced phasing of electron waves and negative magnetoresistance. We show that the resonant component of carrier transport in nanocrystalline Si superlattices (SLs) is solely governed by quantum interference between different paths of elastically scattered electron waves. This phase coherence in carrier transport can be destroyed by dynamic scattering due to the electron-phonon or electron-electron interaction. Using the technique of frequency resolved tunnel spectroscopy we observed and identified resonant transitions associated with hole tunneling via quantized states in nc-Si/ SiO_2 SLs. Under optimized conditions, negative differential resistance with a high peak-to-valley ratio and narrow resonance peaks were observed and identified.

SESSION F2: SILICON QUANTUM DOT DEVICES II

Chair: James A. Hutchby
Monday Morning, November 27, 2000
Constitution A (Sheraton)

10:30 AM *F2.1

SYNTHESIS AND CHARACTERIZATION OF AEROSOL SILICON NANOPARTICLE NONVOLATILE FLOATING GATE MEMORIES. Michele L. Ostraa¹, Richard C. Flagan¹, Harry A. Atwater², California Institute of Technology, ¹Dept. of Chemical Engineering, ²Dept. of Applied Physics, Pasadena, CA; Jan W. De Blauwe, Andreas Kerber, Gary Weber, Martin L. Green, Lucent Technologies, Murray Hill, NJ.

Silicon nanoparticle-based floating gate MOS field effect devices have potential for terabit/cm² density nonvolatile memory applications. We have fabricated nanoparticle memory devices in a conventional MOS ULSI process with channel lengths from 0.2-10 microns with a Si nanoparticle floating gate fabricated by aerosol deposition. SiO_2 passivated Si nanoparticles have been synthesized in an ultra-clean two-stage aerosol reactor that is interfaced to a 200 mm wafer deposition chamber in a class 100 cleanroom. We synthesize silicon nanoparticles by thermal decomposition of silane gas at 950°C to produce single crystal, nonagglomerated nanoparticles. The second reactor stage passivates the silicon particles with a thin thermal oxide grown at 1050°C. Particles are thermophoretically deposited onto 200 mm wafers with densities from 10^{13} particles/cm² at the wafer center to 10^{11} particles/cm² at the wafer edge in tens of minutes. We have fabricated floating gate memory devices in which the dielectric layer contains a discontinuous nanoparticle layer containing either (i) 2 - 4 nm crystalline core diameter with 1 nm thermal oxide; or (ii) 6 - 15 nm crystalline core diameter with 2 nm thermal oxide. Cross-sectional transmission electron microscopy verifies the presence of a silicon nanoparticle floating gate layer and indicates that no significant further oxidation of the nanoparticle core occurs during control gate oxide deposition. Aerosol nanoparticle floating gate devices exhibit normal transistor behavior and have promising nonvolatile device performance. Aerosol nanoparticle devices with 0.2 micron channel length exhibit threshold voltages $< 5V$ with large threshold voltage shifts (~ 2 V), submicrosecond program times and millisecond erase times. No degradation in program/erase threshold voltage swing was

seen during 100,000 program and erase cycles, although some threshold shift due to charge trapping was observed. The effect of nanoparticle size and density on memory characteristics as well as other aspects of electrical characterization will be discussed.

11:00 AM F2.2

CHARGE STORAGE MECHANISM IN NANO-CRYSTALLINE Si BASED SINGLE-ELECTRON MEMORIES. Bruce J. Hinds, Takayuki Yamanaka, Shigeo Hatatani, Shunri Oda, Tokyo Institute of Technology, Tokyo, JAPAN.

An ultimate goal in the scaling of memory devices is to have a single electron in a well defined location and energy state to act as a memory node, thus affecting the current transport in a proximate conduction channel. In particular, it is of interest whether the electron is delocalized over nc-Si dot or whether interfacial states with nc-Si play a dominant role in retention time. Studies of storage lifetimes of single dots involving the variation of temperature and applied potential are required to answer such questions. Remote Plasma Enhanced CVD is used to form 6nm diameter nc-Si dots in the gas phase from pulsed SiH₄ source. This easily scalable process is used to deposit dots over a decanano-scale transistor thus making a memory device. The 80 nm by 20 nm transistor channel is synthesized by E-beam lithography followed by reactive ion etching of thin (20nm) Silicon-on-Insulator (SOI). The small area of the narrow channel allows for the elimination of channel percolation paths around a screening charge. The density of nc-dots is such that statistically 1-3 dots are in the active region of transistor. This method allows a memory device that is sensitive to charge in a single nc-Si dot. A stored electron results in an observed threshold shift of 90 mV. This shift is expected for a 6nm diameter nc-Si dot over 30nm wide channel as calculated by Coulombic shift in channel surface potential. Stepwise increase in channel current shows the loss of several electrons from nc-Si dot. Lifetimes are seen to be 80-120 seconds for each electron at room temperature under bias conditions. Analysis of lifetime as a function of applied potential and temperature show Poisson distributions. Median lifetimes can be modeled by direct tunneling with influence of gate bias and dot size. Temperature dependence also shows that interface states are not the dominant mechanism for electron storage in this device structure.

11:15 AM F2.3

A MEMORY DEVICE UTILIZING RESONANT TUNNELING IN NANOCRYSTALLINE SILICON SUPERLATTICES. L. Montes, G.F. Grom, R. Krishnan, P.M. Fauchet, and L. Tsybeskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY; B.E. White Jr., Digital DNA Laboratories, Motorola Semiconductor Products Sector, Austin, TX.

A quantum structure based on Si/SiO₂ and fabricated using a standard Si technology has strong potential for applications in non-volatile and scaled dynamic memories. Among standard requirements such as long retention time and endurance, a structure utilizing resonant tunneling offers a lower bias operation and faster write/read cycle. In addition, degradation effects associated with Fowler-Nordheim hot electron tunneling can be avoided. In this paper we present definitive experimental observations of resonant carrier tunneling in nanocrystalline Si/SiO₂ superlattices and discuss its application in memory devices with artificially graded barriers between current channel and floating gate. The device properties and limitations including write/read time, "on/off" voltage operation, endurance, retention time and leakage dynamic will be discussed.

11:30 AM *F2.4

INVESTIGATIONS OF SILICON NANO-CRYSTAL FLOATING GATE MEMORIES. Arvind Kumar, J.J. Welser, Sandip Tiwari¹, F. Rana², and K. Chan, IBM T.J. Watson Research Center, Yorktown Height, NY; ¹School of Electrical Engineering, Cornell University, Ithaca, NY; ²Department of Electrical Engineering and Computer Science, MIT, Cambridge, MA.

As memory continues to be scaled to ever smaller dimensions, the floating-gate memory transistor, which offers a single-element storage cell, becomes more attractive. Typically, this structure has been reserved for nonvolatile applications, where the comparatively high voltages, slow write speeds, and limited cyclability could be tolerated. However, if the floating-gate, which is usually a continuous film of polysilicon, is replaced with a discontinuous film of small floating islands (nano-crystals), a new set of tradeoffs in these performance factors becomes possible, opening the door to broader applications. If these islands are further reduced to the point where Coulomb charging or energy quantization effects become relevant, it is possible to control the charge on the islands at a single (or few) electron level, which offers very low power operation and may enable new functionality. This abstract will discuss design and fabrication of these memories, experimental results on fabricated devices, and modeling of what could ultimately be achieved, as well as what limitations will ultimately be reached.

SESSION F3: POROUS SILICON I

Chair: Volker Lehmann
Monday Afternoon, November 27, 2000
Constitution A (Sheraton)

1:30 PM *F3.1

ANALYSIS OF PHYSICAL PROPERTIES OF NANO-STRUCTURED SEMICONDUCTORS VIA NOISE SPECTROSCOPY. Vitali P. Parkhutik, Alcoy School of Engineering, Technical University of Valencia, Alcoy, SPAIN.

Any signal acquired from a complex physical system contains a stochastic component (noise). It has been customary to consider the noise as an artifact of signal acquisition and there exist many tools for filtering it out: smoothing, FFT, etc. We assume that the noise can, in fact, be a source of information about the internal structure and properties of the system, non-equilibrium processes and phase transformations occurring at sub-microscopical level. Knowing how to acquire and process the noise allows one to understand the properties of complex systems. This paper will concentrate on the application of modern statistical theories (first of all - flicker-noise spectroscopy - FNS¹) to the analysis of physical properties of nanostructured semiconductors. The following issues will be considered:

- Classification of elementary events contributing to the noise. It is possible to decompose the noisy signal into elementary components (spikes, steps, their derivatives, etc) and evaluate a contribution of each particular component, thus obtaining knowledge on the structure of the noise;
- Determination of the degree of dynamic memory in a sequence of elementary events contributing into the noise. There exists a pronounced "memory" in the electrical noise in nano-scaled semiconductors, morphological features of surfaces containing imperfections (dots or holes), in their optical properties, etc. Degree of this memory depends on the properties of nanostructures.
- Studies of chaos-order transitions in a system of nano-structured semiconductors. The oscillations of physical properties of macrosystems are due to a synchronization of elementary processes involving their microscopical parts.
- Reproducibility of signals produced by micro-miniaturized devices containing an ensemble of nanostructured components.

Experimental data on electrical conductivity and morphology of porous Si will be used to illustrate the possibilities of analyzing the noise from nanostructured semiconductors. ¹V. Parkhutik, S. Timashev, J. Appl. Phys., 87, 7558 (2000).

2:00 PM F3.2

ELECTRICAL CONDUCTIVITY IN THE CRYSTALLITES OF POROUS SILICON DETERMINED BY AN IMPROVED COMPLEX IMPEDANCE ANALYSIS. Boudjemaa Remaki, Stephanie Perichon, Volodymyr Lysenko, Daniel Barbier, INSA de Lyon, Materials Physics Laboratory (LPM), Villeurbanne, FRANCE.

Porous silicon is a smart material with promising potentialities as a substrate for thermal and electromagnetic devices or an active layer in chemical sensors. However its electrical behavior is not well understood. We present an improved method for the determination of the parameters characterizing electrical transport in meso-porous silicon. Our approach is based on the analysis of separate contributions of the crystallites and their interconnections to the total impedance of the porous layer. We have used Al/SiO₂/porous-Si/Si structures. The samples were prepared on 0.02 Ω·cm p-type Silicon substrates. The SiO₂ layers were used as a protecting mask to avoid metallic contamination of the porous layers during the Al deposition step. Porous silicon samples of different thickness (5 to 100 μm) have been investigated by means of a complex impedance analysis. A wide frequency range from 100 Hz to 10 MHz was used allowing an accurate determination of the impedance components. Combined with thermal stimulation, these measurements provide a powerful tool for the interpretation of basic parameters such as the carrier density in the crystallites and the trap states. Our results can be interpreted in terms of electrically compensated crystallites with semi-insulating interconnections. Besides, the associated nanoscale mobility values differ from that of the porous layer, suggesting a strong individuality of the crystallites in the nano-structure network.

2:15 PM F3.3

ANALYSES OF BALLISTIC ELECTRON TRANSPORT IN NANOCRYSTALLINE POROUS SILICON. Akira Kojima, Xia Sheng, Nobuyoshi Koshida, Tokyo Univ. of A&T, Dept of Electrical and Electronic Engineering, Tokyo, JAPAN.

Nanocrystalline porous silicon (PS) diodes, composed of thin Au films, structure controlled PS layers, n-type Si substrates, and ohmic back contacts, efficiently emit ballistic electrons when positive bias voltages are applied to the Au electrode with respect to the substrate. The emission characteristics suggest that electrons injected into the PS layer from the substrate become ballistic under a high electric field. To confirm this hypothesis, we have investigated the temperature dependence of the energy distribution of emitted

electrons in a temperature range of 100 to 300 K. The energy distributions were measured by an ac-retarding-field method in an ultra-high vacuum system. The carrier transport in PS was also investigated in terms of the temperature dependence of the diode current, the dynamic response, and the drift length. The energy distribution of electrons emitted from PS diodes show a behavior characteristic of ballistic electron emission that is quite different with the Maxwellian distribution. This becomes more apparent at low temperatures below 150 K where the electrical conduction in PS is dominated by the tunneling mode. At a temperature of 100 K, for instance, the low-energy tail component is significantly reduced. As a result, the distribution curve width at half-maximum is decreased by down to about 500 meV. The peak position becomes more close to the energy corresponding to the energy gain expected from ballistic transport without any scattering losses. This result proves that in the interconnected nanocrystalline system, electrons can travel for a long distance under a high electric field via multiple tunneling through some electronic barriers (such as interfacial thin oxide films). This is consistent with the experimental results on both the dynamic response of the electron emission and the drift length estimated from the time-of-flight measurement. The observed ballistic transport in PS indicates the further technological potential of nanocrystalline system.

2:30 PM F3.4
OPTICAL PHOTOLUMINESCENCE STUDY OF POROUS SILICON AT HIGH MAGNETIC FIELDS. J.P. Zheng, Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, FL; X. Wei, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL.

It is now well accepted that the luminescence properties of porous silicon (PS) are mainly due to quantum confinement effects. A number of studies have attempted to correlate the optical properties of PS with the size of its luminescent nanostructures. The PS photoluminescence spectrum obtained experimentally shows a broad band, indicating a distribution of the energy gaps caused by the size inhomogeneity of the PS nanostructures.

In this study, high magnetic fields were applied to the PS sample as a means to study quantum confinement effects. Peak position, intensity and width of the PS photoluminescence spectrum were investigated under magnetic fields from 0 to 30 T and at various temperatures. A blue shift in energy band gap and reduction in bandwidth were observed when increasing magnetic field. The results suggest that the high magnetic field confinement of electron-hole orbits compete with the quantum confinement effect of PS nanostructures, resulting in a more uniform confinement energy. Besides of the position of the peak PL and the bandwidth, the PL intensity under high magnetic fields was also investigated.

2:45 PM F3.5
ELECTROREFLECTANCE STUDY OF POROUS SILICON MADE FROM SUBSTRATES WITH DIFFERENT RESISTIVITIES. Toshihiko Toyama, Yasuharu Nakai, Hiroaki Okamoto, Osaka Univ, Dept of Physical Science, Toyonaka, JAPAN.

We have studied optical transitions in porous Si (PSi) employing electroreflectance (ER) spectroscopy. Previously we have reported ER results on PSi made from Si substrates with high resistivities of 4-10 Ωcm (high- ρ PSi). Here we will report the further ER data using PSi made from Si substrates with low resistivity of 0.018 Ωcm (low- ρ PSi). As like the ER spectra of high- ρ PSi, we observed some ER features being located between 1.2 and 3.1 eV which are never observed in bulk crystalline Si. We have already concluded that the ER features come from interband transitions of quantized states due to quantum-confined electron-hole pairs in PSi. The transition energies are well explained by a simple effective mass approximation model and the mean crystal sizes of low- ρ PSi are estimated to be in the range of 2-3 nm, which is calibrated by those of high- ρ PSi deduced from cross-sectional TEM images. On the other hand, the ER features are observed at transition energies of 3.1-3.4 eV in all of the samples being independent of the substrate resistivity or the mean crystal size. This gives that PSi still keeps the three-dimensional (3D) electronic structure because the optical transitions are caused at $E_1(E_0')$ direct gap of 3.4 eV in c-Si. Interestingly, with an increase in the mean crystal size from 2 to 3 nm, the transition energy tends to decrease from 3.4 eV to 3.1 eV. Namely the direct gap in low- ρ PSi with the mean crystal sizes of 3 nm is less than 3.4 eV found in bulk c-Si or high- ρ PSi with the mean crystal sizes of 1-2 nm. [1] T. Toyama, A. Shimode, and H. Okamoto, to appear in Mater. Res. Soc. Symp. Proc. 609.

SESSION F4: POROUS SILICON II
Chair: Leigh T. Canham
Monday Afternoon, November 27, 2000
Constitution A (Sheraton)

3:30 PM *F4.1
BALLISTIC ELECTRON SURFACE-EMITTING COLD CATHODE BY POROUS POLYCRYSTALLINE SILICON FILM FORMED ON GLASS SUBSTRATE. Takuya Komoda, Tsutomu Ichihara, Yoshiaki Honda, Koichi Aizawa, Matsushita Electric Works, Ltd., Advanced Technology Research Laboratory, Osaka, JAPAN; Nobuyoshi Koshida, Tokyo Univ. of Agriculture and Technology, Faculty of Technology, Tokyo, JAPAN.

It is demonstrated that a porous polycrystalline silicon film on a glass substrate is useful as a ballistic electron emitter for excitation source of a flat panel display. A 1.5 μm polysilicon layer is deposited on a metal layer formed on a glass substrate and anodized in an ethanoic HF solution. The porous polysilicon (PPS) layer is treated by an electrochemical oxidation (ECO) in an H_2SO_4 solution. Finally a thin Au film is deposited onto the ECO-treated PPS layer and used as a top electrode. The electron emission current I_e and the diode current I_{ps} are measured as a function of the bias voltage V_{ps} . The cold emission mechanism has also been investigated in terms of the correlation between the electron emission and the structure of PPS layer. Electron emission of which onset voltage is about 6 V rapidly increases with increasing V_{ps} . The I_e value reaches about 80 $\mu\text{A}/\text{cm}^2$ for $V_{ps}=20$ V at which the emission efficiency defined as I_e/I_{ps} is about 1%. The observed energy distribution curve of output electrons suggest that the PPS layer acts as a ballistic transport medium in a way similar to the case of the porous silicon layer formed on a single-crystalline silicon wafer reported previously. In the PPS sample with a high emission efficiency, a red PL band due to Si nanocrystallites is observed besides a blue PL related to the surface oxide. In the PPS sample with a low emission efficiency, in contrast, only an oxide-related PL is observed. This is consistent with the measured XPS profile that nanocrystalline silicon phase remains in the surface of the high-efficiency PPS layer, whereas the surface of the low-efficiency PPS layer is fully oxidized. These results support the electron emission model based on multiple-tunneling through silicon nanocrystallites and provide an important suggestion for developing the efficient ballistic emitter.

4:00 PM F4.2
A NOVEL SOLID-STATE LIGHT-EMITTING DEVICE BASED ON BALLISTIC ELECTRON EXCITATION. Yoshiaki Nakajima, Akira Kojima, Nobuyoshi Koshida, Tokyo Univ of A&T, Dept of Electrical and Electronic Engineering, Tokyo, JAPAN.

As previously reported, nanocrystalline porous silicon (PS) diodes with a well-controlled structure efficiently emit ballistic electrons. The mechanism of the emission of ballistic electrons is explained by multiple-tunneling effect in PS under a high electric field. This phenomenon is very attractive for possible use of PS for novel ballistic devices owing to the controllability of electron energy and a little scattering loss. We demonstrate here that the ballistic transport in PS is directly applicable to a novel solid-state light-emitting device. The experimental devices are composed of a top contact (semitransparent thin Au film), a fluorescent material (Alq_3), a PS layer (10 μm thick), an n-type Si substrate, and an ohmic back contact. The PS layers are formed by anodization with the current modulation scheme in ethanoic HF solutions. Fluorescent material films were deposited onto the PS layers. The device characteristics are evaluated by optical and electrical measurements. Uniform green luminescence discernible in the daylight is observed when a sufficient positive voltage beyond 10 V is applied to the Au electrode with respect to the substrate. In the diode with a normal structure where ballistic electrons are not generated, no light emission is observed. The luminescence spectrum is exactly the same as that of Alq_3 . The voltage dependences of both the luminescence intensity and the spectrum strongly suggest that the light emission is due to direct excitation of Alq_3 by energetic ballistic electrons generated in the PS layer. For the drift layer and the fluorescent films of this device, porous polycrystalline silicon films and some organic or inorganic materials are also available, respectively. This novel solid-state surface-emitting luminescent device has a potential for applications to large-area light source and display.

4:15 PM F4.3
PROGRESS IN INTEGRATED OPTICAL WAVEGUIDES BASED ON OXIDIZED POROUS SILICON. Marco Balucani, Vitaly Bondarenko, Giulio Lamedica, Aldo Ferrari, Univ of Rome "La Sapienza", Rome, ITALY; Leonid Dolgvi, Nikolay Vorozov, Valentina Yakovtseva, Belarussian State Univ of Informatics and Radioelectronics, Minsk, BELARUS; Guy Vitran, Institut National Polytechnique de Grenoble, Grenoble, FRANCE; Henk Bulthuis, BBV Software BV, Enschede, The NETHERLANDS.

In the present work we review the evolution of integrated optical waveguide (WG) based on oxidized porous silicon (OPS), in keeping with the progression from the first-ever demonstration in 1993 up to date. The distinctive feature of the submitted OPS WGs is that they use the design-technological conceptions of the modern micro-

electronics. Optical parameters of principal interest for OPS WGs made in both p- and n-type silicon substrates are discussed. Propagation losses are reported to be less than 0.5 dB/cm coming about through the improvement of manufacturing technology. Comprehensive approach including experimental studies and computer simulation has been used for the WG elaboration. Consideration is being given to the potentialities of these WGs.

4:30 PM F4.4

BRAGG GRATINGS ON POROUS SILICON WAVEGUIDES.

Patrick Ferrand, Susanna Setzu and Robert Romestain, Laboratoire de Spectrométrie Physique, Université J. Fourier - CNRS UMR 5588, Saint Martin d'Hères, Cedex, FRANCE.

Due to the photosensitivity of the dissolution of porous silicon (PS) in HF electrolyte, the presence of light produces a decrease of optical index. A holographic process, using the illumination by an interference pattern of two laser beams, allows to realize a periodical modulation of the optical index of PS in the plane of the sample. Gratings have been obtained, typically with a period as small as $\Lambda = 300$ nm. For well chosen periods, the effect on waveguides of so called Bragg gratings is to forbid the light to propagate, if β is around π/Λ , producing a reflection of a forward mode of propagation constant β into a backward mode, like it occurs in distributed feedback lasers. We have studied the optical properties of Bragg gratings on porous silicon waveguides, in the near infrared range.

4:45 PM F4.5

SILICON PHOTODIODES WITH ANTI-REFLECTION POROUS LAYERS. Shingo Uehara, Ryudai Murano, Keisuke Iritani and Tadashi Matsubara, Seikei Univ, Dept of Electrical Engineering and Electronics, Tokyo, JAPAN.

Due to the high refractive index, the reflectance of the bare silicon surface exceeds 30%, and its reduction is crucial in enhancing the efficiency of silicon-based optical devices like photodiodes and solar cells. It was demonstrated that, by introducing appropriately designed in-depth porosity grading, we can form a very low reflectance wide-bandwidth anti-reflection porous layer on silicon substrate. Because the porous layer can be formed simply by controlling the anodization current, the porous layer is promising as a low cost high performance anti-reflection coating for silicon optical devices. In this paper, we report on the fabrication and evaluation of silicon photodiodes with the porous anti-reflection layer formed at the incident surface. (100) oriented n-type silicon with 5-10 Ω -cm resistivity was used as the substrate. After forming pn-junction by diffusing boron, the doped p-layer was anodized to form the anti-reflection layer. The anodization current density was varied by a computer control from 25 mA/cm² at the surface to 1 mA/cm² at the silicon interface so as to form gaussian index grading. The resulted anti-reflection layer had reflectance of 2-10% in the 450-900 nm wavelength range. The final reflectance after experiencing junction edge passivation and electrode formation processes was 7-10%. The junction and incident window diameters of the fabricated diode were 10 and 8 mm, respectively. The measured IV characteristics showed reverse current of 4-5 μ A (at -5V) and ideality factor of 1.7-2.6, indicating the possibility of the pn-junction with porous p-region to have IV characteristics comparable with those of the crystalline junction. The measured quantum efficiency at 633 nm was increased to 73% from the 48% of the silicon photodiode without anti-reflection layer. The responsivity improvement in the 450-900 nm range was 1.4-1.6.

SESSION F5: POSTER SESSION
Monday Evening, November 27, 2000
8:00 PM
Exhibition Hall D (Hynes)

F5.1

OPTICAL AND STRUCTURAL CHARACTERIZATION OF NANOCRYSTALLINE SILICON SUPERLATTICES: TOWARD NANOSCALE SILICON METROLOGY. S. Zollner, A. Konkar, R. Liu, M. Canonico, and Q. Xie, Motorola SPS, Process and Materials Characterization Laboratory, Mesa, AZ; G.F. Grom, Q. Zhu, R. Krishnan, P.M. Fauchet, and L. Tsybeskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY.

The possibilities for enormous increase in functionality, integration density, and speed offered by nanoscale-level systems strongly motivate a development of novel metrology for nanometer-sized Si/SiO₂ based structures and devices. Using nanocrystalline silicon superlattices (nc-Si SLs) as a model structure containing layers of Si nanocrystals separated by nanometer-thick SiO₂, we have tested a variety of characterization techniques. We performed optical measurements (UV-visible Raman spectroscopy, spectroscopic

ellipsometry, and modulation spectroscopy), X-ray diffraction measurements, transmission electron microscopy (TEM) and atomic force microscopy (AFM). The AFM images show that the surface of a good quality structure is a continuous film with the RMS roughness better than 5-7 Å. The X-ray diffraction data for superlattices with 75 and 42 Å nominal Si well widths show very well pronounced Si (111) Bragg peaks. The sample with the thinnest (~20 Å) Si wells shows a very broad shoulder (~3 degree FWHM) at the Si (111) position. The ellipsometry spectra were taken in the spectroscopic range of 0.7-6.6 eV. The pseudodielectric function from the sample with 75 Å well width shows an overall shape similar to polycrystalline Si with the interference fringes below the direct band gap of about 3 eV. An excellent agreement is achieved by describing the superlattice as an effective medium containing 35% SiO₂ and 65% of a material with optical properties resembling those of amorphous Si, but with a larger average band gap. This experimental result is in a good agreement with the reconstruction of the pseudodielectric function using the optical reflection data and Kramers-Kronig relations. At the same time, no evidence of the amorphous residue is found in the UV Raman spectroscopy. The ellipsometry measurements may indicate the bandgap opening due to quantum confinement effect in small size Si nanocrystals.

F5.2

CVD GROWTH OF Si NANOCRYSTALS ON DIELECTRIC SURFACES FOR NANOCRYSTAL FLOATING GATE MEMORY APPLICATION. Sucharita Madhukar, K. Smith, R. Muralidhar, D. O'Meara, M. Sadd, B-Y. Nguyen, B. White and R.E. Jones, Materials and Structures Laboratory, Digital DNA Labs, Motorola SPS, Austin, TX.

Initial stages of growth of silicon on dielectric surfaces proceeds through Volmer-Webber growth mode (through island formation) and coalescence of islands to form a continuous thin film layer. Growth of silicon nanocrystals on dielectric surface can be achieved by controlling the nucleation and growth kinetics of these nanocrystals on the dielectric surface. In this study, we present CVD growth of Si nanocrystals on oxide, oxynitride and nitride surfaces using silane based chemistry. The effect of process conditions such as deposition temperature, precursor flow rate, co-flow gas on nanocrystal incubation time, size and density of nanocrystals was studied. The nucleation and growth rate of the silicon nanocrystals is also a strong function of the surface chemistry, surface structure and strain in the dielectric film. We have studied the effect of oxide deposition temperature and surface pretreatments on the nucleation and growth characteristics of the silicon nanocrystals. We have also fabricated MOS capacitors with the nanocrystal floating gate and demonstrated memory operation at room temperature.

F5.3

RETARDATION IN THE OXIDATION RATE OF NANOCRYSTALLINE SILICON QUANTUM DOTS. Jun'ichi Ohmachi, Ryo Nakamura, Katsuhiko Nishiguchi, Shunri Oda, Tokyo Institute of Technology, Research Center for Quantum Effect Electronics, Oda Laboratory, Tokyo, JAPAN.

For room temperature operation of single-electron-tunneling integrated devices, fabrication of a few nanometer structures is required. Using very-high-frequency (VHF) plasma decomposition of silane and pulsed gas technique, we have successfully prepared nanocrystalline silicon (nc-Si) quantum dots having average diameter of 8 nm and dispersion of 1 nm. The role of natural oxide is very important. It controls the electron transport as tunneling barriers. It controls the electron trapping at the Si/oxide interface. It controls the size of nc-Si dots. Of particular interest is that self-limiting oxidation process, due to the stress induced near Si/oxide interface, which allows the fabrication of ultimate monodispersed system. This paper deals with systematic study of oxidation process of nc-Si quantum dots. Nanocrystalline silicon particles, formed in the Ar plasma and silane gas pulse and deposited on Pt mesh, are oxidized for various periods at 750°C and 800°C, and then studied by TEM. The dimensions of the residual nc-Si and the grown oxide are extracted from the micrographs and analyzed. For comparison, field oxide is investigated using ellipsometry. Retardation in the oxidation rate of nc-Si is observed. The mechanism of oxidation in nc-Si is discussed taking into account the stress effect and the surface/bulk peculiarity. This work was supported by CREST/JST.

F5.4

ATOMIC FORCE MICROSCOPY AND RAMAN SPECTROSCOPIC STUDY OF R.F. SPUTTERED Si/SiO₂ THIN FILMS FOR NANOSCALE DEVICE APPLICATIONS. R. Krishnan, G. Grom, P.M. Fauchet, L. Tsybeskov, University of Rochester, Department of Electrical and Computer Engineering, Rochester, NY; S. Papernov, University of Rochester, Laboratory for Laser Energetics, Rochester, NY; G.I. Spoule, D.J. Lockwood, National Research Council, Institute of Microstructural Research, Ottawa, CANADA.

Silicon nanocrystallites grown by controlled crystallization of amorphous Si/SiO₂ superlattices hold considerable promise for ultra-high density/low power memory devices based on quantum processes. In order to fabricate high quality devices with reproducible properties, it is essential that the Si/SiO₂ interfaces be atomically smooth, dense, and chemically and structurally abrupt. These requirements are achievable in Radio Frequency (R.F.) sputtered films, if the deposition parameters are carefully optimized. We used an Atomic Force Microscope (A.F.M.) to study the influence of the various deposition parameters on the morphology and roughness of these films. We demonstrate that amorphous Si/SiO₂ superlattices deposited at non-optimum conditions tend to have a columnar growth and a high void fraction. Using the optimum deposition conditions, we suppressed the columnar growth, and obtained compact, dense, and smooth superlattices with R.M.S. roughness better than 7Å. Auger Microprobe Analysis shows that the Si/SiO₂ interfaces within the superlattice remains chemically abrupt. After the controlled crystallization step, the silicon TO peak becomes asymmetric and shifts towards lower wavenumbers, indicating the presence of silicon nanocrystals. The observation of folded acoustic phonons in low frequency Raman scattering confirms the good periodicity of Si/SiO₂ superlattices and Si/SiO₂ interface structural abruptness. The low intensity Raman signal from thin Si/SiO₂ films ($\leq 1000\text{Å}$) was enhanced using either (a) deposition of the superlattice between cladding layers of silicon dioxide to form a waveguide-like structure, (b) interferometric enhancement of the Raman signal, (c) cross polarized Raman configuration to suppress the signal from c-Si substrate.

F5.5
CHARACTERIZATION OF Si NANOPARTICLES FOR MEMORY APPLICATIONS. A. Konkar, Q. Xie, S. Zollner, R. Liu, G. Rich, S. Madhukar, Materials and Structures Laboratory, Motorola Inc., Mesa, AZ.

With better understanding of the processing, properties, and the attendant control over the fabrication of Si nanocrystals in recent years, these nanocrystals are at a stage where they are prime candidates for incorporation into devices. One such device application is the use of Si nanoparticles as the floating gate for memory devices. In this case the device parameters are strongly dependent on the size and density of the nanoparticles, and the thickness of the tunnel oxide separating the Si nanoparticles from the Si substrate. Characterization of the Si nanoparticles and the gate stack is critical in the development of this technology. However, characterization of these nanoparticles presents some peculiar challenges due to their extremely small size. We have used a variety of techniques to characterize the nanoparticles. Structural characterization has been carried out using SEM, TEM, AFM, and XRD. Results from SEM and AFM analysis will be compared and we will show how complimentary information on the size (lateral and vertical) and density of nanoparticles can be obtained. Plan-view and cross-sectional TEM images evidencing the crystalline nature of these nanoparticles and the 'true' size of the nanoparticles will be presented. XRD results provide information regarding the texture and average size of an ensemble of nanoparticles. Results on the vibrational spectra from UV-visible Raman spectroscopy will be discussed. Some novel results from SPM-based electrical characterization such as Scanning Capacitance Microscopy and Tunneling Atomic Force Microscopy, with the potential of characterizing individual nanoparticles, will also be presented.

F5.6
ION-BEAM SYNTHESIS AND RADIATION PROCESSING OF NANOCRYSTALLINE Si EMBEDDED IN SiO₂ LAYERS AND FUSED SILICA. G.A. Kachurin, S.G. Yanovskaya, V.A. Volodin, V.G. Kesler, T. Hasanov, K.S. Zhuravlev and A.K. Gutakovskiy, Institute of Semiconductor Physics, SO RAN, Novosibirsk, RUSSIA.

In spite of many advantages of Si, it is not suitable for the optoelectronic devices because of its indirect energy band. This physical limitation can be overcome with the use of nanocrystalline Si. Recently, Si nanocrystals (Si-ncs) formed by ion-beam synthesis have received considerable attention. However, the factors governing the formation, properties and stability of Si-ncs remain to be better understood. We studied the formation and radiation stability of Si-ncs synthesized in thin SiO₂ layers and in bulk silica by implantation of 25-150 keV Si ions to the doses of 10-20 at.% followed by (200-1150)^oCx30 mins anneals. Fast electrons and α -particles irradiations were used to introduce the defects. The samples were characterized by Raman spectroscopy, ellipsometry, XPS, HREM, and photoluminescence (PL). The following has been observed. The synthesis starts with the formation of Si-Si bonds as revealed by XPS. This process needs no long-range diffusion and results in appearance of non-phase Si inclusions. Then they transform to the Si phase nanoprecipitates, remaining amorphous until the temperature reaches $\sim 1000^{\circ}\text{C}$. Further annealing leads to the formation of Si-ncs emitting

strong visible PL due to the quantum-size effect. Irradiation induced single atomic displacements were found to quench the emission. On the other hand, such isolated displacements may cause prompt crystallization of Si nanoprecipitates at room temperature. Raman spectroscopy gives evidences the nanoprecipitates may be stressed, depending on whether thin films or bulk substrates were used. Further increase in the irradiation dose amorphizes the Si-ncs. Abrupt phase transition takes place when near 20% of atoms in Si-ncs are displaced. To restore the crystalline lattice 1000°C annealing is necessary, that is much higher than the crystallization temperature of bulk amorphous Si. The results obtained are analyzed and discussed in terms of the balance between the volume and surface free energies in Si-ncs.

F5.7
EFFECT OF AMORPHOUS Si/SiO₂ BOUNDARIES ON STABILITY OF NANOCRYSTALLINE/AMORPHOUS SILICON MIXED PHASE. Vladimir I. Gavrilenko, Ruqian Wu, Dept. of Physics and Astronomy, California State University, Northridge, CA.

Recent success in fabrication of ordered layers of Si nanocrystals in the form of nanocrystalline Si/SiO₂ superlattices has triggered strong interest to their application in nanoscale electronic devices. In order to bring this results to the level of reproducible manufacturing, the development of the theoretical models and numerical simulations of solid-phase crystallization in nanometer-thick *a - Si* layers is necessary. In this work, we study stability of a model nanocrystalline-amorphous silicon mixed phase using total-energy density functional calculations based on *ab initio* pseudopotential scheme. Si nanocrystals surrounded by computer generated amorphous Si phase are studied. The unit cells with up to several hundreds of atoms are considered. Effects of amorphous Si/SiO₂ boundaries are included through explicit calculations of elastic energies of the interfaces. The predicted values of formation enthalpy indicate that nanocrystalline/amorphous Si system with additional amorphous Si/SiO₂ boundaries is energetically favored than that uniformly surrounded by amorphous phase. This issue agrees well with recently observed decrease of crystallization temperature in thin amorphous Si superlattices with respect to thick layers. The results obtained are discussed in comparison with available experimental data on thermal crystallization of amorphous Si.

F5.8
SILICON NANOCLUSTERS IN Si-SiO₂ SYSTEM. Laura Diaz-Flores, Francisco Espinoza-Beltran, Jesus Gonzalez-Hernandez, Yuri Vorobiev, Laboratory of Investigation of Materials, CINVESTAV-IPN, Queretaro, MEXICO.

We investigated the optical properties of the Si-SiO₂ system prepared (i) by thermal oxidation of the Si-powder in air at different temperatures, and (ii) by incorporation of the same powder into sol-gel SiO₂ glass made from the precursor solution with two different water-to-TEOS ratios; the powder was prepared by mechanical milling of silicon (Silicon granular 99.999%, Alfa Aesar production). The infrared absorption and Raman spectra of our samples revealed the lines ascribed to the Si nanoclusters, in particular, those related to the clusters Si₆ and Si₇. The detailed analysis was made of the spectra of SiO₂ phonon bands in the region 1000 - 1300 cm⁻¹ obtained in the samples of different origin and treatment. The well pronounced Berreman effect influencing the relation between the different band intensities was registered, its manifestation depending upon the sample preparation and treatment. On the basis of the intensities of the different bands in this region and their relation to the structural disorder of material, the conclusion is made that the nanoclusters mentioned are formed from the larger ones in the process of their oxidation. Thus, the nanoclusters observed are entrappeded within the SiO₂ cages. The kinetics of formation as well as the possible influence of these cages upon the properties of the clusters are discussed.

F5.9
FABRICATION AND CHARACTERIZATION OF COLD ELECTRON EMITTER BASED ON NANOCRYSTALLINE SILICON QUANTUM DOTS. Katsuhiko Nishiguchi and Shunri Oda, Tokyo Institute of Technology, Research Center for Quantum Effect Electronics, Tokyo, JAPAN; Xinwei Zhao, Science University of Tokyo, Tokyo, JAPAN.

We present an application of nanocrystalline silicon (nc-Si) dots to a cold electron emitter (CEE). Porous Si (PS) has been used for CEE, whose merits are high efficiency, high resolution, and easy fabrication process without requirement of high voltage and high vacuum in device operation. But with PS, a wet process is required. On the other hand, we fabricate nc-Si in gas phase by using very high frequency plasma enhanced chemical vapor deposition (PECVD). Using this method, we can control the size of dots by applying pulsed gas of silane into argon plasma. For CEE, an n-Si substrate is used as an electron source. On this substrate, nc-Si dots are deposited by CVD till the thickness of nc-Si layer becomes 600nm. Then the sample is

oxidized so that the surfaces of dots are covered with SiO₂. Finally, a Au film is formed. Measurements are performed in vacuum of 10⁻⁶ Torr. The Au electrode is grounded, and a metal plate, as a collector of electrons extracted into vacuum, is located in front of the sample and applied a constant positive voltage. While a negative voltage is applied to the Si substrate, a diode current flows. When a negative voltage over 5V is applied, which relates to the work function of Au on Si, electrons begin to be extracted from the sample and reaches to the collector. A possible process proposed for PS emitter is inquired as follows. An electric field is applied mainly to SiO₂ regions covering the dots, so electrons from the wafer go through nc-Si dots without a scattering because of its small size, and then they are accelerated in SiO₂ by the high electric field and transport through the nc-Si layer ballistically. This work was supported by CREST, JST.

F5.10

SINGLE-ELECTRON MEMORY EFFECTS IN MOS STRUCTURES FABRICATED BY LPCVD DEPOSITION OF Si NANOGRAINS. M. Vulpio, C. Gerardi, B. Fazio, G. Renna, STMicroelectronics, Catania, ITALY; S. Lombardo, I. Crupi, Y. Liao, V. Raineri, CNR-IMETEM, Catania, ITALY.

Single electron devices, among which nanocrystal memories, are perceived as the successors of the present MOSFETs when physical and technological scaling limitations will hamper their further development. In this work we have fabricated MOS memory structures containing silicon nanocrystals embedded in SiO₂ which act as nanocrystal floating gates. The dots have been obtained by LPCVD deposition on a 3 nm thermally grown tunnel oxide. A systematic study on deposition rates and annealing conditions has been exploited in order to optimize the nanocrystal density and distribution uniformity. Structural characterization has been carried-out by AFM and TEM. Results of structural analysis show that almost spherically shaped nanocrystals can be obtained with a quite uniform distribution peaked at a diameter of 4 nm. An inter-poly CVD SiO₂ dielectric of ~7 nm has been deposited on top of the Si nanograins. Memory effects have been observed by measuring the flat-band voltage shift in the high frequency CV characteristics after the application of several bias voltages.

F5.11

IN-PLANE SIDE GATE-CONTROLLED COULOMB-BLOCKADE DEVICES FABRICATED ON SILICON-ON-INSULATOR STRUCTURES. S.D. Lee, K.S. Park, J.W. Park, Jung B. Choi, Chungbuk National University, Dept. of Physics, Cheongju, KOREA; K.-H. Yoo, J. Kim, Korea Research Institute of Standards and Science, Taejon, KOREA.

Single electron tunneling through Coulomb-blockade structures has been considered as a new type of spectroscopy technique for exploring of quantized levels of a quantum dot. Unlike optical measurements where electron-hole pairs are created, it allows a direct probe of the additional energy for adding successive charge carriers to the dot. Here, we report a in-plane side gate-controlled Coulomb-blockade device fabricated on silicon-on-insulator(SOI) structure. The SOI structure can remove undesirable Si bulk effects and is very effective to limit the channel width. A quantum dot is defined in the active channel by negatively biasing any two pairs of side gates with keeping the other gates grounded. The side gate were formed by deeply etching into the barrier oxide, followed by nanopatterning by electron beam lithography. They were designed to be located in the same plane as the active channel. Such an in-plane structure of the side gates results in stronger electrostatic effect on the channel current, reducing the dot size down to 70nm. The linear response conductance data for 4.2K at zero magnetic field exhibit up to three paired-peaks, with small intra-pair spacings and large inter-pair spacings. Three intra-pair spacings are found to be nearly a constant value, corresponding to the single charging energy U, whereas two inter-pair spacings are different which are associated with U dE1 and U dE2, i.e., successive quantized level spacings added to U. This simple alternating odd(spin 1/2)-even(spin 0) filling, being a consequence of exclusion principle, indicates that the shape of the silicon dot defined by the side-gate voltage is a significant departure from the x-y symmetry, and level degeneracy is lifted. The deduced quantized level spacings were also revealed in the nonlinear current-staircase, and well explained by a simple model calculation.

F5.12

LATERAL CARRIER TRANSPORT IN ULTRA-THIN LAYERS OF SILICON NANOCRYSTALS. H.B. Kim, L. Montes, R. Krishnan, P.M. Fauchet and L. Tsybeskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY.

Low-dimensional Si/SiO₂ based structures have attracted strong attention due to their interesting physical properties and potential applications in nanoscale electronic devices. In a layered structure with alternating layers of nanocrystalline Si and amorphous, tunnel

transparent SiO₂, the study of carrier transport were focused on vertical (i.e. perpendicular to layers) conductivity. At the same time, a proposed application in ultra-high density memory devices requires the understanding of Si nanocrystal "cross-talk", which most effectively can be studied by means of lateral electrical properties. This work presents a comprehensive examination of lateral electrical properties of ultra-thin layers of Si nanocrystals over a wide range of frequencies, temperatures, and electric fields. Si nanocrystals with sizes controllably varying from 3 nm to 10 nm were prepared by thermal crystallization of initially amorphous Si layers deposited on 100 nm thick, thermally grown SiO₂. The surface morphology of nc-Si layers was studied by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The measurements of ac and dc conductivity were performed in two- and three-terminal geometries. The charging and "cross-talk" between Si nanocrystals strongly depend on nanocrystal size and density, showing the importance of lateral isolation and Coulomb blockade.

F5.13

LATERAL SUPERLATTICES FABRICATED WITH INTERFEROMETRIC LITHOGRAPHY FOR NANOSCALE DEVICE APPLICATIONS. Christopher C. Striemer, Philippe M. Fauchet, Leonid Tsybeskov, Univ of Rochester, Dept. of Electrical and Computer Engineering, Rochester, NY.

Two-dimensional periodic arrays of inverted pyramid holes with nanometer scale have been patterned on the surface of a (100) silicon wafer and studied for possible application in nanoscale silicon based devices. The surface patterning employed a simple microelectronic processing scheme in which the standing wave intensity pattern from two interfering 458nm laser beams was used to expose holes in a photoresist layer. Subsequent dry etching through an underlying oxide mask layer, followed by a KOH etching step yielded a highly periodic, large area array of inverted pyramids. The pyramid geometry is formed during the anisotropic KOH etch, which stops at the (111) pyramid walls. Therefore, the tip of each inverted pyramid is formed by the intersection of (111) silicon crystal planes and has identical geometry. This study focuses on the use of these features as templates for the controlled crystallization of amorphous silicon layers and also as electric field concentrating "funnels" in MOS-type structures. Significant conductivity enhancement through a 200 angstrom oxide grown on this structure has been observed with entirely unexpected electrical properties. We will discuss a proposed device in which silicon nanocrystals will be incorporated into the concentrated electric field region at the tip of each inverted pyramid. With this structure, the charging of identical addressable nanocrystals may be possible, leading to the development of practical nanoscale silicon devices.

F5.14

CHARGING EFFECT IN AMORPHOUS SILICON QUANTUM DOTS EMBEDDED IN SILICON NITRIDE. Nae-Man Park, Sang-Hun Jeon, Hyunsang Hwang, Seong-Ju Park, Kwangju Institute of Science and Technology, Dept of MS&E, Kwangju, KOREA; Suk-Ho Choi, School of Electronics and Information and Institute of Materials Science and Technology, Kyung Hee University, Suwon, KOREA.

Recently some research groups have investigated the electrical properties of Si nanostructures and reported on charge storage in these structures. The nano-memory devices are very interesting in very large scale integrated circuits in the future because this nano-memory has characteristics such as long-term charge storage, fast response, and quasi-nonvolatile. This memory is based on the charging effects such as flatband voltage shifts in metal-insulator-semiconductor (MIS) capacitors. In previous reports of Si nanocrystals in SiO_x as an insulating layer, hole charging was found to occur in Si nanocrystals and hysteresis capacitance-voltage (C-V) curves were observed. In this study, we report on the electron charging in a-Si QDs embedded in silicon nitride as an insulating layer in an MIS structure which were grown by plasma enhanced chemical vapor deposition. This electron charging effect is very important in the fabrication of the Si electronic devices because the electron mobility is about three times as large as the hole mobility. This means that the faster-response-memory can be realized using a-Si QDs. In the MIS capacitor containing a-Si QDs, flatband voltage shift showing discharging was observed without opposite voltage stress when a higher voltage stress was applied. Under illumination condition, the photoionized electrons trapped in a-Si QDs induced a negative photoconductivity at forward bias because these electrons screened the applied bias voltage, resulting in the current decrease. These C-V characteristics and negative photoconductivity are expected to be used in the fabrication of the multi-state memory devices.

F5.15

OXIDATION AND INITIAL GROWTH STAGE OF MICRO-CRYSTALLINE Si FILM DEPOSITED BY PHOTO-CVD AND ITS MEMORY DEVICE APPLICATION. Seung Jae Baik, Koeng Su Lim,

Dept. of Electrical Engineering and Computer Science, Korea Advanced Institute of Science and Technology, Taejeon, KOREA; Jae Hyung Choi, Jeong Yong Lee, Dept. of Material Science and Engineering; Jung H. Shin, KAIST, Dept of Physics, Taejeon, KOREA.

At the previous meeting, nanocrystal memory [1] using self-limited oxidation of microcrystalline Si was demonstrated [2]. Part 1: Nanocrystal memory using that method shows strong dependence of temperature that can be explained by introduction of interface states. Discrete conductance changes manifested by single charge tunneling disappear with slower sweep measurement, and also at lower temperature. Because interface states are more localized than nanocrystals thus they have longer charging time constants. And they respond at lower temperature because higher capture rate of nanocrystal at higher temperature. Part 2: From the study of initial growth stage of microcrystalline Si film, spatial density of nuclei is strongly dependent on the temperature and the hydrogen dilution ratio. They are related to the sticking coefficient and surface mobility of the predeposition species. With optimization procedure, we obtained the spatial density of nanocrystals to be mid $10^{15}/\text{cm}^2$ from atomic force microscopy measurement. We have fabricated nanocrystal memory with the initial growth stage of microcrystalline Si film. In this case, the onset of charge injection does not appear at the transfer characteristics, which is different from the part 1, although similar threshold voltage shift was observed. Interface states show smaller effects in this case. [1] S. Tiwari, et al., Tech. Dig. of IEDM, p. 512, 1995 [2] S.J. Baik and K.S. Lim, MRS 2000 Spring Meeting, Symposium A, San Francisco, 2000

F5.16

ELECTRICAL AND OPTICAL PROPERTIES OF Si NANOCRYSTALS DISPERSED POLYESTER THIN FILMS. Homare Miyamoto, Yoshikazu Ohsawa, Hiroyoshi Naito, Osaka Pref Univ., Dept of Physics and Electronics, Osaka, JAPAN; Yoshikiko Kanemitsu, Nara Institute of Science and Technology, Graduate School of Materials Science, Nara, JAPAN.

Electrical and optical properties of Si nanocrystals (nc-Si) dispersed in electrically-inactive polymer binder are reported. The electrical and optical properties of the material have been studied by means of the optical absorption, steady-state photoconductivity, and dark current-voltage (I - V) measurements. Si nanocrystals with the average diameter of 30 nm were dispersed in polyester. It is found that the steady-state photoconductivity response of the nc-Si:polyester composites is enhanced with increasing nc-Si concentration over spectral range from 1.5 eV to 3.6 eV, indicating that charge carriers are photo-created on nc-Si and transport through nc-Si. The I - V characteristics of Au/nc-Si:polyester/Au exhibit $I \propto V^n$ in nc-Si concentration range from 10 to 50 wt.%, where $3 \leq n \leq 5$. Such varistor characteristics would essentially be interpreted in terms of a barrier model. The nc-Si concentration dependence of the dark conductivity estimated from the Ohmic region in the I - V characteristics shows that the electrical conduction is limited by the percolation of charge carriers in the composite thin films.

F5.17

RELATIONSHIP BETWEEN OPTICAL GAP AND AVERAGE GRAIN SIZE FOR NANOSILICON. Guang-Xu Cheng, Yu-Liang He, Wei Zhang, Xing-Kui Zhang, and Duan Feng, National Laboratory of Solid State Micro-structures, and Center of Materials Analysis, Nanjing University, Nanjing, Jiangsu, CHINA; Jia Cheng, Department of Communication Engineering, Jiaotong University, Shanghai, CHINA; Hao-Yu Chu, The Engineering Institute of the Engineer Corps., Nanjing, CHINA.

A series of nanometer silicon films were deposited on glass substrate using PECVD technique, the substrate temperatures (T_s) are 250, 300°C, respectively, the optical gaps (Tauc gap) were measured by optical absorptive method. We report the results obtained using Raman scattering spectra, which is shown that Raman representation of optical gap is intimately related to the grain size of the nanometer silicon, whole changing process can roughly be divided with three different steps, around 5.0 (nm) grain size, i.e. corresponding to the region which are 1.88 ± 0.03 (eV), the slope of the curve of $E_g^{opt} - \Delta d$ is undergone from positive to zero, and then from zero to negative, it is implied that structural phase transition have been created. This is just characterized by nanometer materials, same as previous works on this field.

F5.18

PHOTOLUMINESCENCE FROM AMORPHOUS Si DIOXIDE/CRYSTAL Si/AMORPHOUS Si DIOXIDE SINGLE QUANTUM WELL STRUCTURES. Y.Q. Wang, Yukari Ishikawa, N. Shibata, Japan Fine Ceramics Ctr, JAPAN.

Since visible photoluminescence (PL) from porous Si was reported by Canham in 1990, several mechanisms have been proposed to interpret

its origin. In porous Si, however, it is difficult to precisely control the structure configuration and size. Therefore, there is little information on quantitative comparison between PL spectra and structures from different papers. A more fundamental two-dimensional system, a single Si quantum well structure enables us to analyze the size effects on PL due to its size defined by the thickness alone and easily being controlled, thus helps us elucidate the origin of PL from low-dimensional Si structures. Amorphous Si dioxide/crystal Si/amorphous Si dioxide single quantum well structures were fabricated by oxygen implantation and thermal oxidation. No photoluminescence was found from these as-grown samples. After annealed in a hydrogen ambient, two peak photoluminescence spectra were measured. The peak positions locate at blue region and yellow-to-blue region, respectively. The blue PL locates at about 425 nm, and its peak position does not change with the thicknesses of Si layers. The yellow-to-blue PL peak positions vary from 600 to 450 nm when the thicknesses of Si layers decrease from 5 to 0.5 nm. When the measurement temperature decreased from room temperature to 8.5 K, peak positions of the blue PL do not change, while those of the yellow-to-blue PL blueshift slightly with temperature. We believe that: 1) the role of hydrogen annealing is to annihilate the irradiate-recombination centers, which were introduced into the samples during the oxygen implantation; 2) the blue PL originates from luminescence centers in Si dioxide, so its peak position does not change with Si layer thickness; 3) the yellow-to-blue PL comes from Si quantum well layer and its peak position changes with the Si layer thickness due to the quantum confinement effects.

F5.19

PHOTOLUMINESCENCE FROM NANOSCALE Si IN a-SiO_x MATRIX. Ikuro Umezū, Ken-ichi Yoshida, Akira Sugimura, Konan Univ, Dept of Applied Physics, Kobe, JAPAN; Mitsuru Inada, Konan Univ, High Technology Research Center, Kobe, JAPAN.

We prepared a-SiO_x ($x < 2.0$) films by co-sputtering of Si and SiO₂ target and found that these films include nano-scaled a-Si region in a-SiO_x matrix. The optical absorption and photoluminescence (PL) spectra of the films are discussed. The structure of the films was evaluated by X-ray photoemission spectroscopy (XPS) and infrared absorption. The XPS spectrum in the a-SiO_x films showed two Si 2p peaks at 99.6 and 104eV. This indicates that the a-SiO_x films are not homogeneous but are composed from Si and a-SiO₂ regions. Optical gap energy of this system rapidly increased when x exceeds 1.0. The rapid increase in the optical gap of this system indicates that nanometer sized Si islands are formed when x is larger than 1.0. The PL peak energy of this material decreased with increasing temperature when x is less than 1.0. On the other hand, when x exceeds 1.0, PL peak energy slightly decreased with increasing temperature until 60 K and began to increase above 60 K. This temperature dependence is explained by an assumption that the PL spectra are superposition of two components; PL emission from the nanoscale Si and from defect in a-SiO₂ matrix. The temperature of PL quenching was also 60 K. This means that 60 K is a critical temperature of recombination mechanism. The optical absorption and PL mechanism of nanoscale Si region surrounded by a-SiO₂ region are discussed.

F5.20

ANODIZATION OF SILICON USING A PREFORMED NANOSCALE TEMPLATE. S.P. McGinnis, P. Sines, C. Garman, and B. Das, West Virginia University, Department of Computer Science and Electrical Engineering, Morgantown, WV.

Silicon nanocrystalline structures were formed by anodization of a silicon substrate using a preformed template of porous aluminum oxide. When anodized in an appropriate oxidizing acid, aluminum thin films have been shown to form a hexagonal array of periodic pores with diameters from 4-100 nm with excellent size uniformity. Using a technique we have previously developed, we have fabricated porous aluminum oxide templates on p-type silicon substrates with pores extending completely through the aluminum film and contacting the substrate surface. These substrates were then anodized using the standard porous silicon fabrication method. The advantage of this approach is that it appears to provide more structural order to the silicon nanocrystals than conventional porous silicon fabrication techniques. We will present the detailed fabrication technique along with structural and optical characterization of the silicon nanocrystals as a function of template pore size.

F5.21

CORRELATION BETWEEN BULK MORPHOLOGY AND LUMINESCENCE IN POROUS SILICON INVESTIGATED BY EVAPORATION INDUCED PORE COLLAPSE. Donald J. Sirbuly, Michael D. Mason, Steven K. Buratto, University of California, Department of Chemistry and Biochemistry, Santa Barbara, CA.

The internal structure of porous silicon (PS) films remains widely debated. In this study, the optical and structural properties of

anodized PS were investigated as a function of the current density (J) and total charge (Q) injected during electrochemical etching. Scanning electron microscopy, fluorescence microscopy and spectroscopy, and laser scanning confocal microscopy were employed on samples that had undergone evaporation induced collapse of the underlying porous structure. From this data two classes of PS samples emerge. Porous silicon samples produced at high and low current density show dramatically different structural and optical properties. Our results indicate that samples produced at high current densities have a 3-dimensional pore network with a narrow distribution of blue-green emitting chromophores. Low current density samples form pores normal to the Si substrate with larger chromophores and exhibit broad red luminescence.

F5.22

SELF-FORMATION OF Au MICROWIRES ON Au-COVERED Si ELECTRODE SURFACE BY ELECTROCHEMICAL ETCHING IN DILUTE HYDROFLUORIC ACID SOLUTION. Yasuo Kimura, Jun Nemoto, Jun Kusakabe, Yusuke Kondo, Michio Niwano, Research Institute of Electrical Communication, Tohoku University, Sendai, JAPAN.

A conventional method of synthesizing porous Si is to apply an anodic (positive) potential to a Si electrode in aqueous etching solutions such as dilute hydrofluoric acid (HF) solution. Previous studies revealed that at electrode potential below approximately 1 V, surface roughening and formation of porous Si occur in the vicinity of the electrode surface, while at higher potentials electropolishing occurs. Etching of Si surface can be controlled by the anodic potential applied to the Si electrode. Then, how is the surface etched in HF solution when the surface is covered with patterned metal overlayer? Microstructures might be fabricated on metal-covered Si surfaces by potential-controlled electrochemical processing. In this study, we investigated the method of fabricating microstructures on the Si surface that was covered with patterned Au mask, by electrochemical etching (anodization) in dilute HF solution. At electrode potentials below approximately 0.5 V, the Si substrate surface is preferentially etched on the fringe of the Au mask overlayer, where a number of pores are formed. Interestingly, at higher potentials, Au microwires with about 1 μm in width formed on the fringe of the Au mask layer. Microwire formation is found to depend both on the anodic potential applied to the Si electrode and the current density. We suggest that electromigration of Au to the fringe of the Au mask induces self-assembling of Au atoms to form microwires. Self-formation of microwires would be beneficial to the fabrication of microstructures on Si.

F5.23

STRONG ENHANCEMENT OF POROUS SILICON PHOTOLUMINESCENCE BY DRY PHOTO-CHEMICAL SURFACE TREATMENT. Sara Stolyarova, Aharon El-Bahar, Yael Nemirovsky, Solid State Institute and Microelectronics Research Center, Technion - Israel Institute of Technology, Haifa, ISRAEL.

A strong enhancement of photoluminescence of porous silicon has been obtained by NF_3/UV photo-chemical surface treatment. The UV photons are provided by an excimer lamp. The increase of PL intensity is about 1–2 orders of magnitude for treatment temperatures in the range of 300–400°C. The enhancement is observed only after contact of the NF_3/UV treated surfaces with air atmosphere. Using AFM and Auger measurements, it is found that the PL enhancement can be correlated with the unusual growth of crystalline SiO_x layer with the x value close to 2, and incorporation of fluorine. The overall effect of photoluminescence enhancement is suggested to be due to the NF_3/UV photochemical etching of the as-formed native oxide, as well as, to the cleaning and passivation of the porous silicon surface with fluorine, followed by a rapid growth of a more stoichiometric oxide SiO_x ($x \approx 2$) layer in air.

F5.24

DEVELOPMENT OF SILICON-BASED UV PHOTODETECTOR PROTOTYPES USING PHOTOLUMINESCENT NANO-CRYSTALLINE SILICON OVERLAYERS. Carlos Navarro, Luis F. Fonseca, Guillermo Nery, O. Resto, and S.Z. Weisz, Dept of Physics, University of Puerto Rico, San Juan, PR.

Commercial silicon-based photodetectors reported maximum photoresponse at wavelengths around 750nm and a significant reduction of this response when approaching the UV region. At the same time nanocrystalline silicon films can be prepared with high transparency above 650nm and highly absorbing for UV radiation. The absorbed UV radiation produces visible emission with a maximum that can be adjusted in frequency according to the synthesis parameters. The preparation details and properties of several silicon-based photodetector prototypes using nanocrystalline silicon overlayers with enhanced UV photoresponse are reported. In particular a prototype with porous silicon/n-type silicon/p-type

silicon/p -silicon/metal configuration and another with Eu-doped silicon-silicon dioxide/n-type silicon/p-type silicon/p -silicon/metal configuration are discussed in detail.

F5.25

METAL/PS/c-Si AND METAL/n-PS/p-PS/p-c-Si PHOTODETECTORS BASED ON POROUS SILICON. Leonid A. Balagurov, Sergei Ya. Andrushin, Vladimir S. Kasatochkin, Dmitrii G. Yarkin, State Institute of Rare Metals, Moscow, RUSSIA; Sue C. Bayliss, Bayram Unal, Solid State Research Centre, Faculty of Applied Sciences, De Montfort University, Leicester, UNITED KINGDOM.

Metal/p-PS/p-c-Si and metal/n-PS/p-PS/p-c-Si photodetector structures were fabricated and investigated. Metal/p-PS/p-c-Si porous silicon (PS) based photodiodes with top grid metal contact demonstrate quantum efficiency of photosensitivity up to 0.7-0.8 in visible range of spectra, detectivity up to $6 \times 10^{11} \text{ cmHz}^{1/2}/\text{W}$ and response time less than 2 ns. Three types of metal/n-PS/p-PS/p-c-Si device structures were fabricated: with ring metal contact, mesa structures and device structures with safeguard rings. For fabrication of the last type of device structures the SiO_2 and Si_3N_4 layers were deposited on the top of p-type c-Si substrates. Phosphorus diffusion was made for formation of c-Si n^+/p junction in open windows of these structures at the depth of 1 μm . For elimination of the leakage current in inverse layer of the substrate appearing due to positive charge of SiO_2 layer p^+ safeguard rings (of square shape) were formed around the device area. Then PS layer with overall thickness of 2-4 μm was formed in open windows. Finally upper metal contact was made by vacuum deposition method. It was obtained that such device structures with safeguard rings possess sufficiently low reverse currents (of $\approx 10^{-8} \text{ A/cm}^2$) as compared to other types of device structures that leads to low noise parameters and high detectivity of photodetectors. Based on the reverse current value and using quantum efficiency of 0.7 for such type of structures, detectivity value of $6.4 \times 10^{12} \text{ cmHz}^{1/2}/\text{W}$ was obtained. Unlike metal/p-PS/p-c-Si device structures metal/n-PS/p-PS/p-c-Si photodetectors are also characterised by photosensitivity that does not depend on the reverse bias.

F5.26

TRANSPORT OF CARRIERS IN THIN METAL/PS/c-Si STRUCTURES BASED ON POROUS SILICON. Leonid A. Balagurov, Elena A. Petrova, Dmitrii G. Yarkin, State Institute of Rare Metals, Moscow, RUSSIA; Sue C. Bayliss, Bayram Unal, Solid State Research Centre, Faculty of Applied Sciences, De Montfort University, Leicester, UNITED KINGDOM.

Metal/PS/p-c-Si structures with relatively thin (1 μm) and high porosity porous silicon (PS) layers were made on moderately and highly resistive substrates. Current-voltage (I-V) and impedance measurements at different temperatures were used for investigation of transport of charge carriers in these structures. Exponential forward bias I-V dependencies for both types of structures spread over several orders of magnitude with low value of ideality factor (close to 2) and have activation temperature dependencies with an activation energy equal to half of the c-Si band gap. Reverse current have a square root dependence on the bias and the activation energy equal to half of c-Si band gap. Therefore it was concluded that generation and recombination of carriers in the depletion region of c-Si substrate determines the reverse and forward currents in thin PS-based device structures. By the analogy to Metal/PS/p-c-Si structures made on moderately doped substrates current rectification for device structures made on highly resistive substrates is found to be caused by the potential barrier in the substrate at PS/c-Si heteroconnection. It was shown that large area spreading current exists in structures made on highly resistive substrates, that appears due to highly conductive inverse (n-type) layer formed in c-Si substrate at the PS/c-Si heterojunction. Spreading effect leads to high reverse current and high capacitance of device structures. Resistivity of the surface channel was found.

F5.27

QUANTUM EFFECTS ON THE DIELECTRIC FUNCTION OF POROUS SILICON. Miguel Cruz, ESIME-UC, IPN, Mexico City, MEXICO; Chumin Wang, IIM-UNAM, Mexico City, MEXICO; Yuri Rubo, Julia Tagüeña-Martínez, CIE-UNAM, Temixco, Mor., MEXICO.

A detailed study of the dielectric function of porous silicon by using a supercell tight-binding sp^3s^* model [1] is presented, in which the pores are columns dug in crystalline silicon and the dangling bonds are saturated by hydrogen atoms. The results of the imaginary part of the dielectric function for the case of 50% porosity are compared with those obtained from the effective medium theory, where the remarkable quantum effects are observed and they are essential for explaining the experimental data. On the other hand, the key participation of the hydrogen atoms in the optical properties of

porous silicon is also analyzed. In particular, a dramatic variation of the dielectric function with the hydrogen concentration is found. The presence of the hydrogen atoms on the enormous surface of the porous silicon causes a significant redistribution of charges in this material, which is particularly important for the dielectric function. [1] M. Cruz, *et al.*, Phys. Rev. B **59**, 15381 (1999).

F5.28

THE EFFECT OF SURFACE ROUGHNESS ON PHOTO-LUMINESCENCE OF POROUS SILICON. Shunsuke Ogawa, Nobutomo Uehara, Masato Ohmukai and Yasuo Tsutsumi, Akashi College of Technology, Hyougo, JAPAN.

We studied the effect of surface roughness of Si wafers on porous silicon by means of photoluminescence (PL), Fourier transform infrared (FTIR) absorption and Raman spectroscopy. We prepared several kinds of Si wafers with a different surface roughness, and then the anodization was performed at a same condition. PL spectra show a blue shift with increasing surface roughness. The particle size of porous silicon nanostructure becomes smaller with increasing surface roughness at the same time. On the other hand, FTIR absorption spectra show no difference regardless of surface roughness. As a result, we suggest that the mechanism for light emission from porous silicon can be explained by quantum effects in silicon nanocrystallites.

F5.29

PHOTOLUMINESCENCE FROM POROUS SILICONS PREPARED BY PHOTOELECTROCHEMICAL ETCHING OF N-TYPE SINGLE CRYSTALLINE SILICON AT VARIOUS CONDITIONS. Chi-Woo Lee, Buem-Suck Kim, Dong-Il Kim, Nam-Ki Min, College of Sciences and Technology, Korea University, Jochiwon, Choongnam, KOREA.

Since the visible photoluminescence from photoelectrochemically anodized porous silicon materials was first observed at the room temperature by Canham in 1990, it has been the subject of considerable interest to develop the materials as silicon-based optoelectronic media. A porous silicon optoelectronic circuit in which a silicon bipolar transistor drives a porous silicon light-emitting diode integrated on the same wafer has been demonstrated. The electro-luminescence observed by utilizing porous silicon diode structures, however, has to be improved in its efficiency and durability to be used as a practical device. The luminescent porous silicon has been usually formed by photoelectrochemical methods in ethanolic solutions of aqueous hydrofluoric acid, but the experimental factors involved are not fully understood. Well-defined photoelectrochemical conditions to produce light-emitting porous silicon materials would be required to fabricate possible well-behaved silicon-based optoelectronic devices. In a previous work, we reported that the micro-porous layer was thickened with the total charge increased but the nano porous silicon remained little changed based on scanning electron microscopic observations. In the present work, we investigated the influence on photoluminescence of the experimental factors in producing them by photoelectrochemical methods. The results show that the characteristics of current-potential as well as chronoamperometric curves strongly depended on the experimental factors involved. Photoluminescence spectra depended on the applied potential, the intensity and wavelength of illumination, and the doping concentration of bulk silicon. When the applied potential and the illumination wavelength increased, the photoluminescence shifted to longer wavelength. However, when the HF concentration increased, the photoluminescence spectra changed little. Multiply-peaked photoluminescence spectra were obtained with the porous silicon produced from the silicon wafer with high doping concentration at some conditions.

F5.30

IDENTIFICATION OF THE LUMINESCENCE CENTER OF POROUS SILICON UNDER LOW TEMPERATURE THERMAL OXIDATION. Kazuo Goda, Meisei Univ, Dept of Physics, Tokyo, JAPAN; Ryuji Tanaka, Koyo Electronics Industries Co. Ltd; Yamanashi, JAPAN; Yukako Honda, Kazuhisa Inoue, Meisei Univ, Dept of Physics, Tokyo, JAPAN; Hideki Ohno, Tokyo National College of Technology, Dept of Physics, Tokyo, JAPAN.

Since the discovery of the efficient photoluminescence (PL) from porous silicon (PS) in 1990, most of the studies have been directed at understanding the mechanism of the PL, especially finding the origin of the light emission. Many researchers are investigating oxidation process of the PS because the PL properties are influenced by the process. In this paper, the relationship between structure and PL spectrum under initial oxidation of inner surface of PS heated at low temperatures (150, 200, 250°C) in air was investigated using an infrared (IR) spectroscopy and PL measurements. The IR measurements show that the IR absorption peaks for Si-H stretching band (2050~2150 cm^{-1}) shift to the higher energy side due to Si-O-Si-H stretching band (2100~2300 cm^{-1}) with increasing thermal oxidation time. On the other hand, the peak top of PL spectrum

shows a blue shift from 820 nm to 710 nm with the oxidation time. The observed blue shift of the PL spectrum is due to the decrease of the initial PL peak intensity at 820 nm and the increase of that at 710 nm. Moreover, the peak top intensities of the PL spectra at 820 nm and 720 nm depend clearly on the amounts of the Si-H bonds and Si-O-Si-H bonds, respectively, with the oxidation time. These results indicate that luminescence center (LC) for as-prepared PS is ascribed to complexes including Si-H bonds and LC for oxidized PS under the oxidation process at low temperatures is to complexes including Si-O-Si-H bonds covering the inner surface.

F5.31

COMPARATIVE SEM AND CATHODOLUMINESCENCE MICROANALYSIS OF POROUS GaP STRUCTURES. M.A. Stevens Kaleff, Univ of Technology, Microstructural Analysis Unit, Sydney, AUSTRALIA; S. Langa, I.M. Tiginyanu, Technical Univ of Moldova, Laboratory of Low-Dimensional Semiconductor Structures, Chisinau, MOLDOVA; J. Carstensen, M. Christophersen, H. Föll, Christian-Albrechts Univ, Materials Science Dept, Kiel, GERMANY.

Depending on etching conditions, electrochemical dissolution of n-GaP crystalline substrates in electrolytes based on sulfuric acid was found to result in the formation of porous structures with different morphologies. In particular, at anodic current densities below a threshold value the pores grow along specific crystallographic directions. For example the preferential pore growth is in the (111) direction for (111)-oriented GaP. We show that alignment of pores along a definite crystallographic direction induces an artificial optical anisotropy. Scanning Electron Microscope (SEM) images of (100)-oriented n-GaP show that the pores branch and form porous domains, both individual pores and domains being separated by walls with characteristic dimensions of twice the thickness of the surface depletion layer. At high anodic current densities ($\sim 100 \text{ mA/cm}^2$) the formation of the so-called current-line oriented pores was observed. Such pores have no specific crystallographic orientation and their morphology reflect the current flow during the anodization process. We present the results of a comparative study of emission characteristics and morphology features of the same areas of layers, free-standing membranes and heterostructures based on porous GaP. Top and cross-sectional views of the spatial distribution of micro-cathodoluminescence (CL) evidenced the dependence of the emission intensity upon the degree of porosity and type of morphology. SEM images and the spatial and spectral distribution of CL measured at accelerating voltages 15-30 keV in the temperature interval from 80 to 300 K are discussed taking into account possible electrochemical dissolution mechanisms of gallium phosphide as well as effects related to surface passivation.

F5.32

TESTING OF POROUS SILICON MEMBRANES AS A NOVEL HUMIDITY SENSOR. Luigi Quercia, Marco Della Noce, Vera La Ferrara, Girolamo Di Francia, Portici Research Center, ENEA, Portici, ITALY.

A new gas sensor device based on a porous silicon membrane has been fabricated. The sensible membrane has been bonded to a $1 \text{ cm}^2 \text{ Al}_2\text{O}_3$ substrate [1], where electrical contacts have been previously deposited by vacuum evaporation. In this work we present preliminary results of DC measurements showing a good response of this device to humidity gradients. Humidity sensors must satisfy a number of requirements, among which a short response time, a high sensitivity, negligible hysteresis and a possibly large operating range for both humidity and temperature. Many materials have been used. Like ceramics, polymers, porous Al_2O_3 and eventually porous silicon [2]. In this frame, the most striking property of our device is its fast and full recovery after exposure to humidity levels up to 90%. The recovery time, $t < 16 \text{ s}$, is limited by experimental conditions and is, anyway, much shorter compared a commercial device, $t = 122 \text{ s}$, obtained in the same conditions. Moreover, the new fabrication process used to realize the sensor merges the advantages typical of porous silicon with thin film ones, by means of a simple process. Further investigations will verify the long term stability of the device, its selectivity and response to low relative humidity. Measurements of porosity size distribution will be performed in order to establish relations between porous silicon membrane morphology and device properties. Such studies will help in understanding the sensor working mechanism tentatively attributed to changes in the percolative paths. References [1] G. Di Francia, L. Quercia, R. Vitiello, F. Roca, D. Ninno, V. La Ferrara, G. Iadonisi, L. Lancellotti, G. Sberveglieri, P. Maddalena: "Metodo per la fabbricazione di dispositivi a stato solido" patent No Ge99A000146 deposited at Italian Patent Office on December 29th 1999. [2] Z.M. Rittersma PhD. Thesis: "Microsensors application of porous silicon", Shaker Publishing B.V., Maastricht (1999).

F5.33

NANOCRYSTALLINE Si VOID-COLUMN NETWORK THIN FILMS DEPOSITED BY HIGH DENSITY PLASMA:

APPLICATION TO HIGH SENSITIVITY AND ULTRA-FAST HUMIDITY MONITORING. A. Kaan Kalkan, Handong Li, Stephen J. Fonash, Nanofabrication Facility, The Pennsylvania State University, University Park, PA.

Deposited high porosity nanocrystalline Si films have been obtained by the combination of two extreme plasma conditions; (1) very low adatom mobility (obtained by low substrate temperature and reduced ion bombardment) and (2) highly reactive chemistry with a high density of hydrogen radicals (achieved by a high density plasma system). Under these conditions, a morphology results that is an array of nanometer-sized rodlike columns oriented normal to the substrate surface and situated in a void matrix. Porosity may be varied up to ~90% by varying the plasma power, which controls the nuclei density and thereby determines the average spacing between the columns as monitored by XRD, TEM, SEM, AFM and optical reflectance. These films can be deposited on plastic, glass, or metal foils and their use as humidity sensors has been demonstrated. The sensitivity is based on conductivity changes (up to 6 orders of magnitude) in response to increases in relative humidity (RH). Moreover, a very fast response has been observed, for example within 0.5 sec to an abrupt RH change of from 20% to 90%. The conductivity-RH behavior of these films shows variations, which can be correlated with nanostructure (e.g., average spacing between the columns). Also, these variations indicate that the dominant charge transport is limited by the dissociation of water into its ions at the column surfaces.

F5.34
ELECTROLESS DEPOSITION OF GOLD, PLATINUM, AND PALLADIUM NANOPARTICLES ONTO NANOPOROUS AND FLAT GERMANIUM (100) SURFACES. Lon A. Porter, Jr., Hee Cheul Choi, Jillian M. Buriak, Purdue University, Dept of Chemistry, West Lafayette, IN.

Monolayers films of gold, platinum, and palladium nanoparticles have been prepared as a result of the immersion of nanoporous and flat germanium (100) substrates into dilute, aqueous solutions of tetrachloraurate (III), tetrachloroplatinate (II), and tetrachloropalladate (II), respectively. The resulting monolayers are composed of metal nanoparticles, ranging in size from 25 to 100 nm, as confirmed by scanning electron microscopy (SEM). However, the sizes of the nanoparticles, and therefore the monolayer thicknesses, may be modulated by variation in substrate immersion times or solution concentrations. This method provides for the facile interfacing of metal nanoparticles with a group (IV) semiconductor. These metal nanoparticle monolayers, with such high surface areas, may prove to be attractive substrates suitable for a myriad of applications, ranging from catalysis to chemical sensing.

F5.35
HETEROJUNCTION-BASED TIN DIOXIDE-SILICON CHEMICAL SENSORS: BARRIER MODULATION AT THE TRIPLE CONTACT. Dario Narducci, Istituto Nazionale per la Fisica della Materia and Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY; Rossella Piagge, Siemens, Settimo M.se, ITALY; Monica Bollani, Consorzio Milano Ricerche, Milano, ITALY, Istituto Nazionale per la Fisica della Materia and Edifis, University of Aix-Marseille III, Marseille, FRANCE; Matteo Oldani, Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY.

Aim of this paper is to provide insights in the mechanism of transconductance modulation in Heterojunction-based Gas Sensors (HJGS's). HJGS's are a class of sensing devices based on the modulation of the barrier height close to the so-called triple contact point, i.e. the triple interface among the semiconducting substrate, the sensing film and the gas. The device considered in this paper is a nanocrystalline film of tin dioxide, grown by spray pyrolysis onto a Si (001) substrate. The film was structurally characterized by High-Resolution Transmission Electron Microscopy and by Nanodiffraction. Tin dioxide was found to grow as a columnar polycrystal, with an unusual preferential orientation along the (100) direction. Nanocrystals were found to have a cross-section of order 5 nm, extending for an overall length of about 50 nm. The HJGS was tested to detect CO in the ppm gas range. We found that the sensitivity of the sensor, defined as $\partial \ln \sigma / \partial p$ reverts its sign when using *p*- or *n*-type Si substrates. In view of the possible models of CO adsorption onto tin dioxide and of the known regime of conduction of the oxide itself we could conclude that the mechanism of gas sensing cannot be explained satisfactorily using the standard theory of surface barrier modulation. Instead, a model based on the modulation of the heterojunction barrier between the sensing film and the substrate must be advanced. The adsorption of CO onto the oxide grains (either specifically or aspecifically) provides an additional effect of band bending which could be successfully modelled through a two-dimensional simulation of the electronic structure at the heterojunction.

F5.36
SURFACE NANODEVICES FOR CHEMICAL SENSING. DETECTION OF GASEOUS MOLECULES BY USING ORGANIC MONOLAYERS COVALENTLY GRAFTED ONTO Si (001). Dario Narducci, Istituto Nazionale per la Fisica della Materia and Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY; Ahmed Charai, CP2M, Marseille, FRANCE; Monica Bollani, Cons. Milano Ricerche, Milano, ITALY, Istituto Nazionale per la Fisica della Materia, ITALY, and Edifis, University of Aix-Marseille III, Marseille, FRANCE; Rossella Piagge, Siemens, Settimo M.se, ITALY; Patrizia Bernardinello, Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY.

In this work we report about a novel class of chemical sensors based on the use of silicon surfaces engineered by grafting organic monolayers. An innovative way to dock aromatic molecules onto Si (100) surfaces has been developed, allowing the formation of direct Si-C bond under mild conditions. These systems were found to act as chemical sensors for gases. The new sensors were obtained by wet chemistry nucleophilic attack of aryl lithium compounds onto halogenated silicon surfaces. Infrared Multiple Internal Reflection experiments and High-Resolution Electron Energy Loss Spectroscopy analyses were used to confirm the formation of Si-C bonds. The devices were tested as gas sensors by measuring their electrical conductivity at 308 K in the presence of trace amounts of reactive gases in Ar. A comparative analysis of the sensor response for different aryl groups showed that functional groups modulate the interaction of the π -system with the gas molecules. A correlation between gas composition and surface conductance was found. Based upon computer simulations, a model could be advanced. We will demonstrate how the sensing mechanism is actually based upon the interplay of three different elemental processes: the activation of the organic molecules at the bare Si surface, the supramolecular interaction between the aromatic ring and the gas, and the consequent modulation of a depletion/accumulation layer at the Si surface, which can be held ultimately responsible for the conductivity modulation experimentally observed. The results obtained pave the way to the development of a new generation of sensing devices, coupling the sensing flexibility of organic chemistry with the structural order typical of single-crystal systems. Specifically, we will comment on the expected capability of these sensors to enhance the selectivity of gas sensing elements in complex gas mixtures, with a special emphasis for applications in the environmental control.

F5.37
INFLUENCE OF SURFACE CHEMICAL MODIFICATIONS ON ELECTRICAL PROPERTIES OF SEMICONDUCTOR NANOMATERIALS: FTIR INVESTIGATION OF TIN OXIDE. Marie-Isabelle Baraton, SPCTS-UMR 6638 CNRS, University of Limoges, Limoges, FRANCE; Lhadi Merhari, Ceramec R&D, Limoges, FRANCE.

It is well-known that surface chemistry is a critical parameter to be controlled during the processing of nanoparticles as it affects properties such as dispersion or sintering. But, surface modifications of semiconductor materials have even more drastic consequences because changes are observed in work function and bulk electrical properties. Therefore, any tailoring of semiconductor surface chemistry must be controlled in close connection with the electrical properties. This becomes critical in the case of gas sensors in which the surface chemical reactions at the gas/sensor interface are directly responsible for the electrical conductivity variations, that is the gas detection mechanism. In this work, surface chemical modifications of a tin oxide nanopowder will be first analyzed by Fourier transform infrared (FTIR) spectrometry. Then, it will be demonstrated that FTIR spectrometry allows the simultaneous investigation of the surface chemical modifications and of their consequences on the electrical conductivity of the semiconductor material. The formation of surface species under different environments will be discussed as a function of the surface chemistry and of the electrical conductivity changes. This work has been funded by the European Commission under the BRITE EURAM III program (contract number BRPR-CT95-0002).

F5.38
TIN-INDIUM OXIDE NANOCOMPOSITES FOR GAS SENSOR APPLICATIONS. Justin T McCue, Jackie Y. Ying, Dept of Chemical Engineering, MIT, Cambridge, MA.

The use of gas sensors for detecting chemical species is important for numerous industrial and consumer processes. Dramatic improvements in industrial process control have been made with the aid of gas sensors. With increasing use of automation, the market size for gas sensors is expected to significantly increase over the next few years. Conventional gas sensors are limited by several characteristics. First, gas sensors tend to have poor long-term stability and response reproducibility from one device to the next. Secondly, the selectivity for various gases that come in contact with the sensor is poor.

Current sensors also suffer in response time. The development of highly selective and thermally stable semiconductor oxide gas sensors is the focus of our research. Novel tin oxide-indium oxide ($\text{SnO}_2\text{-In}_2\text{O}_3$) semiconductor nanocomposites have been designed and synthesized via wet-chemical approaches. They display superb thermal stability and sensitivity to ppm levels of CO and NO_x . By controlling the $\text{SnO}_2\text{-In}_2\text{O}_3$ microstructure and composition, and by introducing active dopants, sensors with excellent selectivity for CO and NO_x have been successfully attained and optimized.

F5.39

NANOSTRUCTURED TiO_2 AND $\text{W}:\text{TiO}_2$ THIN FILMS BY A NOVEL SOL-GEL PROCESSING FOR ALCOHOL SENSING DEVICES. Carlotta Garzella, Elisabetta Comini, Ezio Tempesti, Giorgio Sberveglieri, INFN and Brescia Univ, Dept of Chemistry and Physics for Engineering and Materials, Brescia, ITALY; Cesare Frigeri, CNR-MASPEC Inst, Parma, ITALY.

TiO_2 and $\text{W}:\text{TiO}_2$ thin films have been prepared by a chemically modified sol-gel technique, that implies hydrolysis and condensation of tetraethylortotitanate in the presence of a polymer dissolved in ethanol. The technique results in an effective method for performing nanosized structurally stable titanium dioxide thin films. The role of the polymer as "steric stabilizer" during the film structural evolution and the interesting alcohol sensing performances have been reported in a previous paper [1]. In this work we undertake an experimental study to investigate the doping effects on structural features and sensing characteristics of TiO_2 . To our knowledge this dopant has never been studied for sol-gel titanium dioxide in the gas sensor field. TiO_2 -polymer composite films were deposited by dip-coating; annealing at 500°C resulted in the complete removal of organic phase, as checked by TGA/DTA analysis. For the doping tungsten(V) ethoxide was used in concentration that led to a final W/Ti atomic ratio 1/33 and 5/33. The morphological and structural characteristics of thin films have been studied through microRaman, XRD, SEM and TEM analyses. The W contents were obtained by Microprobe analysis. Both doped and undoped oxide resulted in anatase form and no evidence of W-O oxides resulted. The microstructural comparison between doped and undoped TiO_2 layers highlights that a finer nanostructure can be obtained by doping. Regarding the alcohols sensing properties, the response toward alcohols is always enhanced with the doping content. This behaviour could be ascribed to the finer granularity obtained, that implies a higher surface area to volume ratio. $\text{W}:\text{TiO}_2$ sensors can detect very well ethanol concentration required for breath analysers. [1] C. Garzella, E. Comini, E. Tempesti, C. Frigeri and G. Sberveglieri, TiO_2 thin films by a novel sol-gel processing for gas sensor applications, to be published in Sens. & Act. B 3429 (2000).

F5.40

NANOSIZED MO-W-O THIN FILM GAS SENSOR FOR ENVIRONMENTAL MONITORING. Elisabetta Comini, Giorgio Sberveglieri, INFN and Dept. of Chemistry and Physics, Brescia University, Brescia, ITALY; Vincenzo Guidi, Matteo Ferroni, Leobaldo Casarotto, INFN and Dept. of Physics, Ferrara University, Ferrara, ITALY.

Research on novel materials suitable for gas-monitoring using thin-film technology plays essential role to achieve highly sensitive and selective long-term-operating sensors. WO_3 was recently recognized as a sensor for NO_x with fairly good response owing to exaggerated grain growth [1]. Addition of another element may result in a finer grain of the layer. Molybdenum was chosen because its oxides exhibit sensing capability [2] and it has similar ionic radius to Tungsten. We have deposited thin films of Mo-W-O by r.f. reactive sputtering from a Mo/W target 20/80 in weight. We have first characterized the layers, from the electrical and structural point of view, just after the deposition. Different annealing treatment of the films were performed between RT and 800°C . The layers were characterized by electron microscopy techniques. All the films are very dense with high surface-to-volume ratio. The annealing treatment influences the structure of the films and in turn the sensing behavior: we have comparatively studied the electrical performance of the layers to either oxidizing or reducing gases such as NO_2 and CO in the ranges of interest for environmental monitoring. The gas tests were made at constant relative humidity and constant operating temperature fixed at values from 200 to 500°C . Preliminary measurements show that the thin films obtained are capable to sense CO at concentrations lower than 50 ppm. No effect of poisoning of the surface was recorded and the responses were reproducible. The dynamic of these thin films is very fast, both response and recovery time are in the range of 30 to 90 s. The response of these sensors is high and fast enough to be applied for environmental monitoring. [1] G. Sberveglieri et al., WO_3 sputtered thin films for NO_x monitoring, S&A B, 26-27, 89, 1995 [2] M. Ferroni et al., Characterization of a molybdenum oxide sputtered thin film as a gas sensor, Thin Solid Films, 307, 148-151, 1997.

F5.41

ANALYSIS OF Pt-NANOPARTICLES EMBEDDED ON CRYSTALLINE TiO_2 STUDIED BY HIGH RESOLUTION ELECTRON MICROSCOPY. Jordi Arbiol, Anna Ruiz, Albert Cirera, Francisca Peiró, Albert Cornet, Joan Ramon Morante, Barcelona Univ, Dept of Electronics, Barcelona, SPAIN; Abdelhadi Alimoussa, Marie-José Casanove, CEMES/CNRS, Toulouse, FRANCE.

In this work, we studied the Pt particles embedded on crystalline TiO_2 nanopowders used as a semiconductor gas sensor. As it is well known, metal nanoparticles distributed on TiO_2 surface can improve dramatically the reaction rate and selectivity of reaction in gas sensing. We prepared a wide set of TiO_2 samples grown at different temperatures and with different nominal Pt concentration. The aim of this study was to analyse the Pt distribution on TiO_2 surface (density of Pt, particle size distribution, etc), as well as the different Pt phases (metallic Pt, PtO and PtO_2) existing in our samples. We used high resolution electron microscopy (HRTEM) as a powerful tool to study Pt particles morphology. The HRTEM images were contrasted with computer simulations to confirm the results obtained. After this study we could choose the a priori best Pt/ TiO_2 sample for gas sensing applications and discard those that presented the worst characteristics.

F5.42

A NEW METHOD TO CONTROL PARTICLE SIZE OF SnO_2 NANOPARTICLES FOR GAS SENSOR APPLICATION. Edson R. Leite, I.T. Weber, E. Longo, LIEC-DQ-UFSCar- São Paulo, BRAZIL; J.A. Varela IQ-UNESP-Araraquara, São Paulo, BRAZIL.

This work described the synthesis of a nanostructured material with good potential for gas sensor applications. Nb_2O_5 -doped SnO_2 particles with a narrow particle size distribution and an average 8nm particle size were obtained. A novel approach was used to control particle size during the synthesis of SnO_2 processed by the polymeric precursor method. This new approach is based on the control of particle growth during synthesis through the use of dopants such as Nb_2O_5 . This work involves important aspects that can be applied to the synthesis of nanostructured materials prepared by the polymeric precursor method. The addition of Nb_2O_5 can modify the rate of nucleation during the SnO_2 crystallization process, promoting a high rate of nucleation. After nucleation, Nb_2O_5 can inhibit particle growth, thus preventing the formation of necks between particles and the process of coalescence. Preliminary gas sensing measurements are performed and it is demonstrated that the response time of the Nb_2O_5 -doped SnO_2 is faster than that of the undoped material.

F5.43

THE GAS RESPONSE TO OXIDIZING GASES OF WO_3 THIN FILMS SENSORS PREPARED BY THERMAL EVAPORATION TECHNIQUES. Carlo Cantalini, L'Aquila Univ, Dept. of Chemistry and Materials, L'Aquila, ITALY; S. Santucci, M. Passacantando, L'Aquila Univ, Dept. of Physics, L'Aquila, ITALY.

WO_3 thin films have been deposited on Si/Si 3N_4 substrates provided with platinum interdigital electrodes by Vacuum Thermal Evaporation (VTE) techniques and annealed at temperatures between 300°C and 500°C for 1 to 240 hours in static air. The morphology, crystalline phase and chemical composition of the films have been characterised using SEM, glancing XRD, XPS and SAM techniques. The evolution of the microstructure (Surface roughness, crystallite sizes and chemical composition) has been related to the annealing time and temperature. The thermal annealing process has been optimised in order to stabilize the microstructure and, eventually, the electrical properties of the material, in terms of gas sensitivity, selectivity and Stability (SSS) properties. The electrical response has been measured exposing the films to NO_2 (0.2 - 2 ppm), Cl_2 (0.1 to 1 ppm) NO_x (27 ppm NO and 1 ppm NO_2) at different operating temperatures ranging between 100 and 250°C and different humid air conditions between 20 to 90% Relative Humidity. The gas response to NO_2 and Cl_2 has been found to be at maximum at 180°C . At this temperature and 1 ppm NO_2 or 1 ppm Cl_2 the measured gas response $S = \text{RG} / \text{RA}$ are $S = 30$ and $S = 35$ respectively. The gas response S, has been resulted to be influenced by the annealing time. No cross sensitivity have been found by exposing the WO_3 films to CO and CH_4 . Negligible H_2O cross to NO_2 and Cl_2 response has resulted in the 20% - 90% RH range.

SESSION F6: SILICON QUANTUM DOT PREPARATION

Chair: David J. Lockwood
Tuesday Morning, November 28, 2000
Constitution A (Sheraton)

8:30 AM F6.1

RAMAN SPECTROSCOPY OF Si NANOCRYSTALS IN NANO-

CRYSTALLINE Si SUPERLATTICES: SIZE, SHAPE AND CRYSTALLOGRAPHIC ORIENTATION. G.F. Grom, P.M. Fauchet, and L. Tsybeskov, Dept of Electrical and Computer Engineering, Univ of Rochester, Rochester, NY; H.J. Labbe and D.J. Lockwood, Inst for Microstructural Sciences, National Research Council, Ottawa, CANADA; B.E. White Jr., Motorola, Digital DNA Laboratories, Austin, TX.

Precise control over structural parameters such as size, shape, and crystallographic orientation of Si nanostructures and their microelectronics processing compatibility are required for reliable modelling and fabrication of nanoscale Si-based devices. In this work, Raman spectroscopy is used to study these structural parameters of Si nanocrystals formed by solid phase crystallization of amorphous Si/SiO₂ superlattices (SLs) grown by radio-frequency sputtering. Broadening, position and intensity ratios of the first and second order Raman scattering peaks indicate the presence of nanoscale Si objects with a degree of disorder (grain boundaries) and strain (Si/SiO₂ interfaces). Shapes of Si nanocrystals sandwiched between SiO₂ layers strongly influence the Si/SiO₂ interface roughness, which is inferred from the folded acoustic phonon scattering intensities. The averaged crystallographic orientation of Si nanocrystals is determined by polarized Raman analysis. The rectangular-shaped nanocrystals, as confirmed by transmission electron microscopy studies, exhibit [111] preferred crystallographic orientation along the SL axis due to orientation-dependent crystallization rates. These results demonstrate with certainty that the control over Si nanocrystals structural parameters is attainable using solid phase crystallization of nanometer-thick amorphous Si layers.

8:45 AM F6.2
NUCLEATION AND CRYSTALLIZATION OF ULTRA THIN FILMS - A NEW CRYSTALLIZATION MODEL. Margit Zacharias, Peter Streitenberger, Institute of Experimental Physics, Otto-von-Guericke University, Magdeburg, GERMANY.

We show the exponential scaling of the crystallization temperature and the layer thickness for various superlattices with oxide interfaces. Using an empirical model this behaviour could be reduced to basic material properties like the bulk amorphous crystallization temperature and the melting point. A new crystallization model is presented which takes into account the different interface energies and materials. Using our new model the exponential increase of the crystallization temperature with decreasing layer thickness could be derived in agreement to the empirical model and the experimental data. This has been achieved by introducing the novel concept of an effective interface energy that interpolates between the true oxide/crystalline interface and the true amorphous/crystalline interface energy by means of an ordering parameter varying continuously with interface spacing. The model yields a lower bound for the layer thickness below which no crystallization can occur for the system in good quantitative agreement with our experimental observation. The evidence of a critical crystallization radius and the influence of a non stoichiometric interface are discussed.

9:00 AM F6.3
OXIDATION OF SILICON NANOCRYSTALS. Kristen C. Smith, J.M. White, The University of Texas at Austin, Department of Chemistry, Austin, TX and Digital DNA Labs, Motorola SPS, Austin, TX; Sucharita Madhukar, Ramachandran Muralidar, Michael Sadd, David O'Meara, Bruce White, Bob Jones, Materials and Structures Laboratory, Digital DNA Labs, Motorola SPS, Austin, TX.

Silicon nanocrystals are of interest due to their potential importance in microelectronic [1] and optoelectronic [2] devices. For example, replacing the traditional poly Si floating gate in flash memories with nanocrystals produces more reliable and lower power devices than traditional flash technology [1]. Controlled oxidation of Si nanocrystals is desirable in the processing of Si quantum dots for nonvolatile flash memory devices. Oxidation can be used to control nanocrystal size and achieve good interface quality between the Si nanocrystal and SiO₂ dielectric layer in nanocrystal based flash memory. Although it is known that oxidation kinetics of Si nanocrystals differs from planar surfaces, there are not many reports on the oxidation behavior of Si nanocrystals. In this study, we report on the oxidation of silicon nanocrystals deposited by low-pressure chemical vapor deposition in different oxidizing environments. In the literature, it has been reported that a Si column or dot when oxidized below the viscoelastic temperature of SiO₂ (950°C) will self-limit to a Si core size that is dependent on the oxidizing conditions and the initial nanocrystal size. This self-limiting phenomenon is said to occur because of compressive stress in the oxide layer, which limits the diffusion of the oxidizing agent through the SiO₂ to the Si-SiO₂ interface. This compressive stress is due to the difference in the density of the oxide and the Si and is enhanced by the radius of curvature of the dot. This self-limiting oxidation phenomenon has been studied experimentally using microscopy techniques and the

effect of the constrained structure will be characterized. [1] S. Tiwari, The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface - 3, H.Z. Massoud, E.H. Poindexter, and C.R. Helms, Editors, Proc. Vol. 96-1, The Electrochemical Society, Pennington, NJ, 1996, 250. [2] A.G. Nassiopoulou and S. Grigoropoulos, Appl. Phys. Lett. 69, 1996, 2267.

9:15 AM F6.4
FABRICATION OF SILICON NANO-CRYSTAL DOTS ON SiO₂ BY ULTRAHIGH-VACUUM CHEMICAL VAPOR DEPOSITION. Takayuki Kawashima, Masato Oishi, Supika Mashiro, Junro Sakai, Semiconductor Equipment Div, Anelva, Tokyo, JAPAN; Sucharita Madhukar, Bich-Yen Nguyen, Bruce E. White, Motorola, Materials and Structures Laboratories, Austin, TX.

In this work, fabrication of nano-scale hemispherical shaped Si crystal dots on SiO₂ in a Cold-wall Ultrahigh-Vacuum Chemical Vapor Deposition (UHV-CVD) system is demonstrated. Si₂H₆ gas was used as pre-cursor for this work. In our system, nucleation, growth, and coalescence phases of nano-crystal dots on SiO₂ were found to be related with the optical pyro-meter read-out curve. Thus, optimum irradiation time to obtain highest dot density without coalescence were decided by using the optical pyro-meter, for every gas irradiation condition. Dependence of the optimum gas irradiation time, dot diameter and dot density on gas flowrate and wafer temperature was investigated. Dot diameter was found to be controlled by wafer temperature and Si₂H₆ flowrate, but not by the irradiation time, before coalescence phase. During nucleation and growth phases, dot diameter increased by increasing wafer temperature or decreasing gas flowrate. Dot density decreased by same kind of condition changes as to diameter. Optimum irradiation time was prolonged by decreasing wafer temperature or gas flowrate. Finally, a reproducible process of forming non-coalesced, small-size, and high-density Si nano-crystal dots of about 7nm in diameter with density of 6E11 dots/cm² were obtained. Typical process time to get such dot formation characteristics was about 2 minutes, which were long enough for ensuring precise repeat of process.

9:30 AM *F6.5
THE NOVEL SYNTHESIS OF SILICON AND GERMANIUM NANOCRYSTALLITES. Susan M. Kauzlarich, Qi Liu, Department of Chemistry, University of California at Davis, Davis, CA; Howard W.H. Lee, Boyd Taylor, Lawrence Livermore National Laboratory, Livermore, CA.

Interest in the synthesis of semiconductor nanoparticles has been generated by their unusual optical and electronic properties arising from quantum confinement effects. We have synthesized Silicon and Germanium nanoclusters by reacting Zintl phase precursors with either silicon or germanium tetrachloride or with bromine in various solvents. Strategies have been investigated to stabilize the surface, including reactions with RLi and MgBrR (R = alkyl). This synthetic method produces group IV nanocrystals with passivated surfaces. These particles have been characterized using HRTEM, FTIR, UV-Vis, solid state NMR, and fluorescence. The synthesis and characterization of these nanoclusters will be presented.

SESSION F7: SILICON QUANTUM DOT DEVICES III

Chair: Leonid Tsybeskov
Tuesday Morning, November 28, 2000
Constitution A (Sheraton)

10:30 AM *F7.1
THEORY OF ELECTRONIC TRANSPORT IN SILICON NANOSTRUCTURES. Y.M. Niquet, C. Delerue, G. Allan, IEMN - Dept. ISEN, Lille, FRANCE; M. Lannoo, L2MP, Marseille, FRANCE.

Progress made in the growth of semiconductor quantum dots opens the door to exciting studies of artificial atoms where the electrons are confined in the three directions of space. These studies reveal rich optical and transport properties. If optical spectroscopy probes transitions between valence states and conduction states, transport measurements, on the other hand, can probe separately the discrete states in the bands. Recent experiments based on current or tunneling spectroscopy have been made on semiconductor nanostructures where both the effects of quantum confinement and Coulomb interaction become strong. The theoretical description of these systems requires atomistic approaches to calculate the electronic structure which must be self-consistently solved with the Poisson equation to calculate the electrostatic potential in the system. Our main aim in this talk will be to review the relevant theory on these problems. We will concentrate on empirical tight binding methods. Results of calculations on Si nanostructures will be presented and compared to experiments. A comparison will be made between Si and InAs to show the influence of the electronic structure on I(V) characteristics. Finally we will discuss

the physical and material parameters which determine the charging energy.

11:00 AM F7.2

CHARGING AND DISCHARGING OF SINGLE SILICON NANOCRYSTALS: MEASUREMENT AND MODELING. L.D. Bell, Jet Propulsion Laboratory, Caltech, Pasadena, CA; E.A. Boer, M.L. Brongersma, H.A. Atwater, Caltech, Thomas J. Watson Laboratory of Applied Physics, Pasadena, CA; M. Ostraat, R.C. Flagan, Caltech, Dept. of Chemical Engineering, Pasadena, CA.

Nanocrystal nonvolatile floating gate memories are a good candidate for a commercial nanoparticle device—initial results suggest they are fast, more reliable and consume less power than conventional floating gate memories. To investigate the charge trapping characteristics of nanoparticles suitable for such devices, we have developed an aerosol method for the synthesis and size classification of silicon nanocrystals with ~10-15% control of size in the 7-30 nm size range. We have used conducting-tip atomic-force microscopy (AFM) to spatially and electronically manipulate single silicon nanocrystals on an insulating substrate (a 100 nm thermally grown SiO₂ layer on silicon). By applying voltages of 20-40 V to a conducting AFM tip and contacting the silicon nanoparticle, we have injected charges on the order of 10-100 electrons. We have also used the AFM to observe the discharging of the nanoparticle as a function of time in a dry, nitrogen-purged atmosphere. Typical discharge times range from 1000-10000 s. We have used a simple ('noncontact') and more complex ('tapping') model of the AFM interaction with the sample and electrostatic forces in order to estimate the amount of injected charge and to investigate the discharging dynamics. From the model, we estimate the sensitivity of this charge detection method to be on the order of ~3-5 electrons.

11:15 AM F7.3

ELECTRONIC TRANSPORT THROUGH ULTRASMALL Si NANOPARTICLES USING SCANNING TUNNELING MICROSCOPY: ZERO BIAS CONDUCTANCE. J. Therrien, G. Belomoin, S. Rao, and M.H. Nayfeh Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL.

Ultrasmall, uniform size (~1 nm), ultrabright Si nanoparticles are reconstituted on p- type, n- type Si, and on aluminum grounded substrates. Room temperature electronic transport through the particles is studied, using scanning tunneling microscopy. For p- type substrates, under dark conditions, there is a low visibility staircase structure in the I-V spectra at a spacing of ~0.45 eV. However, under light irradiation, we observe a highly visible regular structure, for negative tip biasing at ~1.0 eV spacing. The second series is discussed in term of light-induced hole states that otherwise are highly infrequent in ultrasmall Si particles, under standard low doping. Unlike the p-type case, the transport in the aluminum case exhibits differential conductance at zero bias that consists of a very sharp single peak, while in the n-type case we have a zero bias response that is split into two sharp peaks. The peaks are observed only after the tungsten tip is first biased at a voltage larger than 3.1 eV. We discuss the zero-biasing conductance in terms of magnetic-exchange coupling in a quantum dot coupled to leads, as in a Kondo effect.

11:30 AM F7.4

SINGLE ELECTRON CHARGING EFFECT IN INDIVIDUAL Si NANOCRYSTALS. Pascal Gentile, Noel Magnea, CEA-Grenoble, Dept. Recherche Fondamentale, Grenoble, FRANCE; Thierry Baron, INSA-Lyon, Labo. Phys de la Matiere, Villeurbanne, FRANCE; P. Mur, F. Martin, M.N. Semeria CEA-Grenoble, LETI, Dept. de Microelectronique, Grenoble, FRANCE.

We present a detailed study of the electronic properties of individual silicon nanocrystals(nc-Si) elaborated by Low Pressure Chemical Vapour Deposition on 1.2 nm thick SiO₂ grown on Si (001) wafers. The combination of ultra thin oxide layers and highly doped substrates allows to image by Scanning Tunneling Microscopy the hemispherical dots. By analysing the STM images, we deduce a size distribution which ranges between 3 and 6 nm with a surface density around 10E12/cm². Spectroscopic studies of single dots are made by recording the I-V curves on the Si nanocrystal accurately selected with the metallic tip. In this double tunnel junction configuration, the capacitance and the resistance of the first junction are defined by the distance between the tip and the Si dot. The characteristics of the second junction are imposed by the thickness of the thin SiO₂ layer and the surface contact of the dots on SiO₂. We will show I-V curves of single dot exhibiting coulomb blockade and resonant tunneling effects through quantum confined states. The first step-like structures appears on the I-V curve when the bias is high enough to allow the electron injection by resonant tunneling and to overcome the electrostatic energy to charge the dot with the first electron. Coulomb pseudo gaps -Ec- between 0.15 and 0.2 eV are measured for different dots. From the width-60 meV- and height-40 pA-of the staircase

observed at bias greater than Ec, capacitance of 0.5 to 1 aF and tunnel resistance of 3-5 E8 and 5-7 E9 Ohms are measured within the "orthodox" approximation for asymmetric junctions. These data will be confronted with the more realistic tight-binding calculations presented by C. Delerue et al. in this symposium.

11:45 AM F7.5

NANOCRYSTAL (NC) BASED NON-VOLATILE MEMORY DEVICES: IMPACT OF NC FABRICATION ON DEVICE CHARACTERISTICS. Jan De Blauwe, Marty Green, Tom Sorsch, Gary Weber, Jeff Bude, Andi Kerber, Fred Clemens, Young Kim, Lucent Technologies, Bell Labs, Murray Hill, NJ; Michele Ostraat, Richard C. Flagan, Harry A. Atwater, California Institute of Technology, Pasadena, CA.

We evaluate the impact of three nanocrystal fabrication processes on the electrical characteristics of 0.20µm, nanocrystal-based non-volatile memory (NVM) devices. The memory operation of this nanocrystal-based NVM device depends on charge storage, similar to conventional NVM devices. In the nanocrystal based NVM device, however, charge is not stored on a continuous poly-Si layer (so-called floating gate), but instead on a layer of discrete nanocrystals. Device performance and reliability are strongly dependent on nanocrystal layer properties (such as crystal size, size distribution, density, and co-planarity) and nanocrystal insulation. In addition, the nanocrystal layer fabrication technique has to be simple, 8" wafer compatible and well controlled. In this study, we have integrated nanocrystal layers in 0.20µm nMOS-FETs based on three nanocrystal fabrication processes. These techniques are:

- *LP-CVD deposition* of n-type doped nanocrystals (0.15 Torr, 580°C), combined with a post-deposition thermal oxidation step;
- *deposition of Si-rich oxide*, followed by a thermal anneal (30min, 1000°C) during which excess Si precipitates and forms the nanocrystals; and
- *formation of a nanocrystal aerosol* through the decomposition of silane at 950°C in an inert carrier gas, followed by an in-situ, pre-deposition thermal oxidation.

Dense ($5 \times 10^{11} \text{ cm}^{-2}$), nearly co-planar nanocrystal layers have been obtained in all three cases, and were investigated by cross-sectional transmission electron microscopy and photoluminescence characterization. Nanocrystal layers were deposited on a thermally-grown tunnel oxide ($t_{ox} = 40-70 \text{ \AA}$), and were encapsulated by a deposited high temperature oxide ($t_{hto} = 80-120 \text{ \AA}$; 800°C) via a SiH₄/N₂O chemical vapor deposition process. The devices can be programmed by using either Fowler-Nordheim (FN) tunneling or Channel Hot Electron Injection; uniform FN tunneling has been used as the erase mechanism. Threshold voltage windows in the range of 2-5V have been obtained for typical program/erase voltages and times, while only limited window closure is observed after 10⁵ program/erase cycles. Preliminary retention data indicate charge retention in excess of 20,000 seconds. Transient, disturb, retention, and endurance characteristics for the different devices will be presented.

SESSION F8: POROUS SILICON III

Chair: Nobuyoshi Koshida
Tuesday Afternoon, November 28, 2000
Constitution A (Sheraton)

1:30 PM *F8.1

SILICON-BASED PHOTONIC BANDGAP DEVICES. Volker Lehmann, Infineon Technologies, Munich, GERMANY.

The existence of a photonic band gap in dielectric or metallic structures that are periodic on a wavelength scale has recently received much attention. Silicon is a potential material for fabrication of photonic crystals for the infrared regime due to its high dielectric constant. It will be shown that macropore formation by electrochemical etching is a favorable technique for manufacturing of two-dimensional photonic band gap structures. Transmission spectra will be presented which show that a triangular lattice of pores in a silicon substrate is sufficient to produce a complete photonic band-gap centered at 5 micrometer. These measurements are in excellent agreement with the theoretically calculated photonic band structure. Furthermore the photolithographic patterning enables us to define defect structures by leaving out pores in the lattice. This has been applied to define optical waveguides, Y-branches and cavities in a well-controlled manner. The integration of silicon based photonic crystals with electronic devices may open new doors for future opto-electronic applications.

2:00 PM F8.2

A NEW WAY TO FORM THREE-DIMENSIONAL MICRO-STRUCTURES BY ELECTROCHEMICAL ETCHING OF SILICON. P. Kleimann, R. Juhasz and J. Linnros, Royal Inst. of Technology, Dept. of Electronics, Kista-Stockholm, SWEDEN.

Anodic electrochemical etching of silicon in a HF containing electrolyte is well-known as a technique of micro or macro-porous silicon formation or electropolishing. Besides being interesting due to the optical properties of porous silicon, this technique has recently emerged in micromachining applications. Indeed it enables to form high aspect ratio pore or trench arrays with a depth up to the wafer thickness. These arrays are used as frames to form 3-dimensional microstructures. However it is commonly admitted that the width of pores and trenches can not easily be extended beyond 20 microns, which is a severe limitation for certain applications. This paper presents a new technique for micromachining which does not require the formation of pores or trenches. The technique is a generalization of macro pore formation by electrochemical etching and is based on electropolishing an n-type silicon sample in a HF containing electrolyte except where vertical walls or pillars are needed. This patterning is achieved by pre-etching steps of a few microns on the sample in a KOH solution prior to the electrochemical etching. Then, due to the electrical field in the space charge region, the etching current lines are bended near the steps which prevents etching of the walls. The wall thickness and shape can be controlled by the etching parameters (light intensity, etching current density, HF concentration, sample resistivity) which enables to form free-standing structures. The feasibility of this technique is demonstrated in this paper by forming pores of 100 microns width as well as micro needles of 5 micron width.

2:15 PM F8.3

A SIGNIFICANT CHANGE IN REFRACTIVE INDEX OF NANOCRYSTALLINE POROUS SILICON INDUCED BY CARRIER INJECTION. Yuichi Toriumi, Morio Takahashi, Nobuyoshi Koshida, Tokyo Univ. of A&T, Dept of Electrical and Electronic Engineering, Tokyo, JAPAN.

As one novel function of luminescent porous silicon (PS), we have shown the usefulness of PS for optical switching by photo-induced [1] and current-induced [2] refractive index change. Details of the carrier injection effect on the optical properties are presented here using PS Fabry-Pérot resonators (PS-FPR). The experimental devices consist of a transparent ITO top contact, an active PS layer sandwiched with upper and lower PS-FPR mirrors, a p-type Si substrate and an ohmic back contact. The resonator was prepared by anodizing p-type Si wafers in an ethanoic HF solution at 0°C. Under the forward biased condition, the reflectance for incident white light was detected at various temperatures. The dynamic response of a relative change in the reflection spectrum was measured as a function of current density. Major experimental results are summarized as follows: (a) When the carriers were injected into the PS-FPR diode, a significant change in the reflection spectrum was induced by a refractive index change with fast and the slow response times. The value of refractive index change was proportional to the number of injected carriers. The fast and slow refractive index changes are explained as a result of carrier injection and subsequent carrier accumulation into localized states, respectively. (b) The refractive index change becomes small at high temperatures. It appears that thermal excitation of the accumulated carriers from localized states to the conduction band is suppressed at lower temperatures. (c) The results of dynamic response measurements show that the turn-on and turn-off time constants are dominated by the recombination rate of accumulated carriers. [1] M. Takahashi, Y. Toriumi, T. Matsumoto, Y. Masumoto and N. Koshida, Proc. Int ECS Symp. Adv. Lumin. Mat. and Quantum Conf. PV99-22, 35 (ECS, Pennington, 1999). [2] M. Takahashi, Y. Toriumi, and N. Koshida, Phys. Status Solidi (2000) (in press).

2:30 PM F8.4

A NOVEL, SIMPLE AND EFFECTIVE METHOD FOR POROUS SILICON FABRICATION AND ITS APPLICATIONS. X. Li, S. Chattopadhyay, R.A. Kruse, J.V. Sweedler and P.W. Bohn, Department of Chemistry, University of Illinois, Urbana, IL.

We present a metal-assisted chemical etching method to produce light emitting porous silicon (PSi). A thin (< 10 nm) layer of Au, Pt or Pd is deposited on a Si(100) surface prior to immersion in a solution of HF and H₂O₂. PSi formation occurs on the time scale of seconds, without external bias, in the dark, on both p- and n- type Si. The morphology and light emitting properties of the PSi can be controlled by adjusting the metal deposited and the Si doping type and level, with emission typically 100 nm to the blue of emission from anodically etched PSi. Of the metals investigated, Pt yields the fastest etching rate and produces the most intense luminescence. A reaction scheme involving microscopic redox reactions with the metal as the cathode is proposed to explain the metal-assisted etching process. The simplicity of this method and the richness of in-plane morphology and

luminescence properties produced allowed us to study the mechanism of desorption/ionization on silicon (DIOS) of macro-biomolecules (Wei, Buriak, Suizdak, Nature, 399, 243 (1999)). Other applications of this method such as fabricating porous silicon with built-in metal contacts will also be explored.

2:45 PM F8.5

SIZE REDUCTION OF SILICON NANOPILLARS BY PHOTO-ELECTROCHEMICAL ETCHING. Robert Juhasz, Jan Linnros, Royal Inst of Technology, Dept of Electronics, Stockholm, SWEDEN; Pascal Kleimann, LENAC, Université Claude Bernard Lyon I, Villeurbanne, FRANCE.

Photo-electrochemical etching has previously been used to create spatially well-defined macropores in silicon as well as random nanoporous structures. This work demonstrates the successful use of this technique for reducing nanometer-sized n-type Si pillars, predefined by electron beam lithography and reactive ion etching, to dimensions far beyond the reach of today's lithography methods. An attempt is also made to explain some of the underlying physics and etching reactions of this system. Etching was performed in a mixture of weak HF solution and ethanol, with a focused red 5 mW laser creating electron-hole pairs within a 200 µm diameter spot where 50 - 100 nm diameter pillars had been formed. A voltage source provided current between the isolated backside of the sample and a Pt counter-electrode in the etching solution. The etched pillars were characterized using scanning electron microscopy. By varying voltage bias and light intensity, different etching reactions (porous Si formation or electropolishing) could be induced. With a proper choice of etching parameters, 100 nm diameter pillars were successfully reduced to 15 nm diameter. Further reduction into the sub-10 nm regime is believed to be possible for structures with smaller initial diameter. SEM investigations also showed that the pillars were etched both at greater speed and in a different regime than the surrounding sample surface. Thus, etching in the porous or electropolishing regime caused etching only at the pillar base or pillar top, respectively, allowing precise three-dimensional control of the etching with a possibility of edge profile enhancement of already defined structures. The key parameter is believed to be the local hole concentration governing the current density and in turn the etch rate. Finally, this setup provides both a nanofabrication tool as well as a model system for gaining insight into the process of porous silicon formation.

SESSION F9: NANOCRYSTALLINE SILICON

Chair: Dmitri Kovalev

Tuesday Afternoon, November 28, 2000

Constitution A (Sheraton)

3:30 PM F9.1

LASER DESORPTION MASS SPECTROSCOPY USING THIN FILM DEPOSITED NANO-POROUS SILICON. Joseph D. Cuiuffi, Daniel Hayes, Stephen Fonash, Electronic Materials and Processing Research Laboratory, Penn State University, University Park, PA.

Obtaining mass spectra of biological and organic samples is done by a variety of methods including matrix assisted laser desorption-ionization (MALDI), secondary ion mass spectroscopy (SIMS), and more recently desorption-ionization on silicon (DIOS). DIOS overcomes the background signal problem inherent in the MALDI technique by eliminating the use of an organic carrier matrix. This has recently enabled the highly sensitive detection of low molecular weight species [Wei et al. Nature, May 1999.]. We report here on a novel deposited thin film nano-porous silicon approach to DIOS. Our deposited Si offers several advantages over conventional porous silicon including its avoidance of electrochemical etching and its capability to be deposited on glass and plastics. With our films, we accomplished detection of molecules in the mass range of 0 to 6000 amu along with specific molecular detection at concentrations in the femto-mole range. To further understand the DIOS process, we characterized molecular detection versus laser intensity and film reflectivity, and we studied the effect of various chemical and thermal modifications to the surface. The results indicate a strong signal dependence on the ability of the silicon films to absorb the incident laser energy, transferring energy to the sample molecules via thermal processes. These films display versatility suitable for biological sensing applications as well as VLSI compatibility that makes them an enabling technology for micro total analysis systems.

3:45 PM F9.2

PHOTOLUMINESCENCE FROM N- (P-) TYPE IMPURITY DOPED SILICON NANOCRYSTALS. Minoru Fujii, Atsushi Mimura, Shinji Hayashi, Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe, JAPAN; Dmitri Kovalev, Frederick Koch, Technische Universität München, Physik-Department, Garching, GERMANY.

Since the discovery of visible photoluminescence (PL) from porous-Si, optical properties of Si nanocrystals (nc-Si) have intensively been studied. However, the subject of impurity doping has not yet been clarified; it has not been fully understood how a dopant atom works in such a confined and dielectric discontinuous medium. In this work, the effect of n- (p-) type impurity doping on the PL properties of nc-Si was studied. Impurity doped nc-Si were prepared by the cosputtering of Si and phosphosilicate (borosilicate) glass, and post-annealing. In the case of P-doping, the PL intensity first increased and then decreased with increasing P concentration. A possible explanation for the observed P concentration dependence is as follows. At low concentration, P-doping electrically passivates P_b centers, which are defects at Si/SiO₂ interfaces and known to act as non-radiative recombination centers. This passivation results in the improvement of the PL efficiency. At high concentration, after completing the passivation of P_b centers, electrically active P atoms supply free electrons in nc-Si, which makes the nonradiative Auger recombination of photo-excited excitons possible, leading to the quenching of the PL. The decrease in the number of P_b centers at low P concentration and the existence of free electrons at high concentration were confirmed by electron spin resonance and optical absorption spectroscopies. In the case of B-doping, the PL intensity decreased monotonously. This suggests that holes supplied by B-doping are not trapped by P_b centers and always act as free holes. The quenching of the PL may be due to the Auger recombination between the hole and a photo-excited exciton. The present results imply that P_b centers act as electron traps, and the trap state exists at the upper-half of the bandgap. Furthermore, it is demonstrated that impurity doping is a useful method for controlling non-radiative recombination centers.

4:00 PM F9.3

PHOTOLUMINESCENCE IN NANOCRYSTALLINE SILICON/SILICON DIOXIDE SUPERLATTICES. V. Timoshenko, J. Diener, H. Heckler, D. Kovalev and F. Koch, Technical University of Munich, Physics Department, Garching, GERMANY; J.P. McCaffrey, J.-M. Baribeau, G.I. Sproule and D.J. Lockwood, Institute for Microstructural Sciences, National Research Council, Ottawa, CANADA; R. Krishnan, G. Grom, P.M. Fauchet and L. Tsybeskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY.

Nanocrystalline silicon superlattice (nc-Si SLs) is a structure consisting of highly crystalline Si nanocrystal layers separated by nanometer-thick SiO₂. Number of characterization techniques such as transmission electron microscopy (TEM) and atomic force microscopy (AFM), Auger elemental microanalysis. X-ray diffraction and X-ray small angle reflection have proved that the nc-Si L exhibits very narrow nanocrystal size distribution (less than 5% in average) and very abrupt and flat nc-Si/SiO₂ interface with a roughness of <5Å. Photoluminescence (PL) in these structures has been studied in details including time-resolved and steady-state PL spectroscopy in a wide range of temperature, excitation wavelength and power. Resonantly excited PL spectra show phonon steps proving that the PL originates in Si nanocrystals. The PL intensity temperature and lifetime dependences are in a good agreement with the spin-orbit interaction model. The PL intensity quenches and PL lifetime increases under applied magnetic field of ≤ 10 T. The PL decay kinetics are found to be exponential in a wide temperature range, in contrast to porous Si where the PL kinetics are mostly stretched-exponential. The PL intensity saturates as a function of the excitation intensity, and the PL spectra show strong blueshift and broadening as the excitation intensity increases. The PL spectra in smaller Si nanocrystals are broader and exhibit a blueshift compared to PL in bulk crystalline Si. We convincingly demonstrate that the major portion of the PL in nc-Si SLs is due to quantum confinement effect in Si nanocrystals.

4:15 PM F9.4

Abstract Withdrawn.

4:30 PM *F9.5

STIMULATED BLUE EMISSION AND SECOND HARMONIC GENERATION IN FILMS OF ULTRASMALL SILICON NANOPARTICLES. M.H. Nayfeh, N. Barry, J. Therrien, O. Akcakir, E. Gratton, G. Belomoin, University of Illinois at Urbana-Champaign, Department of Physics, Urbana, IL.

We dispersed electrochemical etched Si into a colloid of ultrabright, blue emitting, ultrasmall (1 nm in diameter) nanoparticles, and reconstituted it into micro crystallites or uniform films on device quality Si, or silicon oxide. The emission from single particles in colloids or frozen in a gel are readily detectable. When a recrystallized film is excited by near-infrared two photon process at 780 nm, we observe an extremely strong blue band that exhibits a sharp threshold near 106 W/cm², rising by many orders of magnitude, beyond which a low power dependence sets in. We also observe directed blue beams between faces of the micro crystallites. The results are analyzed in

terms of population inversion and stimulated emission in quantum confinement-induced Si-Si dimer phase, found only on ultrasmall Si nanoparticles. We have also observed, under certain conditions, strong radiation at half the wavelength of incident near-infrared radiation. The results are analyzed in terms of second harmonic generation, a process that is not allowed in bulk due to the centrosymmetry. Ionic vibration of or/and excitonic self-trapping on the novel radiative Si-Si dimer phase are suggested as a basic mechanism for inducing anharmonicity that breaks the centrosymmetry.

SESSION F10: BIOLOGY WITH NANOSCALE SILICON

Chair: Jillian M. Buriak
Wednesday Morning, November 29, 2000
Constitution A (Sheraton)

8:30 AM *F10.1

NANOFABRICATED SYSTEMS FOR SORTING AND MANIPULATION OF BIOMOLECULES. J. Han, S.W. Turner and H.G. Craighead, School of Applied and Engineering Physics, Cornell University, Ithaca, NY.

It is possible to fabricate fluidic systems with dimensions comparable to the size of DNA molecules. By controlling the time and spatial dependence of electric fields one can drive, sort and separate molecules by a variety of physical mechanisms. We have created nanoconstrictions in fluidic channels that act as entropic barriers to DNA motion. We have used the size dependence of these entropic effects to separate DNA. In this paper we describe the design and fabrication and performance two such types of devices. One system employs a series of narrow constrictions formed by etching a silicon substrate. The differential electrophoretic mobility of large DNA fragments (~5,000-150,000 base pairs) and electrically controlled spatial focusing can be used to efficiently separate mixtures of different length fragments. In the second device an entropic barrier with time varying electric field can be used to dynamically control the confinement of molecules and selectively permit their motion in a nanofabricated medium. Other applications of narrow fluid channels in molecular analysis will be considered.

9:00 AM F10.2

SIZING OF PROTEINS WITH ELECTROCHEMICALLY MACHINED PORE GRADIENTS IN SILICON. Boyce E. Collins, Keiki-Pua Dancil, Guarav Abbi, Michael J. Sailor, Univ of California at San Diego, Dept of Chemistry and Biochemistry, La Jolla, CA.

Porous silicon films displaying a distribution of pore dimensions ranging from microns to nanometers can be generated by electrochemically etching silicon in an aqueous ethanolic HF solution using an asymmetric electrode configuration. The median pore size and breadth of the size distribution in the film can be set by adjusting the HF concentration, current density, and the shape and position of the counter electrode relative to the silicon electrode. Scanning electron and atomic force microscopies are used to characterize the pore size gradients. It is demonstrated that films with pore gradients in the few nanometer size range can be used as size exclusion matrices to perform an on-chip determination of macromolecule dimensions. Optical reflectivity spectra of a thin porous Si film display distinctive shifts in the Fabry-Perot fringes in regions of the film where the pore dimensions are larger than a critical size, interpreted to be the characteristic dimensions of the molecule.

9:15 AM F10.3

MICRONUTRIENT AND THERAPEUTIC ELEMENT DELIVERY FROM A BIODEGRADABLE SEMICONDUCTOR: MESOPOROUS SILICON. L.T. Canham, C.L. Reeves, P.J. Wright, T.I. Cox, Sensors and Electronics Division, DERA Malvern, UNITED KINGDOM.

The introduction of porosity at the nm scale into silicon renders the semiconductor bioactive and biodegradable (1) We describe here one area of drug delivery which aims to exploit the biodegradability, purity and high temperature processing capability of porous silicon. Many elements of the periodic table (eg. Se, Cr, Mn, Mo) are needed by the body at extremely low levels ("trace elements" or "micronutrients") and yet deficiency effects are well documented. This is often simply due to diet inadequacy and because only a small and highly variable fraction of orally-ingested microminerals are absorbed. Other elements (eg Li, Au, Ag) have widespread use clinically for therapeutic purposes. We have started to investigate the use of micromachined Si tablets, doped with a range of such elements via a recently developed technique of pore impregnation and high temperature anneal. By distributing the element within the Si skeleton itself we hope to eliminate the common 'burst effect' seen with porous implants, and achieve controlled precise delivery over tunable timescales of months to years. (1) L.T. Canham Adv Mater. 7, 1033 (1995)

9:30 AM F10.4

NANOSCALE SILICON MICROCAVITY OPTICAL SENSORS FOR BIOLOGICAL APPLICATIONS. Selena Chan and Philippe M. Fauchet, Univ of Rochester, Center for Future Health and Dept of Electrical and Computer Engineering, Rochester, NY; Yi Li, Lewis J. Rothberg, and Benjamin L. Miller, Univ of Rochester, Center for Future Health and Dept of Chemistry, Rochester, NY.

The large surface area of porous silicon provides numerous sites for many potential species to attach, which makes it an ideal host for sensing applications. The average pore size can be easily adjusted to accommodate either small or large molecular species by controlling the anodization conditions. When porous silicon is fabricated into a structure consisting of two high reflectivity multilayer mirrors separated by an active layer, a microcavity is formed. Multiple narrow and visible luminescence peaks are observed with a full width at half maximum value of 3 nm. The position of these peaks is extremely sensitive to small changes in refractive index, such as that obtained when a biological object is attached to the large internal surface of porous silicon. We demonstrate the usefulness of this microcavity resonator structure as a DNA optical biosensor which displays appropriate sensitivity, selectivity, and response speed. A probing strand of DNA is initially immobilized in the porous silicon matrix, and then subsequently exposed to its sensing complementary DNA strand. Red-shifts in the luminescence spectra are observed and detected for various DNA concentrations. The spectral shifts confirm successful recognition and binding of DNA molecules within the porous structure. Detailed device fabrication procedures and the results of extensive testing will be presented. The detection scheme has also been extended to include the detection of viral DNA. Full length viral DNA strands with approximately 50,000 base pairs have been successfully detected with our optical microcavity sensor. This work will lead to the development of a "smart bandage", where the detection of bacteria or viruses can be diagnosed and an antibiotic treatment can be recommended.

SESSION F11: Si PASSIVATION AND FUNCTIONALIZATION
Chair: Philippe M. Fauchet
Wednesday Morning, November 29, 2000
Constitution A (Sheraton)

10:15 AM *F11.1

FUNCTIONALIZATION OF SILICON SURFACES. Stacey F. Bent, Stanford University, Dept of Chemical Engineering, Stanford, CA.

As the range of applications for silicon-based materials - including micro- and nanocrystalline silicon - continues to expand, methods that can be used to tailor their surface properties become increasingly important. Organic modification is one means of providing new functionality to the silicon surface, imparting properties useful for passivation, molecular recognition, lubrication, or biocompatibility. This talk will focus on organic functionalization of silicon surfaces. Bifunctional and polyfunctional organic molecules have been used to form direct, covalent bonding at the surface in a dry processing environment. A combination of experimental and theoretical methods has been used to identify the bonding and reactivity of the organic layers at the silicon surface. On the Si(100)-2x1 surface, unsaturated molecules such as alkenes or dienes react by cycloaddition chemistry across the Si-Si surface dimers. We show that the [4+2] cycloaddition (Diels-Alder reaction) occurs readily for a range of conjugated dienes at the (100)-2x1 surface of Si, and that the reaction occurs at the surfaces of Ge and C, as well. The reactivity of other functionalities, such as amine groups, with the semiconductor surface has also been explored as a potential means of surface modification. Studies of a series of pyrroles provide insight into the relative reactivities of cycloaddition, N-H bond dissociation, and nitrogen lone pair interactions at the Si(100)-2x1 surface. The use of protecting groups to manipulate the surface reaction will be described, and the potential for these different classes of attachment reactions to impact future applications will be discussed.

10:45 AM F11.2

REACTIONS OF ORGANIC MOLECULES FOR CONTROLLED MODIFICATION OF GROUP IV SEMICONDUCTOR SURFACES: THEORETICAL PREDICTIONS. Jose Barriocanal, Doug Doren, University of Delaware, Dept of Chemistry, Newark, DE.

Theoretical work has played a central role in studies of reactions of organic molecules with semiconductor surfaces. First-principles theory allows accurate predictions of activation barriers and product properties, providing a useful guide to planning and interpreting experiments. This talk will describe calculations on several reaction mechanisms that allow molecules to react with low activation barriers

on (100) surfaces of Si, Ge and diamond. Cycloaddition reactions of alkenes and dienes are the most thoroughly understood reactions of organic molecules on these surfaces, having been studied extensively by both theory and experiment. Much less work has been done with a class of molecules known as 1,3-dipoles which also undergo cycloaddition. Theoretical predictions and initial experimental results indicate that these molecules readily chemisorb to establish an organic monolayer, covalently attached to the surface. However, in many cases the initial products are expected to rearrange, leaving a variety of structures on the surface. For many applications, this disorder is acceptable. However, when more order is desired, it is possible to control the product structure through the choice of precursor molecule. Several examples, and some general principles for predicting the likely rearrangements resulting from different precursors, will be discussed. Finally, a new reaction that attaches an organic molecule to the surface by dissociation (as opposed to cycloaddition) will be described.

11:00 AM F11.3

REACTIVITY PATTERNS AND MECHANISM FOR A WHITE LIGHT PROMOTED HYDROSILYLATION REACTION WITH ALKENES AND ALKYNES AT THE SURFACE OF PHOTOLUMINESCENT POROUS SILICON. Michael Stewart and Jillian Buriak, Department of Chemistry, Purdue University, West Lafayette, IN.

A novel, unprecedented chemical reaction on the surface of porous silicon protects against harsh chemical treatment while preserving the intensity and energy of its visible photoluminescence. White Light Promoted (LP) hydrosilylation uses white light (400 - 600 nm) and exposure times from 5 minutes to 1 hour to give permanently derivatized porous silicon structures. As the LP reaction operates only on photoluminescent porous silicon, active surface states consistent with the quantum confinement model of light emission are thought to mediate the hydrosilylation. The reactivity pattern of substrates suggests nucleophilic attack of surface-localized holes and electrons from exciton pairs. The LP derivatization reaction is unprecedented in that it requires a long-lived exciton to react rather than simple photolysis by light fluence. Experimental evidence for a mechanism involving exciton-mediated nucleophilic attack, along with alternative explanations for the LP hydrosilylation reaction will be discussed.

11:15 AM F11.4

PASSIVATED LUMINESCENT POROUS SILICON. D.J. Lockwood, R. Boukherroub, D.D.M. Wayner, National Research Council, Ottawa, CANADA; L.T. Canham, DERA, Malvern, UNITED KINGDOM.

In freshly prepared porous Si (PSi), the newly exposed Si surface is protected with a monolayer of hydrogen. This monolayer is very reactive and oxidizes in air leading to a loss of photoluminescence (PL) intensity and degradation of the electronic properties of the material. In order to prevent this evolution and to control the stability of the original PL, proper chemical and electronic termination of the surface, limiting the presence of midgap states which act as nonradiative recombination centers, is necessary. Here we describe a new approach based on organic modification of the hydrogen-terminated PSi surface that is well suited to stabilizing the PL of PSi of any porosity. Our strategy is based on the chemical modification of the PSi surface by the formation of stable Si-C and Si-O-C covalent bonds. Ideal passivation of H-terminated light-emitting PSi through the formation of covalently bonded organic monolayers has been achieved by the thermally induced reaction of freshly prepared PSi surfaces with 1-decene, 1,7-octadiene, ethylundecylenate, and octyl and decyl aldehydes. The functionalized surfaces exhibit a similar intensity and the same peak energy of the PL peak as that initially observed from the as-anodized PSi. These organic derivatized surfaces have an unprecedented ability to stabilize the PSi surface, as confirmed by chemography. The surfaces are very resistant against oxidation even when steam treated at 700C for several weeks, a treatment that completely destroys hydrogen-terminated PSi. Aging in ambient air for several months has no effect on the PL. This "pickling" process is thus highly effective in retaining the desired optoelectronic properties of hydrogen-terminated light-emitting PSi such as wavelength tunable PL and high quantum efficiency, and, significantly, lends itself to further chemical modification for integration into chemical or biochemical sensors.

11:30 AM F11.5

DETECTING WARFARE AGENTS WITH POROUS SILICON INTERFEROMETERS. Sonia E. Létant, Honglae Sohn, William C. Trogler, Michael J. Sailor, Univ of California at San Diego, Dept of Chemistry and Biochemistry, La Jolla, CA.

It has been demonstrated that porous silicon interferometers show a high sensitivity to the amount of silicon oxide on their surface, which has been found to be proportional to their optical thickness. In as far as HF is the only gas which can efficiently dissolve SiO₂, its specific

detection can be achieved by monitoring in situ the dissolution of the oxide in porous silicon interferometers via the decrease of the refractive index of the film. The speed of the oxide dissolution is correlated to the HF concentration. Applications of this technique to detect fluorophosphonate warfare agents, which produce HF when they are hydrolyzed, will be presented. The hydrolysis of the fluorophosphonate molecules into HF can be accelerated by the introduction of micelles and of a copper catalyst in the pores of the porous silicon detector. This technique leads to the detection of 800ppm of diisopropylfluorophosphonate (DFP, a Sarin gas simulant) in 5 min.

11:45 AM F11.6

MULTIPARAMETRIC SENSOR FOR AIR POLLUTANTS BASED ON POROUS SILICON OPTICAL MICROCAVITY. Zeno Gaburro, Lorenzo Pavesi, INFN and Department of Physics, University of Trento, Povo (Tn), ITALY; Camilla Baratto, Guido Faglia, and Giorgio Sberveglieri, INFN and Department of Chemistry and Physics, University of Brescia, Brescia, ITALY.

We experimentally demonstrate that porous silicon optical microcavities can be effectively used as multi-parametric gas sensors. In fact, due to the high surface/volume ratio of porous silicon, both the photoluminescence and electrical conduction are strongly dependent on the environment. By fabricating an optical microcavity with porous silicon, it is quite easy to obtain an additional optical parameter, *i.e.* the position of the peak of the cavity, which is also sensitive to the environment. While the peak position depends on the refractive index of the gas, luminescence intensity depends on its low frequency dielectric constant. The combined effects of the environment on the peak position, luminescence intensity and electrical conduction allow discriminating between different substances. We show that porous silicon is very promising material for air pollutants detection. For instance, relative variations of the electrical conductivity $\Delta G/G$ larger than 5 have been observed in presence of NO₂ at 3 ppm concentration. Such detection performance is obtained at room temperature and does not require significant power supply for the sensors. Measurable changes in $\Delta G/G$ are expected at lower concentration due to such performance. A systematic study of the changes of the parameters of porous silicon microcavities, in the presence of several air pollutants like carbon monoxide, ozone, SO₂ and nitrogen oxides, has been performed in this study. The experimental results will be presented and discussed.

SESSION F12: SILICON NANOWIRES

Chair: Christophe Delerue

Wednesday Afternoon, November 29, 2000

Constitution A (Sheraton)

1:30 PM *F12.1

SILICON NANOWIRES: DOPING, ELECTRICAL TRANSPORT AND ASSEMBLY OF FUNCTIONAL NANODEVICES. Charles M. Lieber, Yi Cui, Xiangfeng Duan, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

Semiconductor nanowires represent potentially critical building blocks for emerging nanotechnologies. To achieve the greatest impact in assembling devices will, however, require that the carrier type and concentration be controlled. To this end, we have been investigating the synthesis, electrical properties and assembly of doped semiconductor nanowires, and will present recent results from studies of silicon nanowires (SiNWs). Single crystal n-type and p-type SiNWs have been prepared by laser catalytic growth by introducing either boron or phosphorous dopants during the vapor phase growth. Two terminal, gate-dependent measurements made on individual boron-doped (B-doped) and phosphorous-doped SiNWs (P-doped) show that these materials behave as p-type and n-type materials, respectively. Estimates of the carrier mobility made from gate-dependent transport measurements are consistent with diffusive transport. Temperature-dependent measurements made on heavily doped SiNWs show no evidence for coulomb blockade at temperature down to 1.8 K, and thus testify to the structural and electronic uniformity of our SiNWs. The n-type and p-type SiNWs have also been assembled into p-p, n-n and p-n junctions. The p-p and n-n junctions show non-rectifying current-voltage behavior and suggest good contact between SiNWs. Significantly, p-n junctions show rectification in reverse bias and a sharp current onset in forward bias. The potential for exploiting these nanoscale building blocks for the creation of a wide range of device structures in nanoelectronics will be discussed.

2:00 PM F12.2

INVESTIGATION ON SEMICONDUCTOR NANOWIRES: THEIR SYNTHESIS, STRUCTURE CHARACTERIZATION, AND PROPERTIES. Dapeng Yu, Department of Physics, Mesoscopic

Physics National Lab, and Electron Microscopy Laboratory, Peking University, Beijing, CHINA.

This paper presents an overview of the recent progress on investigation of semiconductor nanowires. In the first part we will introduce the synthesis of a diverse variety of semiconductor based nanowires (such as Si, Ge, GaSe, ZnO) using laser ablation method, or by physical vapor deposition (PVD) approach. A typical example is the synthesis of real free-standing silicon nanowires which have uniform diameter distribution around 12 nm and length up to hundreds of microns. In the second part we will show the microstructure characterization of the nanowires by SEM, TEM, and HREM. The unidirectional growth mechanism of nanowires was investigated based on TEM analysis. In the third part, the quantum confinement effects were evaluated via the measurements of photoluminescence and Raman spectra of the semiconductor nanowires. The doping effect of Li on the Si nanowires was investigated in a cell using Si nanowires as electrode materials.

2:15 PM F12.3

ATOMIC STRUCTURE AND ELECTRONIC PROPERTIES OF SILICON NANOWIRES. Dorothy D.D. Ma, Frederick C.K. Au, C.S. Lee, S.T. Lee, City University of Hong Kong, Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, Hong Kong, CHINA.

We present atomically resolved images of silicon nanowires in different morphologies by using scanning tunneling microscope (STM). The nanowires were prepared via the oxide-assisted growth method (S.T. Lee et al. J. Mat. Res. 14, 4503 (1999)). The oxide layer of the nanowires was removed before STM observation. STM images revealed the presence of silicon nanowires with extremely small diameters (from 10 to 40 angstroms) and lengths longer than 1 micron. They were self-assembled and oriented in parallel direction. Atomic resolution images showed that the silicon nanowires had Si(111) surfaces, which assumed the Si(111)-(1×1) structure. A structural model was proposed which accounts for the observed STM features. STM measurements showed that the electronic properties of the silicon nanowires depended on diameter and morphology. The bandgaps of different types of silicon nanowires were also measured.

2:30 PM F12.4

PSEUDO-MOS OPERATION OF ULTRA-NARROW POLYSILICON WIRES: ELECTRICAL CHARACTERIZATION AND MEMORY EFFECTS. Costin Anghel, Naser Hefyene, Adrian M. Ionescu, LEG-EPFL, Lausanne, SWITZERLAND; J. Tringe, J.D. Plummer, Stanford University, Stanford, CA.

This paper presents a new, simple yet powerful, method for the electrical characterization of polysilicon wires based on the pseudo-MOS effect. The investigated structures are ultra-narrow, four-contact polycrystalline silicon wires (~0.1 micron wide) made of series connection of individual grains, originally designed for resistivity measurements. The vertical structure being SOI-like, the substrate is biased as a MOS-gate and, a dominant accumulation current being imposed at the polysilicon-oxide interface, MOS-like DC characteristics are provided, allowing to investigate interface and bulk characteristics via MOSFET modeling in terms of electrical parameters (carrier mobility, flat band and threshold voltage, mobility reduction coefficient, etc). Complementary 1/f noise measurements, based on the four-contact design of polysilicon wires are shown to be a useful characterization tool for material investigation, especially if polysilicon is anticipated to serve for sensor applications. Information provided by the electrical I-V MOS-like characteristics and 1/f noise is correlated with the structural investigation (TEM) of the polysilicon wires in order to obtain more physical insights about material electrical properties. Particular attention is paid to the investigation of observed transient phenomena in pseudo-MOS operation of polysilicon wires. First, significant hysteresis is experimentally revealed in the I-V DC characteristics, when high voltages are applied on the substrate acting as a gate. Systematic measurements of long current relaxation (duration of few minutes) in accumulation and depletion, in darkness and under illumination, demonstrate the dominance of carrier trapping at grain boundaries over oxide charging and SRH g.r. in-grain phenomena. The transient analysis, highlighting remarkable retention duration, appears to be extremely useful for further memory design and applications based on similar polysilicon wire structures.

2:45 PM F12.5

LASER ABLATION FABRICATED NANO-COMPOSITE OF METAL CRYSTALLINES IN SILICON WIRE. Jifa Qi¹ and Yasuaki Masumoto^{1,2}. ¹Japan Science and Technology Corporation, Single Quantum Dot Project, Tsukuba, Ibaraki, JAPAN. ²Univ. of Tsukuba, Inst. of Physics, Tsukuba, Ibaraki, JAPAN.

We have fabricated a nanometer scale composite of the metal copper

nanocrystallines embedded in silicon nanowire by laser ablation of Si/metal mixture targets at 1200°C in argon gas flow. The samples were characterized by transmission electron microscope and energy dispersive x-ray spectroscopy. Both silicon nanowires and the copper nanocrystallines possess uniform diameters and smooth surfaces. The diameters of the nanowires and nanocrystals ranged 30-50 nm and 10-25 nm, respectively. The size of the copper nanocrystalline was found to depend on the diameter of silicon nanowire. The growth of the composite nanowires appears to follow vapor-liquid-solid growth process. Because of semiconducting silicon nanowire and metallic copper nanocrystalline materials have distinctive characters in electronic and optical domain, the composite materials based on them are promising for new concept silicon related optoelectronic elements.

SESSION F13: ALTERNATIVE Si
NANOSTRUCTURE SYNTHESIS

Chair: Jan Linnros
Wednesday Afternoon, November 29, 2000
Constitution A (Sheraton)

3:30 PM F13.1

FORMATION OF NANOSTRUCTURES IN SILICON BY PULSED-LASER ABLATION. J.D. Fowlkes, A.J. Pedraza, S. Jesse, Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN; and C.M. Rouleau, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Nanoparticles of silicon and silicon oxide are formed during UV pulsed-laser ablation of silicon substrates. It is shown that the nanoparticles' size is controlled by the initial micro-topography present on the target and by the base pressure of the gas present during irradiation. The generation of nanoparticles is strongly enhanced if the initial silicon substrates are laser textured. This treatment is performed by multiple irradiations in a reactive atmosphere that generate a very pronounced roughness with micro-holes over 100 μm -deep and 10- μm in diameter, and cones protruding tens of microns over the initial surface. The micro-hole /micro-cone ensemble becomes completely covered with a filamentary nanostructure when further irradiations are performed in an oxygen rich atmosphere. Photoluminescence spectra, high-resolution electron microscopy and scanning tunneling microscopy are used to determine the nature and size of the nanoparticles. A new method to separate nanoparticles by their size and charge is described and examples are shown. This research was sponsored by NSF Grant DMR-9901238 and by the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

3:45 PM F13.2

SIZE CONTROL AND OPTICAL PROPERTIES OF SILICON NANOPARTICLES FORMED BY PICOSECOND PULSED LASER ABLATION. M.H. Wu, W.J. Yost, R. Mu, A. Ueda and D.O. Henderson, Fisk University, Dept of Physics, Nashville, TN.

Silicon nanostructures hold great promise for advanced optoelectronic applications. We describe here the size control and optical properties of silicon nanocrystals produced by picosecond pulsed laser ablation. Results observed for nanocrystals produced by picosecond pulse widths differ from those reported earlier for nanosecond pulses, where energy densities of 1 - 10 J/cm^2 and backing gas pressures of 1 - 10 torr are typically used to produce nanometer sized particles. Energy densities required for nanocrystal production with picosecond pulses are considerably lower, with small nanocrystals produced at densities of 0.1 J/cm^2 . Nanocrystal can also be produced by picosecond pulses in vacuum, with particle densities of up to 100 μm^{-2} observed on a mica substrate 4cm from the target. Higher backing gas pressures, such as those used for nanosecond experiments, result in formation of particles larger than 25 nm. Control of the size of nanocrystals deposited on a substrate facing the ablated target and on nanocrystals backscattered onto the target can be achieved by varying the energy density of the laser pulse, the gas pressure and the distance from the center of the ablation plume where the measurement is taken. Average particle size, as measured by ex-situ atomic force microscopy, can be varied from 1 nm to > 5 nm. This particle size range is theoretically predicted to result in bandgaps spanning the visible spectrum. Optical absorption and photoluminescence measurements demonstrate a considerable blueshift of the bandgap, with absorption onsets and photoluminescence peaks occurring throughout the visible region of the spectrum.

4:00 PM F13.3

GROWTH MECHANISM OF CHAINS OF SILICON NANOCRYSTALLITES. Hideo Kohno, Seiji Takeda, Osaka University, Department of Physics, Osaka, JAPAN; Koji Tanaka, Osaka National Research Institute, Department of Material Physics, Osaka, JAPAN.

We have reported growth of self-organized chains of silicon nanocrystallites: silicon nanocrystallites of about 10-20 nm in diameter are connected by necks of amorphous silicon oxide at a nearly equal spacing. Chains were synthesized by a simple thermal treatment of a gold-coated silicon substrate via an extension of the vapor-liquid-solid (VLS) growth process. In the VLS process, gold works as a liquid-forming catalyst at the tips of the growing chains. The novel self-organized phenomenon had been attributed to the periodic instability of the catalyst at the tip of a growing chain and oxidation during the growth of silicon nanowires. However, the growth mechanism had been controversial. In this study, chains were examined with energy-filtered transmission electron microscopy (TEM) to reveal the growth mechanism of the chains. Energy-filtered TEM images showed tails of silicon each of which ran toward the core of the neighboring oxide neck. This is direct evidence that the oxidation process from the surface of wires plays an essential role in formation of chains, namely at a neck of a wire, the oxidation reaches the core, while at a knot, the core remains unoxidized. Additionally, we have performed simple numerical simulations of the periodic instability in the chain growth. We could reproduce the periodic variation of the diameter of a wire and simulated periodic instabilities were in good agreement with our experimental results. The results of energy-filtered TEM observations and simulations strongly support our growth model.

4:15 PM F13.4

SYNTHESIS OF MONODISPERSE, NONAGGLOMERATED SILICON NANOCRYSTALLITES. Toshiharu Makino, Nobuyasu Suzuki, Yuka Yamada, Takehito Yoshida, Matsushita Electric Industrial Co., Ltd., Advanced Technology Research Laboratories, Kawasaki, JAPAN; Takafumi Seto, AIST, MITI, Mechanical Engineering Laboratory, Tsukuba, JAPAN.

We have synthesized monodisperse, nonagglomerated silicon (Si) nanocrystallites of the diameter less than 5 nm, using a novel integrated process system under clean processing condition. The integrated process system has the ability for carrying out formation of nanocrystallites by pulsed laser ablation in inert background gas (PLA-IBG), size classification using a low-pressure operating differential mobility analyzer (LP-DMA), and deposition by nozzle jet onto a substrate, sequentially. Si nanoparticles formed by PLA-IBG were introduced into LP-DMA with an inert background gas (a carrier gas) through an ionization unit using a differential evacuation system. The ionized Si nanoparticles were classified by LP-DMA, then deposited onto the substrate through the nozzle. In order to collect the classified nanoparticles efficiently, bias voltages were applied between the nozzle and the substrate. The size, morphology, and crystallinity of the deposited nanoparticles were characterized using a high resolution transmission electron microscope (HRTEM). The monodisperse, nonagglomerated Si nanoparticles were successfully synthesized (e.g. 3.8 nm mean diameter, 1.2 geometrical standard deviation). It was clarified the crystallinity of the deposited Si nanoparticles was really crystalline from the HRTEM analysis. When we adopt the Si nanocrystallites for active regions of quantum dot structure functional devices (e.g. Si based visible light emitting devices (LEDs)), it is important to increase the nanocrystallite yields. We increased the laser pulse energy to increase the nanocrystallite formation quantity, and the carrier gas flow rate to suppress the deposition of nanocrystallites on the inside wall of the transporting tube. Consequently, the particle concentration of classified Si nanocrystallites increased at the whole range of mean sizes (3-10 nm). The monodisperse, nonagglomerated Si nanocrystallites, which are deposited onto the substrate at high deposition rate, can be adopted for the Si based visible LEDs.

4:30 PM F13.5

ENLARGEMENT OF CRYSTALLINE GRAIN SIZE AND SIGNIFICANT INCLUSION OF HEXAGONAL DIAMOND PHASE IN ULTRA PURE MICROCRYSTALLINE SILICON. Toshihiro Kamei, CIS, Dept of Electrical Engineering, Stanford, CA.

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) is a composite film of nanometer-sized Si crystallites and amorphous Si, which is typically made by plasma decomposition of a gas mixture of SiH_4 and H_2 . As is inferred from the observation by infrared reflection absorption spectroscopy, its growth surface is totally covered with hydrogen due to the low temperature process. The surface hydrogen coverage would reduce surface reactivity with contaminants and, thus, maintain the clean growth surface. As a result, it is often argued that impurity would not affect the crystalline formation so much. In this paper, however, we demonstrate a reduction of atmospheric impurity (O, C, N) levels during the growth of $\mu\text{c-Si:H}$ enlarges crystalline grain size at higher substrate temperatures than 250°C. While grain size of (111) and (311) oriented crystallites is almost independent of substrate temperature, that of (220) oriented crystallite increases with substrate temperature, and, in particular, it shows rapid increase above 250°C

and then reaches 100 nm (Scherrer method) at 350°C. This rapid increase is not seen until this purification is achieved. It might be associated with a switch of surface hydrogen bonding configuration from SiH₂ to SiH, for SiH may favor (110) surface. Another interesting feature is the significant inclusion of diamond hexagonal phase which is accompanied by the enlargement of crystalline grain size. X-ray diffraction pattern of $\mu\text{-c-Si:H}$ grown at 350°C shows additional peak which is clearly observed in the lower diffraction angle (26.9° for Cu-K α line) than that of (111) diffraction peak. We believe that this stems from (10-10) crystalline plane of hexagonal diamond Si. The formation mechanism of hexagonal diamond Si is discussed in terms of the intersecting (111) stacking faults inside (220) oriented crystallites.

4:45 PM F13.6

FULL COLOR LUMINESCENCE FROM AMORPHOUS SILICON QUANTUM DOTS EMBEDDED IN SILICON NITRIDE. Nae-Man Park, Tae-Soo Kim, Chel-Jong Choi, Tae-Yeon Seong, Seong-Ju Park, Kwangju Institute of Science and Technology, Dept of MS&E, Kwangju, KOREA.

Although silicon (Si) is in a widespread use in the area of micro-electronic technology, bulk silicon is excluded from optoelectronic applications since it is an indirect bandgap semiconductor. However, many research groups have attempted to obtain an efficient luminescence from silicon during the past decade largely by taking advantage of quantum confinement effects (QCE) in the nano-sized silicon structures. We report on the successful growth of amorphous Si quantum dots (a-Si QDs) embedded in silicon nitride and the precise control of QD size, which permits the tuning of the luminescence wavelength. In this study, the tuning of the luminescence wavelength from red to deep blue and eventually white luminescence from a-Si QDs were demonstrated for the first time. a-Si QDs were grown by plasma enhanced chemical vapor deposition and the formation of a-Si QDs was confirmed by high-resolution transmission electron microscopy. The formation and the size control of the QDs in the silicon nitride film were controlled by the growth rate of the silicon nitride film. The wavelength of emitting light from a-Si QDs could be modulated from red to deep blue by controlling the QD size. Photoluminescence and optical absorption spectroscopy also showed that the confinement effect is a major origin of the change in the optical band structure. Pure white photoluminescence was also demonstrated by combining an orange-light emitting a-Si QDs layer with blue-light emitting one. Light-emitting devices (LEDs) with metal-insulator-semiconductor (MIS) structure were also fabricated and they showed a low threshold voltage (< 5V).

SESSION F14: POSTER SESSION
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

F14.1

SYNTHESIS OF Ge NANOCRYSTALS IN SILICON OXIDE MATRIX BY RAPID THERMAL ANNEALING. W.K. Choi, V. Ng, Y.W. Ho, T.B. Chen, Microelectronics Laboratory, Department of Electrical and Computer Engineering, National University of Singapore, SINGAPORE.

Raman, transmission electron microscopy (TEM) and photoluminescence (PL) results of Ge nanocrystals in co-sputtered Ge SiO₂ samples synthesized by rapid thermal annealing (RTA) will be presented. The samples were prepared by co-sputtering a SiO₂ target with six pieces of Ge attached. All the samples were rapid thermal annealed for a fixed duration of 300s. Raman results showed that a transition from amorphous to nanocrystalline Ge when the samples were annealed at a temperature higher than 700°C. The Raman spectrum of sample annealed at 1000°C is very similar to that of the as-deposited amorphous sample. TEM results showed spherical Ge nanocrystals well dispersed in the oxide matrix for sample annealed at 800°C. For samples annealed at 1000°C, Ge nanocrystals with a diameter of 200-280Å were observed near the Si-SiO₂ interface. These nanocrystals have a multiple twinned structure. The TEM results suggest that when annealed at 800°C, only nucleation of Ge occurs. When annealed at 1000°C, Ge diffuses to the silicon oxide/silicon interface and precipitates at the interface. The significant reduction in the Raman peak of sample annealed at 1000°C may be due to the broadening caused by the nanocrystal size distribution. PL results showed a peak at ~3.0 eV and the peak intensity increases as the annealing temperature increases from 600 to 800°C. Further increase in annealing temperature to 1000°C resulted in a reduction in PL intensity.

We aim to synthesize Ge nanocrystals of different sizes by varying the Ge concentration in the SiO₂ matrix or by manipulating the RTA profile. Preliminary results on nanocrystal growth with different RTA profiles showed a critical thermal budget for maximum PL response.

Detailed results on this will be reported. We are also carrying out X-ray photoelectron spectroscopy experiments to examine possible contribution of defects associated with Ge or in SiO₂ to the PL results.

F14.2

SYNTHESIS OF DEPOSITED Ge-NANOCRYSTALS OUT OF THE GAS PHASE. C. Bostedt, T. van Buuren, N. Franco, M. Balooch, L.J. Terminello, Lawrence Livermore National Lab, T. Möller, Hasylyab at DESY, GERMANY.

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over additional parameters in the growth process - like surface passivation - often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor that is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. The clusters are spherical in shape and their sizes are determined by atomic force microscopy (AFM) and confirmed by transmission electron microscopy (TEM). The sizes exhibit a log-normal distribution and the mean sizes range from 1.5 to 7 nanometers. The parameters for making the Ge-nanocrystals are discussed and compared to other cluster experiments, so that general rules for the synthesis of these nanostructures can be established. We find, that the clusters are crystalline in structure, measured by both X-ray diffraction and TEM. However, we do not find hints of a tetragonal phase in small particles as reported in the literature for small cluster sizes [1] and this finding is supported by theoretical calculations [2]. Additionally we see indications for strong substrate-cluster interactions, which can in extreme cases lead to the destruction and/or rearrangement of the clusters. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL. [1] S. Sato et al, Appl. Phys. Lett., 66, 3176, 1995 [2] L. Pizzagalli, G. Galli, J. Klepeis, private communications

F14.3

PREPARATION AND FUNCTIONALIZATION OF HYDRIDE TERMINATED POROUS GERMANIUM BY BIPOLAR ELECTROCHEMICAL ETCHING (BEE). Hee Cheul Choi, Jillian M. Buriak.

Porous germanium (PG) has been prepared via a novel bipolar electrochemical etching (BEE) technique using an ethanolic HCl electrolyte. An initial period of anodization of the germanium electrode followed by cathodization leads to formation of a porous layer with nanoscale features. Both n-type and p-type germanium (100) wafers result in high surface area hydride-terminated PG as determined by transmission FTIR and SEM, similar to silicon hydride surfaces of porous silicon (PS), although the mechanism of the etch is quite different. Homogeneous red photoluminescence is observed across the entire etched PG surface at 77 K in a darkened room upon illumination with 365 nm UV irradiation. In contrast to the 3 previous literature reports utilizing HF for the preparation of PG, in our hands, this route leads to a highly oxidized, rough interface. The HCl system, however, provides a highly reproducible methodology for production of PG. Artificial color changes of the samples during BEE, due to Fabry-Perot fringes, also indicate formation of the thin porous layer. The hydride terminated PG material is quite resistant to oxidation, even under thermal conditions, but can be induced to undergo hydrogermylation by thermal reactions with alkenes and alkynes.

F14.4

FORMATION OF Ge NANOCRYSTALS PASSIVATED WITH Si BY GAS EVAPORATION OF Si AND Ge. J.J. Si, H. Ono, K. Uchida, S. Nozaki and H. Morisaki, Univ. of Electro-Communications, Dept. of Electronic Engineering, Tokyo, JAPAN.

There are various techniques to fabricate semiconductor nanocrystals. However, most of the techniques do not have a good control over the surface of semiconductor nanocrystals, and the surface often becomes unintentionally oxidized. Uncontrolled oxidation of the surfaces makes it difficult to experimentally observe physical effects from a zero-dimensional quantum structure such as quantum confinement. In order to form an ideal quantum dot we made an attempt to passivate the surface of a Ge nanocrystal with Si by gas evaporation of Si and Ge. Two methods are employed in the gas evaporation technique to realize such a quantum dot. One is to use a single boat with SiGe alloy as a source, by taking advantage of a lower melting point of Ge. The other is to use two boats with Si and Ge each as source materials. It is referred to as the gas co-evaporation process, in which Ge is placed in the lower boat so that the formed Ge nanocrystals can travel through the Si vapor before reaching the substrate. Ge nanocrystals were formed by both methods, and their structures including the surface of the nanocrystals were characterized by X-ray Diffraction, Raman and

X-ray Photoelectron Spectroscopy. In the case of a single boat with a SiGe alloy source, Ge nanocrystals are found to be oxidized and appear to be coated with a SiGeO shell. In the gas co-evaporation, the XRD pattern shows presence of Ge nanocrystals without Si or SiGe alloy, while the Raman spectrum clearly shows a Si-Ge peak. Furthermore, the XPS spectrum does not show Ge oxide but Si oxide. Therefore, it is concluded that the surface of Ge nanocrystals is well passivated with Si, and the surface of the Si outer shell is oxidized. The FWHM of the Si-Ge peak in Raman is as small as those reported for a Ge quantum dot coated with Si by Molecular Beam Epitaxy.

F14.5

STRUCTURAL, COMPOSITIONAL AND OPTICAL PROPERTIES OF SELF ORGANISED Ge QUANTUM DOTS GROWN ON Si [001]. Matthew Halsall, Alan Dunbar, Philip Dawson, Uschi Bangert, Department of Physics, UMIST, Manchester, UNITED KINGDOM; Yasuhiro Shiraki, Makoto Miura, RCAST, University of Tokyo, Tokyo, JAPAN; Isabelle Berbezier, Mario Abdallah, CRMC2, Marseille, FRANCE.

The structure of the Ge quantum dots, grown by gas source molecular beam epitaxy on Si (001) substrates, has been examined by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Uncapped Ge quantum dots examined by AFM are seen to have a bi-modal size distribution: domed quantum dots, of approximately 100nm base width and 12nm in height, occurring alongside smaller pyramidal quantum dots of approximately 50nm base width and 6nm in height. Cross sectional TEM measurements show that capping the quantum dots with Si causes them to flatten such that the pyramids and domes are much more alike in overall shape, the main difference being their size. Energy dispersive X-ray analysis shows that the material between the quantum dots is pure Si whilst the 2D layer on which the quantum dots form and the quantum dots themselves consist of SiGe. The concentration of Ge in this 2D layer is nominally 8% and in the quantum dots it is approximately 27%, also the distribution of Ge within the quantum dots was found to be asymmetric, with the greatest Ge concentration occurring at the apex of the quantum dots. The low temperature photoluminescence spectrum exhibits a broad feature with a peak energy of 0.8 eV which we attribute to recombination involving the quantum dots. The time decay of the photoluminescence from the quantum dots was observed to be non-exponential and that it could be described as a bi-exponential decay with time constants of 2 and 30 microseconds. Time-resolved photoluminescence spectroscopy suggest that the two different time constants are associated with recombination from the two size distributions of quantum dots with the faster time constant being associated with the smaller of the two size distributions due to the greater degree of overlap of the spatially separated electron-hole wavefunctions.

F14.6

ON THE STRUCTURE AND STABILITY OF SMALL Ge DOTS. Laurent Pizzagalli, Giulia Galli, John E. Klepeis, Francois Gygi, Lawrence Livermore National Laboratory, CA.

Understanding the influence of surface reconstruction and passivation on the ground state properties of semiconductor nanodots is a key prerequisite in designing biological applications, as well as for controlling deposition and aggregation processes of nanoparticles on surfaces. In order to tailor the properties of nanodots, it is important to separate the effects of quantum confinement from those due to the surface, and to gain insight into the mechanisms by which preparation conditions can influence the dot structure. Here we focus on small Ge dots (1-3 nm), whose structure is at present the subject of controversy. Using first principles calculations, we have studied the influence of both H-saturated and bare reconstructed surfaces on the relative stability of diamond and tetragonal, ST12-like structures for clusters smaller than ~ 2.5 nm. Our results show that over a wide temperature range the diamond structure is more stable than ST12-like structures, with the magnitude of the energy difference between the two geometries being strongly dependent on the surface properties. Based on our calculations, we propose a mechanism which may be responsible for the formation of metastable ST12 clusters in vapor deposition experiments, by cold quenching of amorphous nanoparticles that have unsaturated, reconstructed surfaces. Our results suggest that the pressure exerted on the inner core of the dot by an unsaturated surface can induce an amorphous-to-ST12 transition in clusters with diameters smaller than 2.5-3.0 nm. In conclusion, our study indicates that by tuning the surface properties of nanodots, the pressure exerted on the dot core can be modified and used to tailor the structural and electronic properties of the nanoparticles. This work was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

F14.7

COMPOSITION AND STRAIN IN FREESTANDING Ge ISLANDS. J. Stangl, A. Daniel, V. Holý, G. Bauer, Univ. Linz; I. Kegel, T.H. Metzger, Univ. Munich; Th. Wiebach, Humboldt Univ. Berlin, GERMANY; O.G. Schmidt, K. Eberl, MPI Stuttgart, GERMANY.

Combining different x-ray scattering techniques, we have conclusively established the strain *and* composition distribution in uncapped Ge islands, which were deposited at 600°C by MBE on Si(001). Using grazing incidence diffraction for recording 3D reciprocal space maps around the (220) and (400) reciprocal lattice points (RLP), combined with grazing incidence high angle exit diffraction around the (202) RLP, and coplanar diffraction around the (113) RLP, the experimental data and their comparison with simulations of the scattered intensity based on finite element calculations show conclusively the following: albeit pure Ge is deposited, the islands (diameter: 110 nm, height: 13 nm), exhibit a concentration gradient from $x = 0.5$ at the base to $x = 1.0$ at the top, in conjunction with an averaged in-plane strain gradient along growth direction from $\epsilon_{xx} = 0$ (at $z = 0$ nm) to 0.025 ($z = 13$ nm). Consequently, the composition and strain profiles which we obtained show, that the islands consist of pure Ge only at their top, but they are nowhere fully relaxed.

F14.8

OPTICAL AND STRUCTURAL ANALYSIS OF Ge QUANTUM DOTS EMBEDDED IN STRAINED Si QUANTUM WELLS GROWN ON PATTERNED SUBSTRATES. A. Beyer, D. Grützmacher, C. David, E. Müller, S. Stutz, Laboratory for Micro- and Nanotechnology, Paul-Scherrer-Institute, Villigen, SWITZERLAND.

Ge quantum dots embedded in Si have been used in the past to improve the opto-electronic properties of Si based materials. The idea is to overcome the limitation of the indirect band gap of Si by a strong localisation of the carriers in quantum dots. However, the Ge quantum dots provide a strong carrier confinement only for the holes, the electrons are only weakly confined in the Si. In this study we embedded the Ge quantum dots in strained Si quantum wells grown on relaxed SiGe buffer layers. The strained Si quantum wells provide a 2-dimensional confinement of the electrons. The structures were deposited on planar as well as on patterned substrates by molecular beam epitaxy. The structural and optical properties of the samples were analysed using high resolution cross sectional transmission electron microscopy as well as low temperature photoluminescence. The Si quantum well width, the amount of Ge deposited and the size of the mesa structures have been used as experimental parameters. Pure Ge dots as well as C-induced Ge dots have been embedded in the strained Si quantum wells. Relaxed buffer layers grown on square and line shaped mesa structures show a strongly reduced dislocation density. Consequently the deep luminescence attributed to dislocations in the buffer layers is strongly reduced and pronounced photoluminescence of the quantum structures grown on top of the buffer layers can be observed.

F14.9

Abstract Withdrawn.

F14.10

Si/Ge INTERMIXING AND ISLAND-ISLAND INTERACTION INFLUENCE ON THE Ge/Si(100) ISLAND SIZES. G. Capellini, M. De Seta, and F. Evangelisti Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica Università di Roma Tre, Roma, ITALY.

In this work we present a detailed study of the influence of the deposition temperature and growth rate on size, size distribution and density of self-assembled Ge islands grown on Si(100) substrates by UHV Chemical Vapor Deposition (CVD) technique. The samples have been characterized by atomic force microscopy (AFM), X-ray photoemission spectroscopy (XPS) and reflection high-energy electron diffraction (RHEED). We find that the deposition temperature strongly influences the base size of the Ge self-assembled islands at the 3D nucleation onset (critical base) as well as the strained island mean size. The critical base increases from 25 to 270 nm and the strained island mean base size increases from 50 to 370 nm on going from deposition temperature of 450°C to 850°C. We explain this effect as a temperature enhanced Si/Ge intermixing that reduces the effective epilayer-substrate lattice mismatch. By combining AFM and XPS measurements we have determined the actual composition of the Ge islands as a function of deposition temperature. We found that the intermixing is present above $T_{dep} = 600^\circ\text{C}$. The Ge content x in the alloyed epilayer decreases upon increasing the deposition temperature. The scaling relationship connecting the alloyed island sizes and the effective mismatch with the Si substrate has been determined. By changing the growth rate at fixed deposition temperature we were able to modify the island density. The influence of the island density on the islands size has been investigated. We found that by tuning the island density from 10^9 to $2 \times 10^{10} \text{ cm}^{-2}$, at $T_{dep} = 600^\circ\text{C}$, the mean

island size changes from 90 to 60 nm. Island-island interaction effects on the growth dynamic will be discussed.

F14.11

MICROSTRUCTURE OF STRAIN-RELAXED SiGe LAYERS.
P.M. Mooney, J.L. Jordan-Sweet, IBM T.J. Watson Research Center, Yorktown Heights, NY; C.B. Stagarescu, D.E. Eastman, James Franck Inst., University of Chicago, Chicago, IL; B. Lai, Z. Cai, Advanced Photon Source, Argonne National Lab, Argonne, IL.

Strain-relaxed $\text{Si}_{1-x}\text{Ge}_x$ alloy films on (001) Si substrates serve as buffer layers for field-effect transistors having strained Si or $\text{Si}_{1-y}\text{Ge}_y$ ($y > x$) carrier channels. At low mismatch strain (<2%), SiGe/Si(001) heterostructures relax by the formation of 60° misfit dislocations with attendant microstructure and broadened x-ray diffraction peaks. Samples investigated are step-graded structures consisting of a series of thin layers, with increasing Ge mole fraction, followed by a uniform-composition $\text{Si}_{1-x}\text{Ge}_x$ ($x \approx 0.15$) layer of varying thickness. Measurements taken at the NSLS (X20) using a divergent ($\approx 0.3^\circ$) capillary-focused beam ($\approx 1.0 \times 5.0 \mu\text{m}$) show that all regions of the top $\text{Si}_{1-x}\text{Ge}_x$ layer have the same lattice parameter ($\Delta\theta_{Bragg} < 0.01^\circ$) but different average tilt angles whose variation depends on the misfit dislocation density. High angular resolution x-ray rocking curves measured at the APS (2-ID-D) from a 3 μm -thick $\text{Si}_{0.83}\text{Ge}_{0.17}$ layer show many discrete tilt angles with sharp lines ($\approx 0.01^\circ$ wide) that correspond to individual tilted regions ("micro-grains") illuminated by the 3.0 μm pinhole-apertured beam. Various illuminated spots show a range of tilt angles of $\approx 0.08^\circ$ to 0.22° with complex and varying rocking curve line shapes. Using a model in which the local tilted regions are considered to be columnar "micro-grains" extending from the misfit dislocation network up to the sample surface, we find that some illuminated regions show a few "micro-grains" with the largest size $\approx 4.0 \mu\text{m}$ while others show 10-15 "micro-grains" with an average size $\approx 1.5 \mu\text{m}$. The dimensions are smaller than previously estimated and are consistent with cross sectional TEM images and with measurements of the surface morphology. Partially supported by DOE contracts DE-AC02-76CH00016 and W-31-109-Eng-38.

F14.12

NUCLEATION-CONTROL AND ENHANCEMENT OF SOLID-PHASE-CRYSTALLIZATION OF SiGe HETERO-STRUCTURE. S. Yamaguchi, S. Park, N. Sugii, Hitachi Ltd., Central Research Lab., Tokyo, JAPAN.

Formation of high-quality polycrystalline Si on insulating substrate has been widely investigated for application in many device fields (e.g., polycrystalline gates of FET, channels of TFT). The paper reports on the effect of SiGe heterostructures on the size and shape of crystallites and on crystallization properties on SiO_2 . We have composed SiGe heterostructures ($\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{SiO}_2$; $x = 0 - 1$) and observed nucleation process during solid-phase-crystallization by TEM, AFM, and ellipsometry. We have found that the incubation time of the nucleation in SiGe layer significantly decreases with an increase of x ; the nucleation rate of $x = 0.3$ sample was nearly one-hundred times higher than that of $x = 0$ sample. The time to complete the crystallization of the covered Si layer has been significantly reduced as well as the incubation time. The composed SiGe crystallites have larger grain size than that of Si/ SiO_2 . We have used patterned (sub- μm) SiO_2 to modulate the surface geometry and found that the nucleation-site of SiGe crystallites strongly related to the surface tension between the SiGe layer and the substrate. The size, shape and crystallographic orientation of microcrystallites and their effects on transport properties (e.g., mobility, resistivity) of SiGe heterostructure will be discussed. A part of this work was carried out under the ASET program supported by NEDO, Japan.

F14.13

LOW TEMPERATURE GROWTH OF POLY-CRYSTALLINE FILM OF SILICON-RICH SILICON-GERMANIUM BY REACTIVE THERMAL CHEMICAL VAPOR DEPOSITION. Kousaku Shimizu, Jianjun Zhang, Jeong-woo Lee, Jun-ichi Hanna, Imaging Science and Engineering Laboratory, Tokyo Institute of Technology.

Low temperature growth of poly-SiGe has been investigated by reactive thermal chemical vapor deposition (RTCVD) method, which is a newly developed technique for preparing poly-SiGe by using redox reactions in a set of source materials, i.e., Si_2H_6 and GeF_4 . This technique gives quite low inhomogeneity in film thickness as well as no polymeric silane particles, which can be applied to large-area electronic devices such as TFT arrays for flat-panel liquid crystal displays (LCDs) and solar cells, because the source gases are decomposed to afford the films in the vicinity of heated substrate surface under the conditions where gas flow and substrate temperature are uniform on substrates area. Interestingly, GeF_4 promotes the crystal growth in spite of a small gas flow rate compared with that of Si_2H_6 , e.g., $\text{GeF}_4/\text{Si}_2\text{H}_6 = 0.1\text{sccm}/2\text{sccm}$. In order to

prepare silicon-rich poly-SiGe of high mobility, a series of experiment on total pressure, gas flow rates of the source materials and dilution gas of He, and residence time of the gases at 450°C was investigated. Raman Scattering and XRD (X-Ray Diffraction) measurements were used for evaluating the crystallinity of the films, and XPS (X-ray Photoelectron Spectroscopy) and XRFs (X-ray Fluorescence Spectroscopy) methods for evaluating silicon content [Si/(Si+Ge)]. For evaluating the morphology, SEM (Scanning Electron Microscope) and TEM (Tunneling Electron Microscope) were used. At 0.45 Torr, high crystallinity films with high silicon content was prepared, however, the inhomogeneity of film thickness was quite serious and reproducibility of the film growth was poor for device application. This issue is probably attributed to the difficulty in establishing uniform distribution of substrate temperature in such a growth condition. For overcoming this problem, the growth condition was surveyed especially in higher pressure range of 5-20 Torr. Simple increase of the total pressure resulted in degradation of Si-content and crystallinity of the films, although the distribution of film thickness was suppressed drastically. Appropriate choice of the residence time and the gas flow ratios lead to significant improvement in the Si content in the films. Finally, silicon-rich poly-Si($>0.95\text{Ge}<0.05$) films, which has 7.5 cm^2/Vs of Hall mobility (p-type) and (220) orientation, have been prepared at 10 Torr and 450°C under satisfactory reproducibility enough to fabricate devices.

F14.14

PHOTOLUMINESCENCE AND ESR STUDY OF $\text{Si}_{1-x}\text{Ge}_x$ ALLOY NANOCRYSTALS. Kimiaki Toshiakiyo^a, Masakazu Tokunaga^a, Shinji Takeoka^a, Minoru Fujii^b and Shinji Hayashi^{a,b}; ^aGraduate School of Science and Technology, ^bDepartment of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe, JAPAN.

Nanometer-size Si crystals (nc-Si) have extensively been studied. It has been demonstrated that the photoluminescence (PL) energy of nc-Si is changed in a wide range by just controlling the size. The tuning range can be expanded by $\text{Si}_{1-x}\text{Ge}_x$ alloy formation, because the PL energy of $\text{Si}_{1-x}\text{Ge}_x$ alloy nanocrystals (nc- $\text{Si}_{1-x}\text{Ge}_x$) depends on the Ge concentration as well as the size. In our previous work, we demonstrated that the PL energy of nc- $\text{Si}_{1-x}\text{Ge}_x$ changes from the widened band gap of nc-Si to that of nc-Ge by increasing the Ge concentration. However, the PL efficiency decreased rapidly with increasing the Ge concentration. For the applications of nc- $\text{Si}_{1-x}\text{Ge}_x$ as optoelectronic devices, the improvement in the PL efficiency is indispensable.

The purpose of this work is to explore the origin of the PL quenching and propose a method for the improvement of the PL efficiency. We prepared nc- $\text{Si}_{1-x}\text{Ge}_x$ as small as 4nm in diameter embedded in SiO_2 matrices by a cosputtering method. In pure nc-Si, a PL peak was observed around 1.45 eV. With increasing Ge concentration, the PL peak shifted to lower energies and reached 1.21 eV for the sample with $x=0.31$, while the PL intensity decreased about two orders of magnitude. It was found that the decrease in the PL intensity is accompanied by a drastic change in ESR spectrum. For nc-Si, the ESR signal due to Si dangling bonds at the interface between nc-Si and SiO_2 matrices (P_b centers) was observed. By $\text{Si}_{1-x}\text{Ge}_x$ alloy formation, in addition to the signal from nc-Si, a broad signal appeared. The intensity of the broad signal increased with increasing Ge concentration, indicating that the broad signal is related to Ge. These results suggest that defects at the interface between nc- $\text{Si}_{1-x}\text{Ge}_x$ and surrounding SiO_2 matrices induced by alloying are responsible for the PL quenching.

F14.15

TEM STUDY OF NANOCRYSTALLINE DIAMOND FILMS GROWN FROM Ar-CH₄ WITH OR WITHOUT ADDED H₂. S. Jiao, A. Sumant, M.A. Kirk, D.M. Gruen, A.R. Krauss, O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Nanocrystalline diamond (NCD) films, grown from microwave plasma-enhanced chemical vapor deposition (MPCVD) from a gas mixture of Ar ~1percent CH₄ or Ar ~1% CH₄ ~5% H₂, have been examined with transmission electron microscopy (TEM). The films consist of equiaxed nano-grains (2-10nm in diameter) and elongated twinned dendritic grains. The area proportion of these dendritic grains increases with an addition of H₂. High resolution electron microscopy (HREM) shows an absence of detectable amorphous phase at grain boundaries, which are typically one or two atomic layer thick (0.2 - 0.4nm). Cross-section view reveals non-columnar structure of the films. The initial nucleation of diamond occurs on Si matrix directly when H₂ is present otherwise from a carbon layer, which is about 10-15nm thick above the matrix Si. This distinction indicates the enhancement of diamond nucleation by H₂. The relation between diamond nuclei and Si is primarily random and occasionally epitaxial.

F14.16

NOVEL BULK NANODIAMOND/PYROCARBON SEMI-CONDUCTOR MATERIALS. Sergey K. Gordeev, Central Research Inst of Materials, St. Petersburg, RUSSIA; Peter I. Belobrov, Nikolai I. Kiselev, Eleonora A. Petrakovskaya, Kirensky Inst of Phys & Inst of Biophysics SB RAS, Krasnoyarsk, RUSSIA; Thommy C. Ekstrom, Royal Institute of Technology, Stockholm, SWEDEN.

Novel semiconductor materials from nanodiamond/pyrocarbon composites (NDC) consisting carbon > 99 mass % were produced using synthesis-by-design method. Nanodiamond particles of 4-6 nm are connected into a bulk solid composite by pyrolytic carbon matrix. The high-porous NDC has the narrow pore-size distribution and effective pore size of 8-10 nm. Main features of NDC are controlled by $\gamma = \text{mass ratio of } sp^2/sp^3 \text{ phases}$. The changing of γ from 0 to 0.5 modifies volume electrical conductivity by 12 orders of magnitude. The effective thickness of pyrocarbon on the surface of nanodiamond particles is varying from 0.2 to 1 nm and the pore volume is ranging from 30 to 60 vol. %. The physical nature of cooperative states in NDC was studied. The volume electrical conductivity σ (T) was measured in the temperature range 77 - 290 K. The dependence of EPR data and values of σ (T) on γ was determined. Nanodiamond has paramagnetic invariant with $g = 2.0027(1)$, $\Delta H = 0.86(2)$ mT which conserves in NDC. Both g-factor and line width are not depending on γ and temperature. Concentration of unpaired electrons is $3.5 \cdot 10^{19}$ spin/g that is equal to one dangling bond per nanodiamond particle. Semiconducting properties of NDC was established. The activation energy of NDC electrical conductivity depends on γ and has value of 0.03 - 0.3 eV. The check for variable-range hopping conduction is to measure σ against T and to observe a $T^{1/4}$ dependence at low T. A strongly positive thermoelectric power is evidence that NDC is p-semiconductor with narrow gap. Correct consideration of NDC should take into account Tamm levels of surface electrons. Observed zero value of magnetoresistance and the absence of Hall potential for all NDC are accounted for by Tamm - Lifshitz - Pekar electronic conduction mechanism within one-dimensional band of surface states.

F14.17

MOLECULAR DYNAMICS SIMULATION OF N IMPURITIES IN ULTRANANOCRYSTALLINE DIAMOND GRAIN BOUNDARIES. Peter Zapol, Larry A. Curtiss, Dieter M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; Michael Sternberg, Thomas Frauenheim, Department of Physics, University of Paderborn, Paderborn, GERMANY.

Ultrananocrystalline diamond films grown from hydrogen-poor plasmas have a number of highly desirable mechanical and electronic properties. High-angle grain boundaries with rather high formation energy are believed to be dominant in these films. Due to the small grain size of 3 to 15 nm, about 5 to 10% of all the atoms in the films are located in the grain boundaries. High-energy twist grain boundaries in diamond have been shown to have a large fraction of three-coordinated carbon atoms in sp^2 configuration. We find that N is likely located at the grain boundaries, which play a crucial role in controlling important characteristics of the films, such as electrical conductivity and electron emission. Density-functional based tight-binding (DFTB) molecular dynamics simulations were performed for diamond high-energy high-angle (100) twist grain boundaries with N. It is shown that N substitution in the grain boundaries is more favorable energetically than in the grain bulk. The low-energy atomic structures and their electronic properties are reported, and we conclude that N in ultrananocrystalline diamond decreases the coordination of carbon atoms near the interface. Electronic levels associated with N atoms are discussed. (Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.)

F14.18

CHARACTERIZATION OF DEFECTS IN BORON DOPED CVD MICROCRYSTALLINE DIAMOND FILMS. V.I. Polyakov, A.I. Rukovichnikov, N.M. Rossukanyi, L.L. Golik, Z.E. Kun'kova, Institute of Radio Engineering and Electronics, RAS, Moscow, RUSSIA; V. Ralchenko, General Physics Institute, RAS, Moscow, RUSSIA; V.P. Varnin, I.G. Teremetskaya, Institute of Physical Chemistry, RAS, Moscow, RUSSIA.

Despite many years of diamond research little is known about a variety of electronic properties, such as doping induced defect formation. In this paper electrical properties of the semiconductor boron doped p-type CVD diamond films were studied. Isothermal Charge-based Deep Level Transient Spectroscopy (Q-DLTS) was applied to explore the density, activation energies, and capture cross-sections of trapping centers (TC) - electrical active defects in CVD diamond films. The Transient Spectroscopy showed that TC have the continuous energy spectrum with two peaks at low temperatures - two discrete energy levels. Analysis of the Q-DLTS spectra for all samples, measured at different conditions, was shown

that discrete levels have the same activation energies about 0.3 eV with strongly difference in capture cross-sections and are induced by boron. The obtained density of these defects was less than the uncompensated acceptor concentration, which is calculated from capacitance-voltage (CV) data. From Hall effect measurements the carrier (hole) concentration and mobility were found. Experimental data were used to determine the degree of compensation and concentration of compensating donors (nitrogen) in growing diamond films. The results are discussed in comparison with data available in the literature. This work was supported by Grant No of the 98-02-16679 of the Russian Foundation of Fundamental Research.

F14.19

STABILITY STUDIES OF THERMALLY-CARBONIZED POROUS SILICON. J. Salonen, V-P. Lehto, M. Björkqvist, E. Laine, Turku Univ, Dept of Physics, FINLAND; L. Niinistö, Helsinki Univ Tech, FINLAND.

Thermally-carbonized porous silicon (TCPS) films have been prepared by exploiting a dissociation of an acetylene. Since SiC is quite inert, the TCPS surface could be assumed to demonstrate similar behavior. Indeed, reduced thermal oxidation, enhanced adsorption of water molecules and only slightly reduced specific surface area have been already observed. In addition to this, the thermal carbonization process is quite simple and many advantages of porous silicon (PS) are retained considering, for example, sensing applications, MEMS, etc. In this work we go on the stability studies of the TCPS using calorimetric methods. The long-term stability studies of water adsorption behaviour indicates that the TCPS samples are more stable than thermal oxidized PS samples. Also, the reaction rate in KOH aqueous solution is smaller in TCPS than, for example, in dodecene treated sample. Several other promising results will be presented and future prospects of TCPS in applications will be discussed.

F14.20

INTERBAND TRANSITIONS IN Si QUANTUM WIRES GROWN IN {100} PLANE. X. Zianni and A. Nassiopoulou, Insitute of Microelectronics, NCSR, 'Demokritos', Attiki, GREECE.

The growth of Si quantum wires and their optical properties have been the subject of research in recent years. We discuss the interband transitions in Si rectangular quantum wires grown in {100} plane. The transition rates are given by second order perturbation theory. In the indirect-phonon assisted transitions both Γ - Δ electron-phonon and hole-phonon scattering are considered. The eigenstates of electrons and holes are calculated within the effective mass approximation. For holes, the minimum of the one dimensional sub-bands is at the Γ -point for all the three bands, (heavy hole, light hole and split-off band), considered. For electrons, the six anisotropic valleys near the X point in bulk Si are taken into account. The position of the minimum of the one dimensional sub-bands of electrons depends on the growth direction and for some angles in the {100} plane it is at the Γ -point. The six valleys are not equivalent and the phases of the electrons wavefunctions depend on the direction of growth. The overlap integrals for interband and intrasubband transitions exhibit strong directional dependence. These effects explain the dependence of the calculated emission rates of Si quantum wires on the growth direction and on the dimensions of the quantum wires.

F14.21

A NEW SYNTHETIC ROUTE FOR THE SYNTHESIS OF SILICON NANOPARTICLES. Qi Liu, Susan M. Kauzlarich, University of California-Davis, Department of Chemistry, Davis, CA.

We describe the synthesis and characterization of nanocrystalline Si (R-n-Si) prepared by the reaction of Zintl phase silicide MSi (M= Na, Mg, K) with different oxidants, such as I_2 , Br_2 , in solution. Glyme, diglyme, tetrahydrofuran, and hydrocarbon have been investigated as solvents. Different reaction conditions have been explored. These reactions produce crystalline Si nanoparticles R-n-Si with surfaces that can be chemically modified (R= alkyl, H), along with amorphous material. The resultant nanoparticles can be suspended in organic solvent, and are characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), UV-vis absorption, and photoluminescence spectroscopy. The results from this work are compared to those from previously reported synthesis by the reaction of MSi with $SiCl_4$.

F14.22

NANOCRYSTALLINE SILICON BY MICROWAVE CVD FOR THIN FILM TRANSISTORS AND SOLAR CELLS. Young J. Song, Hak-Gyu Lee, Lihong Teng and Wayne A. Anderson, SUNY at Buffalo, Dept. of Electrical Engineering, Buffalo, NY.

Microwave chemical vapor deposition (MCVD) is utilized to deposit nanocrystalline silicon (nc-Si) thin films onto a variety of substrates for application to thin film transistors (TFT's) and solar cells. It is

especially important to gain reproducible control of the processing. Thus, an in-situ mass spectrometer (MS) records the plasma conditions with variation of process conditions such as gas selection, pressures, partial pressures, and substrate temperature. These data are correlated with electrical and optical properties of the films. Raman spectra show a FWHM of 11/cm with position at 522/cm as desired for crystalline Si. Typical film thickness is 100 nm with grain size of 20-30 nm, using standard deposition, and 50-80 nm when the substrate is intensely optically illuminated during deposition, called photon assist (PA). Hydrogen dilution serves to increase the crystallinity of the films. The ratio of photo- to dark conductivity exceeds 10^5 with dark conductivity as low as 1.5×10^{-10} S/cm. Thin film transistors have been fabricated with I_{on}/I_{off} of 10^7 . Heterojunction solar cells were fabricated using amorphous Si/n-Si/crystalline Si giving a conversion efficiency of above 10.5%, without an antireflection coating. The use of MS in device design will be emphasized.

F14.23
PULSED DEPOSITION OF MICROCRYSTALLINE SILICON THIN FILMS. N.H. Nickel and P. Lengsfeld.

General drawbacks of microcrystalline silicon (μ c-Si) films prepared by rf-glow discharge of silane-hydrogen gas mixtures are the low deposition rate and a small average grain size of about 10 nm. In this paper, we investigate the influence of a pulsed rf-glow discharge on the properties of μ c-Si films. The pulse frequency was varied between 100 and 30000 Hz for duty cycles between 0.75 and 0.9. The crystalline fraction of μ c-Si was determined from Raman backscattering data. Information on hydrogen bonding was obtained from Si-H_x stretching local vibrational modes (LVM) at 2000 and 2100 cm⁻¹ and from H evolution measurements. With decreasing pulse frequency the deposition rate increases by up to 60%. The crystalline fraction X_C is independent of pulse frequency and duty cycle. In addition, a change of the deposition pressure from 0.4 to 1.0 mbar did not affect X_C at a given frequency and duty cycle. However, pulsed deposition has a significant impact on the hydrogen microstructure. The H microstructure parameter R=I(2100)/I(2000) I(2100) decreases by more than a factor of two in response to a decrease of the pulse frequency from 30000 to 3000 Hz indicating that the amount of H incorporated in large clusters decreases. This is accompanied by the vanishing of a third local vibrational mode centered around 1906 cm⁻¹ that commonly is observed in μ c-Si. The H evolution spectra of μ c-Si films are distinctively different from those measured on amorphous silicon. They show a low temperature peak at T=420°C and two high temperature peaks centered at 610 and 670°C. The results are discussed in terms of current models for the growth of hydrogenated microcrystalline silicon.

F14.24
CHARACTERIZATION OF MICROCRYSTALLINE Si FILMS BY MeV ION SCATTERING TECHNIQUES. W. Bohne, J. Röhrich, B. Selle, M. Birkholz, F. Fenske, W. Fuhs, J. Platen, P. Reinig, Hahn-Meitner-Institut, Berlin, GERMANY.

Rutherford Backscattering Spectrometry (RBS) and channeling studies with 1.4 MeV ⁴He ions as well as Heavy-Ion Elastic Recoil Detection Analysis (HI-ERDA) with 230 MeV ¹²⁹Xe ions have been applied to characterize structural properties and the impurity content of thin Si films. The depth profiles of impurities such as H, O and Ar can be determined by HI-ERDA without any need of calibration. The analytical potential of these ion-beam techniques is demonstrated by two examples: (1) μ c-Si films prepared by dc magnetron sputtering in a pure Ar plasma and (2) transition from oriented to disordered growth in homoepitaxial Si films deposited by electron cyclotron resonance CVD at low temperatures. In case (1) we compare the atomic area density N-d obtained by RBS and the optical thickness n-d (n=refraction index) derived from the interference structure of IR reflection spectra and use the ratio n/N as a figure of merit for the structural quality of the films. This quantity correlates well with the deposition parameters. For example, a decrease of n/N was found for increasing growth temperature which suggests an enhancement of the film density. The Ar content in these films has a uniform depth distribution and increases linearly with a negative substrate bias. In case (2) we evaluate disorder profiles from the ion channeling spectra. Comparing these with the impurity profiles determined by HI-ERDA we observe that hydrogen and also oxygen are accumulated in the disordered parts of the films. This is explained by preferential incorporation of hydrogen in amorphous regions of conical shape which appear at the transition from oriented to defective growth and which have been visualized by electron microscopy. The HI-ERDA results suggest that with progressing film growth oxygen is increasingly involved in the evolution of disorder.

F14.25
NANOCRYSTALLINE SILICON STRUCTURES FOR ELECTRON FIELD EMISSION APPLICATIONS. Anatoli A. Evtukh, Ella B.

Kaganovich, Volodimir G. Litovchenko, Yuri M. Litvin, Eduard G. Manoilov, Sergei V. Svechnikov, Inst. of Semiconductor Physics, Dept. Physical Bases of Microelectronics, Kiev, UKRAINE.

A new method of silicon multitip electron emitter array formation have been developed by laser technology in air. The laser direct-write process has been applied, one by one (single) laser pulses formed the single rather uniform conical structure arrays. In this process a silicon substrate (n-Si) is locally heated above its melting point by a pulse YAG : Nd3+ laser. The laser ablation of n-Si took place in air. Owing to air pressure ((105 Pa) most of Si particles were deposited back on the target, on conical surface too. As a result the conical surface was very developed with many protrudes on it, covered with the nanocomposite film. This film consists of the nanocrystalline silicon in SiOxNy matrix. Several samples were stain etched, and porous silicon (PS) layers were formed on the conical surface. These PS layers present the composite structure which contains nanocrystalline silicon in porous SiOxNyHz matrix. The Fowler - Nordheim current-voltage characteristics were usually observed on samples tested. Relatively high emission parameters: effective emission areas (=10-8 cm2, local field enhancement factors (=105 cm-1 have been obtained. The resonant tunneling phenomenon have been discovered on some samples. The resonant peaks have been observed. Due to the quantum-size effect there are some energy levels in quantum well region which cause increased tunneling probability under definite electric field.

F14.26
EXCITON-MEDIATED EXCITATION OF Er³ IN ERBIUM-DOPED SILICON-RICH SILICON OXIDE. Se-Young Seo and Jung H. Shin.

A great interest has been aroused in doping silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded in a SiO₂ matrix, with erbium to obtain a Si-compatible photonic material operating at the important telecommunication wavelength of 1.54 μ m. Recently, there have been reports that by tailoring the quantum effects and taking advantage of the strong coupling between the Er³ ions and the nanoclusters, it is possible to greatly enhance the efficiency of Er³ luminescence to such a degree that practical photonic applications may be possible. In explaining the Er³ luminescence mechanism of Er-doped SRSO, however, the trapped-exciton mediated excitation model of Er-doped bulk Si is often used with little modification. But unlike bulk-Si, SRSO is an inhomogeneous material with diverse possible Er locations and electron states. Thus, the excitation mechanism of Er in SRSO must be explored in detail and its components identified if further improvements are to be made. In this paper, we report on the time-resolved measurement of Er³ luminescence from Er-doped SRSO. The time evolution of Er³ luminescence from erbium-doped SRSO with 0.1 at.% Er and nm-sized Si nanoclusters under pulsed excitation and under two-beam conditions indicate that more Er can be excited under weak and long excitation pulses than under strong but short pulses. Based on the results of fitting the data with various models and simulating the time-evolution of Er³, we propose that the formation of the trapped exciton is the limiting step in the Er excitation mechanism, and that the exciton is erbium-related rather than cluster-related. The implication of the results on the design and performance of possible devices will be discussed.

F14.27
EFFECTS OF THE SUBSTRATE TEMPERATURE AND OF HYDROGEN PRESENCE DURING SPUTTERING ON THE LUMINESCENCE OF Eu-DOPED NANOCRYSTALLINE Si/SiO₂. Guillermo A. Nery, Luis F. Fonseca, Oscar Resto, S. Zvi Weisz, Dept of Physics, University of Puerto Rico, San Juan, PR; Huimin Liu, and Aziz Mahfoud, Dept of Physics, University of Puerto Rico, Mayaguez, PR.

We co-sputtered Eu₂O₃, Si and SiO₂ for different substrate temperatures and with and without the presence of H₂ gas during sputtering. The samples were then annealed. The photoluminescence intensity versus substrate temperature and versus presence or absence of H₂ is presented, with a focus on Eu(III). The effects of annealing are also presented.

F14.28
RESONANT EXCITATION OF Er³⁺ BY THE ENERGY TRANSFER FROM Si NANOCRYSTALS. Kei Watanabe^a, Minoru Fujii^b and Shinji Hayashi^{a,b}. ^aGraduate School of Science and Technology, ^bDepartment of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe, JAPAN.

Er-doped Si nanostructures such as porous Si and Si nanocrystals (nc-Si) have recently been attracting much interest, because Er³⁺ incorporated into these materials emits light at 0.81 eV, which corresponds to the absorption minimum in silica optical fibers. In our

previous work, we have studied photoluminescence (PL) from SiO₂ films containing nc-Si and Er and discussed the excitation mechanism of Er³⁺ via nc-Si. The samples exhibited strong 0.81 eV PL at room temperature as well as 1.5 eV PL due to the recombination of excitons in nc-Si. We found that the 0.81 eV peak becomes strong as the Er concentration increases, while the 1.5 eV peak becomes weak. These results suggest that the excitation of Er³⁺ is made by the energy transfer from nc-Si.

However, details of the energy transfer mechanism are not yet understood. Since the electronic states of Er³⁺ are discrete and the bandgap of nc-Si changes with the size, nc-Si with some specific sizes can resonantly excite Er³⁺. However, such specific sizes are not found. In this work, we studied PL and PL decay dynamics of SiO₂ films containing nc-Si and Er. The average size of nc-Si was changed in order to tune the exciton energy of nc-Si to the energy separations between the discrete electronic states of Er³⁺. This wide tunability provides valuable information to understand the energy transfer mechanism. We will demonstrate that phonon-related periodic features appear on the PL spectra of nc-Si. The appearance of the features implies the existence of a resonant energy transfer process. We will also show that the 4f shell PL of Er³⁺ exhibits a delay after the pulsed excitation of nc-Si hosts, and the rise-time depends strongly on the size of nc-Si.

F14.29

IMPACT OF ERBIUM-DOPED SILICON NANOCRYSTALS ON THE PROPERTIES OF POLYPHENYLENE VINYLENE (PPV) FILMS. Jeffery L. Coffey and Junmin Ji, Texas Christian University, Ft. Worth, TX.

Reducing the dimensions of crystalline silicon structures in one, two, or three dimensions in the presence of an optically-active dopant is an area of considerable fundamental and technological importance. Our recent synthesis of erbium-doped discrete Si nanoparticles is of particular relevance since its observed luminescence band at 1540 nm lies in an absorption minimum for silica-based waveguides. This type of silicon-based light emitter, when coupled to a suitable waveguide, would prove vital to the construction of an all Si-based optoelectronic device of nanoscale dimensions. A key issue in fundamental studies of these nanoparticles involves carrier transport from an external medium. Efficiency issues dictate the use of a processible conducting/semiconducting polymer such as poly(phenylene vinylene). Compared to conventional inorganic electroluminescent materials, they have several advantages for photonic applications such as high fluorescence efficiencies, wavelength-tunable emitting light, and mechanical flexibility. Most of these conjugated polymers can be solution processed to form large-area thin films. In this presentation, we report our studies of Er-doped Si nanocrystal/poly(phenylene vinylene) (PPV) composites. Preliminary results have focused on the characterization of these materials via atomic force microscopy (AFM), profilometry, absorption/fluorescence spectroscopies, and current-voltage measurements. A point of emphasis here concerns the influence of the Er-doped Si nanocrystals on PPV photoluminescence and carrier transport.

F14.30

EFFECT OF HYDROGEN TREATMENT ON HIGH EFFICIENCY ELECTROLUMINESCENCE DEVICE USING SILICON NANOCRYSTALS. Keisuke Sato and Tomio Izumi, Department of Electronics, School of Engineering, Tokai University, Hiratsuka-shi, Kanagawa, JAPAN; Mitsuo Iwase, Department of Electrical Engineering, School of Engineering, Tokai University, Hiratsuka-shi, Kanagawa, JAPAN; Yoshiyuki Show, Shinji Nozaki and Hiroshi Morisaki, Department of Communications and Systems, The University of Electro-Communications, Chofu-shi, Tokyo, JAPAN.

Since strong visible light emission from silicon (Si) nanocrystals is observed, the application to light emitting devices based on the Si has been extensively studied. Previously, we reported the improvement of the photoluminescence (PL) from the Si nanocrystals with hydrogen treatments. In this paper, we fabricate the electroluminescence (EL) devices using hydrogen treated Si nanocrystals and report the effect of the hydrogen treatment on the EL device.

The Si nanocrystals in the SiO₂ films were deposited by RF sputtering method. A sputtering target was 16 pieces of 5 × 5 mm² Si chips on a silicon dioxide (SiO₂) substrate of 100 mm in diameter. The deposited sample was annealed at 1100°C in Ar atmosphere for 1 hour. The annealed sample was carried out hydrofluoric (HF) acid solution treatment. The indium tin oxide (ITO), deposited by sputtering method, was used for the top electrode of the EL devices. The aluminum (Al) electrode was formed by the evaporation method on the back side.

EL spectrum was not observed from EL device using annealed Si nanocrystals because the resistance of the EL device was high (10MΩ) and the electrons were not injected into its device. On the other hand, the EL spectrum at the peak of 670 nm was obtained from EL device using HF treated Si nanocrystals under forward bias of 4.5 V, because

the Si nanocrystals appeared by HF treatment of the substrate and the resistance of the EL device decreased. The EL intensity from the EL device increased with increasing the forward bias. The red light emission can be seen with the naked eye under room illumination by applying the forward bias of 5 V. Furthermore, its device has a good stability for aging of 4 hours.

F14.31

COMPUTER SIMULATION OF PULSED LASER PROCESSING OF Si. Sebastiano Tosto, ENEA Casaccia, Roma, ITALY.

A paper recently published has introduced a 3D model to simulate the surface microstructure resulting after pulsed laser processing of Si. The dependence of thermal and optical properties of Si on temperature is taken into account. The melting and solidification process is described by introducing for each volume element of heat affected zone the characteristic times of beginning of melting, end of melting and nucleation of a stable nucleus. The microstructure after solidification is inferred comparing the various nucleation times and the respective interface growth rates at any point of the undercooled liquid phase: this analysis discriminates whether a given volume element can nucleate a new grain or it merely increases the size of another grain nucleated earlier. Of course these characteristic times have different values if calculated through the physical properties of the amorphous or crystalline phase; then the simulation predicts also which phase is locally allowed to form by kinetic reasons. The present paper evidences that this kind of approach, apparently deterministic as concerns the microstructure, has really a probabilistic character: in fact, the formulae to calculate the characteristic times are obtained assuming spherical nuclei whose critical radii correspond to the minimum total free energy resulting from the surface and volume terms. However, it is reasonable to expect that in the pulsed laser processing conditions, typically out of equilibrium and characterized by temperature transients rapidly changing, the minimum energy condition is not really fulfilled. Some examples of computer simulation show how the microstructure changes when the critical radii of the nuclei are allowed to deviate from the values of minimum free energy.

F14.32

ATOMISTIC SIMULATION OF LASER-INDUCED RECRYSTALLIZATION OF AMORPHOUS SILICON. Luigi Brambilla, Dip. to Scienze dei Materiali, Università di Milano "Bicocca", Milano, ITALY; Luciano Colombo, Dip. to di Fisica, Università di Cagliari and INFN, Cagliari, ITALY; Fabrizio Cleri and Gregorio D'Agostino, ENEA, Divisione Materiali, Centro Ricerche Casaccia, Roma, ITALY and INFN; Vittorio Rosato and Massimo Celino, ENEA, High-Performance Computing and Networking Project, Centro Ricerche Casaccia, Roma, ITALY and INFN; Mario Rosati, CASPUR, Roma, ITALY.

It is well known that amorphous silicon (a-Si) exhibits a melting temperature lower than the melting temperature of the crystalline phase (c-Si). The existence of a well defined thermal region separating the two melting temperatures plays a key role in the process of production of micro-crystalline Si film from a-Si precursor, upon laser melting and recrystallization. Classical MD simulations using the EDIP potential have been performed with systems with a number of atom of the order of 10⁵ for times of the order of nanoseconds. A first series of simulations has been performed with a bulk liquid system to investigate its behavior upon quenching in the thermal region between the two different melting temperatures (T-region). Data analysis has been mainly devoted to studying the nucleation kinetics of the homogeneous liquid. The presence, the orientation and the growth velocity of the growing crystalline seeds have been also evaluated. A second series of simulations has been carried out on a model system, of a similar size, containing a free surface and a fixed substrate. This has been used to study the early stage of the laser interaction with the a-Si structure, in order to investigate the process of inhomogeneous nucleation of the liquid. The same model has been also used to study the effects of the presence of a free surface and the substrate on the process of the nucleation of the crystalline phase upon quenching of the liquid in the T-region. A comparison between the growth kinetics in the homogeneous and heterogeneous nucleation regimes has been made. This work has been performed in the frame of the ENEA-MURST project "FOTO" (laser recrystallization of amorphous silicon).

F14.33

MOLECULAR DYNAMICS SIMULATIONS OF AMORPHOUS GERMANIUM AND SILICON, AND OF CRYSTALLIZATION IN THE AMORPHOUS MATRIX. J.K. Bording, Department of Physics, University of Oslo, NORWAY.

By molecular dynamics simulations we have performed rapid quenching of molten germanium and silicon.¹ The quenching is sufficiently slow to produce a simulated material with radial distribution function (RDF) in very good agreement with experiment.

This material has no medium or long range order, and falls in the category of a Continuous Random Network model. To address nucleation and growth of crystallites in the amorphous material, we embedded crystallites of different diameters in the amorphous matrix at different temperatures. Crystallites annihilate or grow depending on their size. At a temperature about halfway between absolute zero and the melting temperature the critical size for growth was 2 nm. At lower temperatures the evolution of the crystals slows down dramatically and so they appear to be stable. We observe that such small crystals can comprise at least 20% of the total volume without significantly changing the RDF from that of an amorphous material. Due to the high spatial and temporal resolution of molecular dynamics simulations we were also able to study the crystalline/amorphous boundary at an atomic level. Thus we were able to infer a free energy barrier by realizing that the outer atomic layer of the crystal was topologically ordered while heavily strained. ¹J.K. Bording, *Phys. Rev. B* Scheduled to be published June 15 2000.

F14.34

DEPOSITION OF SILICON CLUSTERS ON SILICON. A MOLECULAR DYNAMICS STUDY. A.M. Mazzone, C.N.R.-Istituto LAMEL, Bologna, ITALY.

The synthesis of nanostructured materials is of primary technological importance in modern electronic devices manufacturing. The preparation of these materials can be achieved by the deposition already formed units onto a support. This possibility has stimulated the interest on the physics of cluster deposition and theory and experiments show a wealth of new phenomena. This study presents a molecular dynamics simulation of deposition of silicon clusters on a silicon substrate. The purpose is to gain insight into cluster-cluster coalescence, cluster fragmentation and cluster-surface interaction and inter diffusion. In order to illustrate these effects three structures, i.e. the isolated cluster, a cluster dimer and a cluster deposited on a substrate, have been chosen. The calculations describe the evolutions of the three structures at high temperature. The focus of the calculations is on the structural aspects of the temperature increase and the aim of the simulations is to clarify whether or not crystallinity in the growing film may be sustained by properly selected the cluster size and the deposition temperature.

F14.35

SHRINKAGE OF NANOCAVITIES IN AMORPHOUS SILICON DURING IRRADIATION. X.F. Zhu, Department of Electronic Materials Engineering, Research School of Physical Science and Engineering, Australian National University, Canberra, AUSTRALIA and Frederick Seitz Materials Research Laboratory and Department of Materials Science and Engineering University of Illinois at Urbana, IL; J.S. Williams, M.C. Ridgway, J. Conway, Department of Electronic Materials Engineering, Research School of Physical Science and Engineering, Australian National University, Canberra, AUSTRALIA; F. Fortuna, M-O. Ruault, H. Bernas, Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse, Centre National Recherche Scientifique, Orsay Campus, Orsay, FRANCE; Ian Robertson, Frederick Seitz Materials Research Laboratory and Department of Materials Science and Engineering University of Illinois at Urbana, IL.

The production and properties of nanostructures in semiconductors is currently a hot topic. Nanocavities have recently been produced in crystalline silicon and these small voids exhibit intriguing properties, such as providing efficient sinks for diffusing interstitials, especially fast diffusing metals [1]. Although the nonequilibrium thermodynamic properties of nanoparticles have been extensively studied in terms of their nanosize effects, such properties of their counterparts (i.e. nanocavities) have not been studied. In this paper, we show experimentally that nanocavities in silicon exhibit some intriguing properties when irradiated with energetic ions. Following irradiation with energetic silicon ions at various doses and temperatures, silicon (100) was examined by ion channeling and transmission electron microscopy (TEM). In-situ TEM (during irradiation) and time resolved reflectivity (during annealing) were also used to characterise the samples. Depending on the irradiation conditions, ion bombardment can induce preferential amorphization around cavities or the cavities can act as efficient sinks for silicon interstitials, thus reducing the residual damage in the vicinity of cavities. Cavities are also found to shrink during ion irradiation but again the mechanism is dependent on irradiation conditions. For example, at low temperatures the region around the cavities is first amorphised and then cavities shrink during subsequent irradiation. At higher temperatures, the cavities appear to shrink via capture of silicon interstitials. This behaviour is explained in terms of nonequilibrium properties of such open-volume, nanometer-sized cavities surrounded by defective silicon. Some implications for silicon technology are also discussed.

F14.36

CONTROL OF THE ARRANGEMENT OF NANOHOLES ON SILICON SURFACE. Y. Ohno and S. Takeda.

We have found the new method to introduce various kinds of diperiodic and nonperiodic arrays of nanoholes, about 6 nm in diameter and several nanometers in deep, on {100}, {111}, and {110} silicon surfaces. Electron irradiation in the temperature range from 4 K to about 100 K introduced the array at the electron exit surfaces of a thin silicon crystal, while nanoholes distributed nonperiodically were formed at higher temperatures. The primitive cell of the two-dimensional nanohole lattice depended on the surface structure, i.e., the square, hexagonal, and centered rectangular nanohole lattices were formed on {100}, {111}, and {110}, respectively. The lattice constants were about 10 nm. This method may be utilized for fabricating nanometer-scale structures in silicon. We have suggested that the formation of the nanohole lattice is attributed to the surface diffusion of surface vacancies introduced by electron irradiation. The fact that nanoholes were arrayed diperiodically suggesting an anisotropy in the surface diffusion. We have found that the lattice constants of the nanohole lattice were nearly constant regardless of the irradiation temperature. This result indicates a temperature-independent diffusivity of surface vacancies under the irradiation condition. We have considered that the anisotropic and nonthermal surface diffusion of surface vacancies occurs due to an electron-irradiation effect.

F14.37

ATOMICALLY SHARP ARTIFICIALLY REORDERED STRUCTURES OF VARYING LENGTH SCALES IN Si(100). P. Sen, J. Akhtar, School of Physical Sciences, Jawaharlal Nehru University, New Delhi, INDIA.

The ability to organize materials in two or three dimensional structures forms the basis for approach worldwide to construct nanometer sized arrangements. In a recent publication¹, we showed the formation of irradiation interfaces following MeV ion irradiation. These interfaces are formed as a result of electronic energy loss suffered by the ions. Here we show the interaction of 200 MeV silver ions with a Si(100) single crystal lattice which has been studied to look for defects with atomic resolution. Employing scanning tunneling microscopy (STM), we demonstrate that the deposited energy is not stored as random defected arrangements at the irradiation site but as spatially extended structures at predetermined locations. These artificially reordered structures consist of random Si atoms, placed atomically sharp next to the the single crystalline lattice. The structures are stable (to 1150K) and are characterized by modified band gaps and Si-Si distances. Scaling of the structure size with temperature and primary ion energy loss will be presented.

¹P. Sen, G. Aggarwal and U. Tiwari, *Phys. Rev. Letters*, 80, 97 (1998)

F14.38

HIGHLY STABLE 1D NANOSTRUCTURES ON 3C-SiC: FROM A SINGLE ATOMIC CHAIN TO A LARGE SUPERLATTICE OF MASSIVELY PARALLEL ATOMIC LINES. V. Derycke, P. Fonteneau, Nga Phuong Pham, V.Yu. Aristov, P. Soukiassian, Commissariat l'Energie Atomique, Saclay, and Dept. de Physique, Universite de Paris-Sud, Orsay, FRANCE; J. Gautier, CEA-LETI, Dept. de Microelectronique, Grenoble, FRANCE.

We investigate the self-formation of Si atomic lines and dimer vacancy chains on the 3C-SiC(100) surface by variable temperature atom resolved scanning tunneling microscopy (STM). We show that, using a rigorous protocol in surface preparation, it is possible to build very long, very straight and defect free Si atomic lines. These lines are found to be very stable (up to 1200 K) and are derived from the dimer rows of the 3C-SiC(100) 3x2 surface reconstruction by selective Si removal resulting, at the initial step, in very long dimer line vacancies. Using the capability of the scanning tunneling microscope to probe simultaneously both filled and empty electronic states, we show that these atomic lines are composed of Si-Si dimers perpendicular to the line direction. These Si atomic lines are derived from the 3C-SiC(100) 3x2 surface dimer rows by surface thermal dismantling including, at the initial step, Si removal "dimer row by dimer row" leaving very long dimer line vacancies. On the 3x2 surface, the Si-Si dimers are asymmetric in marked contrast with the dimers forming the Si atomic lines which are symmetric. Such a behavior is understood in terms of decreased lateral interaction between atomic lines when the spacing between them is increased. Through a single process, thermal annealing, it is possible to control atomic line density/spacing leading to arrangements ranging from a large superlattice of massively parallel atomic lines to a single isolated atomic chain. These highly stable atomic lines reveal a novel aspect of SiC in its ability to also be a very suitable material for nanotechnologies.

F14.39

MICROSTRUCTURING OF SILICON BY PULSED-LASER ABLATION UNDER REACTIVE ATMOSPHERES. A.J. Pedraza, J.D. Fowlkes, Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN; A. Puzetky, D.H. Lowndes and J. Budai, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Deep micro-holes, bottoming 120 μm below the initial surface, surrounded by micro-cones, protruding 40- μm over the initial surface, form in silicon as a response to multiple UV pulsed-laser irradiation in an SF_6 atmosphere. The micro-holes and micro-cones are arranged in a characteristic ensemble displaying a self-organizing pattern. Similarly, ensembles composed of deep-holes and tall micro-columns form when the irradiation is performed in an oxygen-rich atmosphere. The formation mechanism of micro-columns and micro-cones in these reactive atmospheres has been studied using transmission and scanning electron microscopy, profilometry and x-ray diffraction. Laser-ablated silicon-rich molecules are deposited preferentially at the top of the columns and the top and sides of the cones because these regions are melted by the laser irradiation. Using an ICCD gated camera coupled to a long distance microscope the first stages leading to the cone formation have been studied. The relation between the plasma generation during laser ablation and the formation of diffraction-like patterns preceding the cone formation is established. Laser-induced fluorescence is used to analyze the chemical components of the laser induced-plasma. Applications of laser microstructuring to solar cells and sensors are discussed. Laser irradiation conditions leading to nanostructure formation are briefly mentioned. This research was sponsored by NSF Grant DMR-9901238 and by the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

F14.40

FLUCTUATION MICROSCOPY STUDIES OF MEDIUM-RANGE ORDER STRUCTURES IN TETRAHEDRAL SEMICONDUCTORS. Xidong Chen, J. Murray Gibson, Materials Science Division, Argonne National Laboratory, Argonne, IL.

We applied fluctuation microscopy technique to study medium-range order in tetrahedral semiconductor materials, such as amorphous silicon, amorphous diamond like-carbon films. It is shown that this technique is very sensitive to local structure changes in the medium range order and promises solutions to open questions that cannot be answered by current techniques. For as-deposited amorphous germanium and silicon, we identified a fine-grain para-crystallite structure, which will be relaxed into the lower-energy continuous random network structure after thermal annealing. With the same fluctuation microscopy technique, we however found that thermal annealing introduces medium-range order in amorphous diamond-like carbon films. Future studies will be focused on modeling and systematic exploration of annealing effects.

F14.41

Abstract Withdrawn.

F14.42

TRANSFER OF III-V VERTICAL-CAVITY SURFACE-EMITTING LASERS ONTO SILICON WAFERS. Jie Zhu, Univ. of Albany, SUNY, Dept. of Physics, NY; Mengbing Huang, Univ. of Albany, SUNY, Dept. of Physics, NY.

Silicon is a dominant electronic material in the semiconductor industry. However, due to its indirect energy bandgap, Si cannot be used for fabrication of optical devices. On the other hand, gallium arsenide (GaAs), a direct bandgap semiconductor, has been identified as an important optical material. In this work, we investigate the possibility of transferring GaAs-based vertical-cavity surface-emitting lasers (VCSELs) onto silicon wafers. The VCSEL structures with size of 5-15 μm , first produced on a GaAs wafer, are transferred onto a silicon wafer via ion beam induced layer splitting and wafer bonding techniques. The VCSEL structures on the silicon wafer are evaluated with various analytic methods (e.g. scanning/transmission electron microscope, photoluminescence measurement). The study suggests a promising method for integrating III-V VCSELs with the silicon technology.

F14.43

DOPANT PROFILING OF SEMICONDUCTOR TRANSISTOR STRUCTURE BY ELECTRON HOLOGRAPHY. Y.C. Wang, E. Van Cappellen, X. Da, M. Weschler, M. Bernas, FEI Company, Hillsboro, OR; P. Midgley, S.J. Lloyd, A.C. Twitchett, University of Cambridge, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM; M. Lehmann, Technische Universität Dresden, Institut für Angewandte Physik (IAPD), Dresden, GERMANY.

Two-dimensional dopant mapping with nanometer spatial resolution for the transistor structure is urgently needed for the ULSI semiconductor devices. Typical dopant levels do not alter the amplitude of the incident electron wave sufficiently to depict visible contrast in conventional TEM (Transmission Electron Microscopy) mode. However, electric fields generated by the dopant atoms will modulate the phase of the incident electron wave and this will be visible in the phase image. Due to its ability to recover phase information, electron holography provides a means of observing and

measuring microscopic objects and fields that are inaccessible to detection by other techniques. In various pioneering works, electron holography has been established and proven to be a promising candidate for dopant profiling. In this work, TEM samples were prepared by FIB (Focused Ion Beam) with a sample thickness ranging from 200 to 400 nm. The use of the FIB will provide site-specific capabilities for TEM sample preparation as well as reproducible thickness of the sample and the electrically inactive layers. Dopant profiling of different channel length n- and p-metal-oxide-semiconductor transistors will be discussed in the presentation.

F14.44

DIFFUSION LENGTH MEASUREMENTS OF MINORITY CARRIERS IN Si-SiO₂. Y. Posada, L.F. Fonseca, O. Resto, S.Z. Weisz, Dept of Physics, University of Puerto Rico, San Juan, PR; I. Balberg, The Racah Institute of Physics, The Hebrew University, Jerusalem, ISRAEL.

The interest on developing opto-electronic devices from Si-SiO₂ has raised the necessity of study its photo-transport properties. Five measurements of transport properties were made in Si-SiO₂ at room temperature using the Photo-grating Technique. The Si/SiO₂ films were prepared by R.F. Co-Sputtering on quartz substrates. The measurements were made for different concentrations and sizes of Si particles, starting from a barely luminescent site to non-luminescent sites. Diffusion length measurements, minority and majority carriers were found for each site including their photoconductivity properties.

F14.45

THREE-DIMENSIONAL SILICON BASED NANOSTRUCTURES IN OPAL MATRIX: PREPARATION AND PROPERTIES.

A.B. Pevtsov, V.G. Golubev, V.A. Kosobukin, D.A. Kurdyukov, A.V. Medvedev, Ioffe Physico-Technical Institute RAS, St. Petersburg, RUSSIA.

We have prepared 3D arrays of silicon nanostructures using artificial opals as matrices. Both "direct" silicon opal composites and silicon inverted opal structures have been fabricated. An amorphous-nanocrystalline silicon film was deposited on the inner surface of opal cavities by silane thermal decomposition. The designed thermal CVD technique allows to deposit on the inner surface of pores a solid and uniformly thick silicon layer and to control the thickness, the fill factor, the nanocrystallite size and phase composition of substances in the pores. The inverted structure was obtained by etching out substance of the opal matrix (silica spheres) in an aqueous solution of hydrofluoric acid. The prepared samples were studied by XRD, SEM, TEM and optical methods. The above materials are expected to form 3D array of active elements with the density up to 10^{14} cm^{-3} , which is much larger than that produced by state-of-the-art planar technologies. As well, a photonic-crystal electromagnetic structure, in particular, a photonic band gap (PBG) and some related optical effects are believed to occur due to a long-range order of the opaline matrices on the light wavelength scale. The inverse opal structure is found to be a photonic crystal with refractive index contrast $\sim 3.5:1$, and in accord with theoretical predictions such a composite might possess a complete PBG. Using a transfer matrix technique, we calculated both reflectivity spectra and electromagnetic-mode dispersion for a few high-symmetry directions in the opal-matrix crystal structure. Being in a good correspondence with our experimental data, the results evidence definitely for the existence of a stop band in the crystal directions under study. It is also demonstrated that the degree of filling of opal pores can be controlled precisely with the designed CVD technique, which fact allows to hope for obtaining "tunable" photonic crystals with prescribed location and width of the stop band.

SESSION F15: Ge AND SiGe QUANTUM DOTS

Chair: Susan M. Kauzlarich

Thursday Morning, November 30, 2000

Constitution A (Sheraton)

8:30 AM F15.1

SHOCK SYNTHESIS OF NANOCRYSTALLINE HIGH PRESSURE PHASES IN Si, Ge, AND CdTe BY HIGH-VELOCITY THERMAL SPRAY. J. Parise², R. Goswami^{1,3}, S. Sampath¹, R. Gambino¹, H. Herman¹, Y. Zhu³ and D. Welch³. ¹Center for Thermal Spray Research, SUNY at Stony Brook. ²Center for High Pressure Research, SUNY at Stony Brook. ³Brookhaven National Laboratory, Energy Sciences and Technology Department, Upton, NY.

Shock synthesis of high-pressure phases of Si, Ge and CdTe was accomplished using thermal spray. In this technique powders are injected into a high energy flame, where they melt and accelerate, and then impact on a substrate, promoting the formation of high pressure forms. Thermal spray can be treated as a "dynamic-pressure anvil"

allowing synthesis of high-pressure metastable forms of nanocrystalline Si and diamond, where it is estimated shock pressures of 0 to 30 GPa are achieved. The broader implications of this work include the production of other high pressure phases whose bulk synthesis is precluded by economic considerations. Following thermal spraying a number of metastable phases were observed to have formed including nanocrystalline (2-5 nm) Si-IX, Si-IV (hexagonal diamond Si), R-8 and BC-8 phases. This is consistent with results of static high pressure experiments, which shows cubic Si (Si-I) transforms to Si-II, which poses a beta-Sn type structure at GPa and forms metastable phases upon decompression. In Ge, a metastable phase, ST-12, was observed. The ST-12 is a decompression product of Ge-II with a beta-Sn type of structure. The transformation pressure of Ge-II is slightly lower than that of Si-II. In the case of CdTe, a fine dispersion of hexagonal CdTe particles (Wurtzite) with an average size of 10 nm was obtained. The paper presents the synthesis and characterization of these nanocrystalline semiconductor materials. This work was supported by the MRSEC program of the National Science Foundation under Award No. 96-32570 through the Center for Thermal Spray Research and by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886.

8:45 AM F15.2

OPTICAL PROPERTIES OF Si AND Ge QUANTUM DOTS STUDIED BY LIQUID CHROMATOGRAPHY. J.P. Wilcoxon, G.A. Samara, and P.N. Provencio, Nanostructures and Advanced Materials Chemistry Dept. 1122, Sandia National Labs, Albuquerque, NM.

We have been investigating the cluster size distributions and optical properties of quantum dots of Si and Ge dispersed in organic solvents using high pressure liquid chromatography (HPLC), and transmission electron microscopy (TEM). These nanosize indirect semiconductors are formed by the inverse micelle synthetic process at room temperature in inert oils in the complete absence of water and oxygen and range in diameter from 1-10 nm. HPLC is used to size select, remove all other chemicals, and study the absorbance and photoluminescence (PL), in an oxygen-free mobile phase. HPLC is sensitive enough to discern changes in dot diameter corresponding to less than 2 Å (i.e. ~ 1 additional shell of atoms). Simultaneously we obtain the optical absorbance, PL, and PLE spectra of these dots. We find that these size selected clusters exhibit structural features in their absorbance which we have recently reported. These include both indirect and direct transitions, the latter blue shifted by as much as ~ 0.4 eV compared to the bulk. The most intense PL occurred for the smallest, $d \sim 1.8$ nm clusters and had an efficiency of about 2-3% at room temperature, without any post-synthesis surface treatment. In the case of Ge the shifts of the various transitions were even larger, nearly 1 eV for the smallest clusters, $d = 2.0$ nm. These Ge clusters had the most intense PL centered at 420 nm which was attributed to direct recombination at the band center.

1. J.P. Wilcoxon, G.A. Samara, and P.N. Provencio, Phys. Rev. B, 60, 2705, 1999.

Acknowledgment

This work was supported by the Division of Materials Sciences, Office of Basic Energy Research, U.S. Department of Energy under contract DE-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

9:00 AM F15.3

THE ORIGIN AND NATURE OF STABLE RED TO ULTRAVIOLET LIGHT EMISSION FROM SILICON AND GERMANIUM QUANTUM DOTS. Howard W.H. Lee, Lawrence Livermore National Laboratory; Peter A. Thielen, Dept of Applied Science, University of California-Davis, CA; Boyd R. Taylor, Gildardo R. Delgado, Lawrence Livermore National Laboratory; Susan M. Kauzlarich, Chung-Sung Yang, Dept of Chemistry, University of California-Davis, CA.

Inducing efficient visible light emission from indirect bandgap Group IV materials and understanding the underlying physics have long defined fascinating scientific and technological challenges. We present comprehensive new results addressing light emission from Si and Ge QDs: (i) these QDs can be made to emit light that is stable in ambient (several years) and continuously tunable from red to UV through a single mechanism, i.e., quantum confinement (QC), (ii) the energy gap can widen considerably from QC (~ 3.80 eV with our smallest QDs), (iii) the experimental size-dependent energy gap agrees with pseudopotential and tight binding calculations but not with effective mass results, (iv) despite strong QC, the lowest optical transition remains predominantly indirect (phonon absorption and emission observed in vibronic absorption and emission) even for small QDs (~ 1.4 nm diameter), and (v) the PL lifetime reflects the effects of QC and the indirect nature of the lowest optical transition. Single dot experiments verify these conclusions. Our results generalize earlier results by showing that QC affects optical and electronic properties

much more extensively and over a much broader range than previously realized, provided the QD surface is appropriately terminated. We show that this can be achieved with a variety of surface passivating materials (oxides and organic groups). Red to UV light emission can also result from non-QC such as traps. This underscores the caution required for the interpretation of visible light emission from nanostructured Si and Ge. With the appropriate surface termination, trapping can be mitigated or eliminated and the full range of QC effects can be observed that might otherwise be obscured by non-QC effects. Organic termination with covalent bonds results in mainly quantum confined light emission. We show for the first time that oxide termination can also be made stable in ambient and essentially trap-free so as to display a similarly wide range of QC effects and thus becomes a viable surface passivation. We will discuss how these results offer realistic opportunities for Si- or Ge-based optoelectronics, biological applications, and single electron nanoelectronics.

9:15 AM F15.4

ELECTRONIC STRUCTURE OF Ge-NANOCLUSTER FILMS PROBED WITH SYNCHROTRON RADIATION. C. Bostedt, T. van Buuren, N. Franco, L.J. Terminello, Lawrence Livermore National Lab T. Möller, Hasylab at DESY, GERMANY.

Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic properties. Germanium clusters are of particular interest since, as recent publications suggest, they display a strong blue luminescence. However, it is not clear, if this luminescence is due to surface species, oxide layers or quantum confinement. X-ray absorption spectroscopy (XAS) and Photoemission (PES) was performed on thin films of Germanium (Ge) clusters. The clusters were synthesized in situ by thermal vaporization of Ge in a He buffer gas and subsequently deposited. The average diameter of the clusters could be varied between 1nm and 7nm. Characterization of the nanoclusters in size and shape was done by non-contact atomic force microscopy. X-ray absorption spectroscopy at the Ge L-edge was used to measure the shift of the conduction band of the Ge-clusters as a function of particle size. We find, that the conduction band of the clusters is blueshifted compared to bulk-Ge, in agreement with the quantum confinement theory. The blueshift ranges from 0.2eV to 0.4eV for clusters between 4nm and 2nm. Photoemission data shows a very small shift of around 0.1eV of the valence band in clusters of around 3nm in size. Measurements of the Ge3d plasmons show a strong increase of the surface plasmon compared to the bulk plasmon in clusters. Comparison of this work to previous work done on Si-clusters of the same size and prepared in the same manner show, that the conduction band shift in Ge-clusters is much larger for clusters of the same size. Effective mass calculations of Si and Ge clusters confirm this effect. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

9:30 AM *F15.5

FORMATION OF Ge NANOISLANDS BY SELECTIVE GROWTH USING ULTRATHIN SILICON DIOXIDE FILMS ON Si(001). Masakazu Ichikawa, Yoshiki Nitta, Motoshi Shibata, and Ken Fujita, Joint Research Center for Atom Technology, Ibaraki, JAPAN.

Selective growth of nanometer-scale is an important technique for fabricating well-ordered nanostructures in given areas. Previously we reported that the 20-nm scale Si islands with pyramidal shape grew on Si(001) windows in ultrathin SiO₂ films and the islands were stable during high temperature annealing. The stability was originated from a difference in the adsorption energy of Si adatoms on SiO₂ and these on Si(001) [1]. In this work, we report Ge nanoisland formation by selective growth using ultrathin SiO₂ films on Si(001). The growth was observed in real time by scanning tunneling microscopy (STM). Si windows with 20-nm size were formed by electron-beam-induced thermal decomposition of SiO₂ using field emission electron beam from STM tip. Then, selective growth was achieved by introducing germane gas (GeH₄) at 683 K. In a Si (001) window, Ge film grew in layer-by-layer manner up to 3-4 monolayers and then several Ge islands started to grow in the window. During further growth the Ge islands coalesced forming one hut island with {1, 0, 5} facets. This enabled us to form an array of nanometer-scale Ge hut islands by the selective growth in the windows formed by the STM tip. We also formed Ge nanoislands on pyramidal Si islands in the windows using their stability at high temperature. During GeH₄ supply at 703 K, pyramidal Si nano-islands with {1, 1, 13} facets gradually changed to hut-like islands with {1, 0, 5} facets due to Ge overgrowth on the Si islands. This indicates that hetero-nanoislands composed of Ge and Si could be grown in the window areas. These results manifest that selective growth using ultrathin SiO₂ films can fabricate Si-based nanostructures in given areas. [This work was supported by NEDO.] [1] M. Shibata, Y. Nitta, K. Fujita, M. Ichikawa, Phys. Rev. B61, 7499 (2000).

10:00 AM F15.6

ORGANOMETALLIC FUNCTIONALIZATION OF POROUS SILICON AND GERMANIUM SURFACES. Jillian M. Buriak, Michael P. Stewart, Hee Cheul Choi, Purdue University, West Lafayette, IN.

Because of the numerous technological applications envisioned for porous group IV semiconducting materials with nanoscale architectures, it is important to control the interfacial characteristics of these materials. We will describe recent results concerning organometallic derivatization of hydride terminated porous silicon and germanium layers through efficient chemical protocols. The highly improved stability of the surfaces and generality of this chemistry will be described, along with future directions and novel applications.

SESSION F16: DIAMOND NANOCRYSTALS

Chair: Robert J. Nemanich

Thursday Morning, November 30, 2000

Constitution A (Sheraton)

10:30 AM *F16.1

NANOCRYSTALLINE DIAMOND FILMS: PROPERTIES AND APPLICATIONS. Dieter M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL.

Nanocrystalline diamond films (3-5 nm) are synthesized by plasma-enhanced CVD methods using C_{60}/Ar or CH_4/Ar gas mixtures. Phase purity has been established by a variety of techniques: HRTEM, electron diffraction, EELS, XRD, and carbon 1s photoabsorption. A new growth and nucleation species, carbon dimer, C_2 , has been identified using plasma diagnostics. Density functional calculations provide theoretical insight into the mechanisms underlying the insertion of C_2 into the (110) and (100) faces of the diamond lattice (L. Curtiss, et al.). Molecular dynamics calculation have shown that the carbons are largely π -bonded (sp^2) across two-atom-wide grain boundaries, a quite unique occurrence (P. Kebabinski et al.). Recent work reveals that the electrical conductivity can be controlled by nitrogen doping over many orders of magnitude so that the films range in behavior from insulating to semiconducting to semimetallic. Theoretical work is in progress to elucidate the nature of nitrogen impurities in the grain boundaries and their possible role in conductivity. Tribological, electronic, and MEMS applications of these unusual materials will be presented. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

11:00 AM F16.2

LOW-FIELD ELECTRON EMISSION PROPERTIES FROM INTRINSIC AND S- INCORPORATED NANOCRYSTALLINE CARBON THIN FILMS GROWN BY HOT-FILAMENT CVD. S. Gupta, B.R. Weiner, B.L. Weiss and G. Morell, Department of Physics, Univ. of Puerto Rico, San Juan, PR.

Results are reported on the electron field emission properties of intrinsic and S- doped nanocrystalline carbon thin films grown on molybdenum substrates by hot-filament CVD technique from methane-hydrogen and methane-hydrogen sulphide gas mixtures respectively. For the intrinsic nanocrystalline diamond thin films the positive bias is used to produce a continuous flow of electrons from the filament onto the substrate, while the negative bias is used so that the ions bombard the substrate continuously. The films grown by the electron- and ion- assisted CVD technique show changes in their electron field emission (EFE) properties (turn-on fields and emitted current). Low-field electron emission for the best samples was observed at 6-8 V/micron. The continuous bias also causes microstructural changes, as characterized with ex situ techniques such as SEM, AFM and Raman spectroscopy (RS). The properties of electron and ion bombarded CVD films are compared to the films grown without electron and ion bombardment by either HFCVD or microwave CVD technique. The nanocrystalline diamond thin films were also incorporated with sulphur (S) and the field emission properties of which were compared with the intrinsic nanocrystalline diamond thin films under no bias. We have found a correlation of the EFE characteristics with the nanocrystalline diamond band observed at around 1180 cm^{-1} in the Raman spectra of these films, suggesting a significant role of the tetrahedrally-bonded carbon (ta-C) in the electron emission. Films grown under electron bombardment show smoother surfaces and smaller grains than those grown without it and ion bombardment. These studies are preformed to understand low-field emission mechanisms and the role of ta-C towards improving the emission from the nano-crystalline carbon thin films. This research work is supported from the Department of Defense (DoD ONR Grant No. N00014-98-1-0570), the Department of Energy (DoE Grant No. DE-FG02-99ER45796), and the University of Puerto Rico (UPR FIPi Grant No. 880244).

11:15 AM F16.3

N-TYPE DOPING OF NANOCRYSTALLINE DIAMOND FILMS WITH NITROGEN. Somnath Bhattacharyya, John Schlueter, Dieter M. Gruen, and Alan R. Krauss, Materials Science and Chemistry Division, Argonne National Laboratory, Argonne, IL.

Nanocrystalline nitrogen doped diamond (NCD) films were prepared in a microwave chemical vapor deposition plasma from a mixture of argon and methane (1%) using up to 20% nitrogen in the gas phase. Films prepared without nitrogen consist of 2-5 nm diamond crystals surrounded by 3-4 Å wide grain boundaries. Such films are good insulators. The conductivity of the films is found to increase rapidly when nitrogen gas is introduced into the plasma. From measurements of electrical conductivity and Hall voltage as a function of temperature down to 4K one concludes that the conductivity in the doped films is due to localized states as well as to an extended electronic state close to the conduction band. The negative carrier sign and high carrier concentration suggest that n-type doping of NCD has been accomplished. For the first time, nitrogen is shown to create a shallow donor level, which occasions an increase in conductivity of diamond films leading to a semi-metallic state. As a result, a remarkable enhancement of field emission current and a decrease of the on-set voltage from the n-doped NCD have been observed. Applications of these doped films as electronic devices therefore suggest themselves. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-98.

11:30 AM F16.4

EFFECT OF sp^2/sp^3 IN N-DOPED DIAMOND FILMS ON THE ELECTRON EMISSION PROPERTIES. T. Yamada and A. Sawabe, Dept of Electrical Engineering and Electronics, Aoyama-Gakuin Univ, Tokyo, JAPAN; S. Koizumi, NIRIM, Ibaraki, JAPAN; J. Itoh, ETL, Ibaraki, JAPAN; T. Kamio and K. Okano, Dept of Physics, ICU, Tokyo, JAPAN.

The low-threshold electron emission from CVD-grown polycrystalline diamond doped with N was reported in our previous study [1]. Although there were many reports to understand its electron emission mechanism [2, 3], it has not yet been established. It was also reported that the electron emission from amorphous carbon (a-C) and diamond-like-carbon (DLC) were observed at relatively low voltage/field and the electron emission from diamond was speculated to be due to the amorphous/graphitic components in diamond. In this paper, sp^2/sp^3 ratio in the diamond emitters is modified by changing the substrate temperature, and their electron emission properties are compared. In the obtained electron emission properties, the threshold voltage of the sp^2 -rich emitter has been confirmed to be much higher than that of the sp^3 -rich emitter. This result suggests that the difference in the electron emission properties should be explained by the quality of the emitters. References [1] K. Okano et al. Nature 381 (1996) 140. [2] P. Lerner et al. J. Vac. Sci. Tech. B 16 (1998) 900. [3] S.R.P. Silva et al. J. Vac. Sci. & Tech. B 17, pp. 557-561 (1999).

11:45 AM F16.5

X-RAY ABSORPTION AND EMISSION STUDIES OF DIAMOND NANOCCLUSERS. T. van Buuren, C. Bostedt, L.L. Chase, L. Terminello, Chemistry and Material Science Department, Lawrence Livermore National Laboratory, Livermore, CA.

The conduction and valence band structure of bulk diamond and diamond nanoclusters have been measured using x-ray absorption and x-ray emission spectroscopies. The diamond nanoclusters are commercially available products from the Straus chemical corporation and are synthesized in a detonation wave from high explosives. X-ray diffraction and TEM show that the nanodiamond powder is crystalline and approximately 3.5 /- 1.0 nm in diameter. The nanodiamond K-edge absorption and emission show the same spectral features as bulk diamond with low impurity levels. The C1s core exciton feature clearly observed in the K-edge absorption edge of bulk diamond is not observed in the nanodiamond spectra. A possible explanation for this is a broadening due to a distribution of particle size. The depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond. This effect has been observed previously and attributed to quantum confinement. We note that no blue shift measured in the position of nanodiamond conduction edge when compared to the bulk diamond contrary to a recent publication that has reported large conduction band shifts in CVD grown diamond nanoclusters. [1] Experiments are in progress to measure the nanodiamond conduction band edge from the EELS spectra acquired with a field emission TEM. We compare our conduction band data to the published measurements and comment on the differences. Soft x-ray emission measurements of the valence band structure of the diamond nanocluster will also be presented. The electronic structure of the nanodiamond will be compared to recent results on Si and Ge nanoclusters and the effects of reduced sizes on the electronic structure of group IV semiconductors will be discussed. [2] The work

is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL. [1] Y.K. Chang et.al. PRL 82, 5377 (1999). [2] van Buuren et.al. PRL 80, 3803 (1998).

SESSION F17: RARE EARTHS IN
NANOSTRUCTURES
Chair: Lionel C. Kimerling
Thursday Afternoon, November 30, 2000
Constitution A (Sheraton)

1:30 PM F17.1

LUMINESCENCE IN SILICON NANOSTRUCTURES AND THEIR INTERACTION WITH RARE EARTH IONS. F. Priolo, G. Franzu, D. Pacifici, V. Vinciguerra, INFN and Physics Department, University of Catania, Catania, ITALY; F. Iacona, A. Irrera, CNR-IMETEM, Catania, ITALY.

The luminescence properties of several different low dimensional silicon structures will be analyzed and compared. It will be shown that both Si ion implantation and chemical vapor deposition represent quite powerful tools to achieve nanometer sized Si structures embedded within SiO₂. Depending on the preparation conditions the dimensions can be properly varied. Moreover, nanocrystalline Si/SiO₂ superlattices can be formed with the Si nanocrystals (nc) being almost completely isolated among themselves. All of these structures present a strong room temperature optical emission, a weak luminescence temperature dependence and a clear blue shift of the luminescence with decreasing crystalline size. Moreover, the interaction mechanisms between Si nc in SiO₂ and Er ions will be investigated. When nanocrystals are doped with Er they absorb energy which is then preferentially transferred to the rare earth. Indeed, room temperature luminescence yields two orders of magnitude higher are observed for Er-doped SiO₂ in presence of nanocrystals than in pure SiO₂. Moreover, since Er is now embedded within a SiO₂ matrix, the non-radiative decay channels typically limiting Er luminescence in Si are absent. This further improves the luminescence yield which is almost temperature independent in the range 15-300 K. From a detailed characterization in terms of pump power dependencies and time decay it will be demonstrated that the number of Er ions per Si nc is a quite critical parameter in determining the final properties of the overall system. Moreover, the excitation cross section of Si nc with and without Er have been measured under several different conditions. These data will be presented, a plausible phenomenological model on the energy exchange between Er and nanocrystals proposed and the future trends and applications discussed.

1:45 PM F17.2

ERBIUM EMISSION FROM SILICON BASED PHOTONIC BANDGAP MATERIALS. Herman A. Lopez, J. Eduardo Lugo, Christopher C. Striemer, Sharon M. Weiss and Philippe M. Fauchet, Univ of Rochester, Dept of Electrical and Computer Engineering, Rochester, NY.

Control over the 1.5 micron emission from erbium is desirable for communication and computational technologies because the erbium emission falls in the window of maximum transmission for silica based fiber optics. Tunable, narrow, directional, and enhanced erbium emission from silicon based one-dimensional photonic bandgap structures will be demonstrated. The structures are prepared by anodic etching of crystalline silicon and consist of two highly reflecting Bragg reflectors sandwiching an active layer. The cavities are doped by electro-migrating the erbium ions into the porous silicon matrix, followed by high temperature oxidation. By controlling the oxidation temperature, porosity, and thickness of the structure, the position of the erbium emission is tuned to emit in regions where the normal erbium emission is very weak. The erbium emission from the cavity is narrowed (FWHM of 12 nm) with a quality factor Q of 130, highly directional with a 20 degree emission cone around the normal axis, and enhanced by more than one order of magnitude when compared to its lateral emission. The ability to control erbium emission in two-dimensions is a significant step towards achieving all-optical silicon based circuits. Results from erbium-doped two-dimensional photonic bandgap structures will also be presented and discussed.

2:00 PM F17.3

Er³⁺ PHOTOLUMINESCENCE PROPERTIES OF ERBIUM-DOPED Si/SiO₂ SUPERLATTICES WITH SUB-NM THIN Si LAYERS. Yong Ho Ha, Sehun Kim, Department of Chemistry, School of Molecular Science, Korea Advanced Institute of Science and Technology (KAIST), Taejeon, KOREA; and Dae Won Moon, Surface Analysis Group, Korea Research Institute of Standards and Science (KRIS), Taejeon, KOREA; Ji-Hong Jhe and Jung H. Shin, Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), Taejeon, KOREA.

Erbium doping of silicon has been identified as one of the most promising methods for developing silicon-based optoelectronics, yet has so far had only a modest success. Recently, it has been demonstrated that by using silicon nanoclusters, much of the problem facing erbium doping of silicon can be solved such that efficient Er³⁺ luminescence at room temperature can be obtained and population inversion of Er may be achieved. However, with silicon nanoclusters, the size and the number of the clusters and the location of Er, which all play a significant role in determining the Er³⁺ luminescence, are difficult to control. One possible way of obtaining such control is using Si/SiO₂ superlattices instead. In this paper, we report on the Er³⁺ photoluminescent properties of erbium-doped Si/SiO₂ superlattices with sub-nm thin Si layers. The superlattices were deposited by UHV-ion beam sputter deposition method at room temperature and subsequently annealed at 950°C. Erbium was doped only into the SiO₂ layers whose thickness was fixed at 4.8 nm. The thickness of the Si layers was varied from 0.6 to 4.8 nm. The structure and the composition of the films were confirmed using transmission electron microscopy and medium energy ion spectroscopy. We find that the Er³⁺ luminescence increases very strongly as the film thickness decreases, and that one monolayer of silicon is sufficient for carrier-mediated excitation of Er to dominate. The temperature dependence of Er³⁺ luminescence, however, is nearly independent of the Si layer thickness, indicating that quantum confinement effect is not a major factor controlling the Er³⁺ luminescence. The differences between Si nanoclusters and superlattices will be discussed, and photonic application (e.g. waveguides) demonstrated.

2:15 PM F17.4

STRONG EXCITON-ERBIUM COUPLING IN Si NANOCRYSTAL DOPED SiO₂ OPTICAL WAVEGUIDES. P.G. Kik and A. Polman, FOM-Institute AMOLF, Amsterdam, THE NETHERLANDS.

We have observed strong coupling between optically generated exciton states in Si nanocrystals and intra-4f electronic states of erbium ions implanted into the nanocrystal-doped SiO₂ matrix. The energy transfer rate is larger than 10⁶ s⁻¹, much larger than the radiative decay rate of the nanocrystals at 300 K. As the optical absorption cross section of Si nanocrystals is some four orders of magnitude higher than that of Er ions, this effect can be used to dramatically enhance the excitation rate of Er in optical waveguide amplifiers and lasers operating at 1.54 μm.

Silicon nanocrystals were formed in SiO₂ using Si ion implantation and thermal annealing. The nanocrystal-doped SiO₂ layer was implanted with different doses of Er, resulting in Er peak concentrations in the range 0.015 at.%-1.8 at.%. All samples show a broad nanocrystal-related luminescence spectrum centered around 800 nm and a sharp Er luminescence line at 1.54 μm. In our experiments we measured, as a function of Er concentration, the nanocrystal and Er photoluminescence intensity, the nanocrystal excitation rate, the Er excitation and decay rate, and the Er saturation with pump power. We conclude that the maximum amount of Er that can be excited via exciton recombination in Si nanocrystals is 1-2 Er ions per nanocrystal. We attribute this to Auger de-excitation or pair-induced quenching, that can both occur at high pump power. We also find that the excitable Er ions are most likely located in an SiO₂-like environment.

Channel waveguides based on index guiding through the high-index nanocrystal doped region show excellent mode confinement. At a typical nanocrystal concentration of 10¹⁹ cm⁻³, the maximum optical gain at 1.54 μm of an Er doped waveguide amplifier based on Si nanocrystal doped SiO₂ is estimated to be ~0.6 dB/cm. In these waveguides we also observe an effect of trap-assisted free carrier absorption in the Si nanocrystals.

2:30 PM F17.5

HIGH PRESSURE SPECTROSCOPIC INVESTIGATIONS OF ERBIUM-DOPED SILICON NANOCRYSTALS. Jeffery L. Coffey, Robert Senter and John St. John, Texas Christian University, Ft. Worth, TX.

Studies of the preparation and fundamental properties of three dimensionally-confined Si nanoparticles doped with optically-active species have important implications for the future fabrication of Si quantum dot optoelectronic devices. We have recently devised a process which permits the incorporation of optically-active rare earth dopants such as erbium (Er) into discrete Si nanoparticles and systematically investigates these nanocomposites as a function of their size. Characteristic Er near IR luminescence at 1540 nm is detected in these doped nanoparticles; excitation and power dependency measurements of this luminescence suggest a Si carrier-mediated emission mechanism. In this presentation, we focus on the effects of high pressure (via the use of a diamond anvil cell) on both the fluorescence and absorption spectra of these doped nanoparticles. For crystalline Si, pressure alters the conduction band minima of the nanophase host and subsequently should affect the extent of energy transfer to the Er center(s) (and its resultant PL intensity). For

optical absorption measurements, the emphasis here is with respect to (a) the effect of particle size on pressure dependence of the bandgap as well as (b) an indirect examination of the structural impact of the erbium dopant on the pressure-induced phase transition(s).

2:45 PM F17.6

SUPER FINE STRUCTURE OF PHOTOLUMINESCENCE SPECTRA FROM ERBIUM CO-INCORPORATED WITH IRON IN POROUS SILICON. Nikolay Kazuchits, Belarussian State Univ, Minsk, BELARUS; Svetlana Volchek, Vladimir Petrovich, Leonid Dolgyi, Nikolay Vorozov, Valentina Yakovtseva, Vitaly Bondarenko, Belarussian State Univ of Informatics and Radioelectronics, Dep of Microelectronics, Minsk, BELARUS.

We report for the first time the observation of the highly defined Stark structure of photoluminescence spectra from Er co-incorporated with Fe in porous silicon. To incorporate Er and Fe in porous silicon we used an electrochemical procedure followed by high temperature annealing/oxidation. We observed more than 11 super sharp emission bands related to highly resolved transitions between splitted spin-orbit levels of the 4 I 13/2 first excited multiplet and the 4 I 15/2 ground multiplet. The spectral width of the emissions peaks did not exceed 0.4 meV at 77K that is many times less than that for Er incorporated by ion implantation in silica glasses (4.5-13 meV FWHM at 77K), crystalline silicon (2-3 meV FWHM at 77K), and GaN (1.1 meV FWHM at 6K). To explain the experimental results we proposed that electrochemically co-deposited Er and Fe can form after high temperature treatment well organized nanoclusters in porous silicon matrix.

SESSION F18: LIGHT-EMITTING DEVICES

Chair: Howard W.H. Lee
Thursday Afternoon, November 30, 2000
Constitution A (Sheraton)

3:30 PM *F18.1

ION BEAM SYNTHESIS BASED FORMATION OF Ge-RICH THERMALLY GROWN SILICON DIOXIDE LAYERS: A PROMISING APPROACH FOR A SILICON-BASED LIGHT EMITTER. L. Rebohle¹, T. Gebel¹, J. Zhao¹, D. Borchert², J. v. Borany¹, and W.Skorupa¹; ¹Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, GERMANY; ²Department of Electrical Engineering, Fernuniversitat Hagen, GERMANY.

There is no doubt that silicon-based light emission is a key feature to make a real step into the world of high performance optical communication because of their integrability into dedicated integrated circuits. One of the most promising approaches to form a silicon based light emitter bases on ion beam synthesis. In this paper we will report on our recent progress in extracting blue-violet (~400 nm) electroluminescence (EL) from an Ge-rich silicon dioxide layer thermally grown on silicon. The thickness of this layer was in the range of 100 .. 200 nm. High dose Ge-implantation was performed with fluences of 6.3×10^{14} .. 1.2×10^{16} cm⁻² at energies of 50 .. 100 keV followed by different annealing steps. To extract EL a top electrode of indium tin oxide (ITO) was formed. The power efficiency of the EL was as high as 0.5 % (!) one of the best values ever reported. The EL duration time without special measures of stabilising the EL-active layer against ionic or other contamination can reach several hours. Moreover, results are reported dedicated to the investigation of the excitation mechanism of this strong EL. A first silicon-based integrated optocoupler device combining the light emitter with a low-temperature processed pin - photodiode will be demonstrated.

4:00 PM F18.2

SILICON NANOCRYSTALLITE LIGHT EMITTING DEVICES FABRICATED BY FULL PULSED LASER ABLATION PROCESS. Yuka Yamada, Toshiharu Makino, Nobuyasu Suzuki, Takehito Yoshida, Matsushita Electric Industrial Co., Ltd., Advanced Technology Research Lab, Kawasaki, JAPAN; Seinosuke Onari, Univ of Tsukuba, Inst of Materials Science, Ibaraki, JAPAN; Ikurou Umezui, Akira Sugimura, Konan Univ, Dept of Applied Physics, Kobe, JAPAN.

We have developed visible light emitting diodes (LEDs) whose active regions are silicon (Si) nanocrystallite layers showing remarkable quantum confinement effects. The Si nanocrystallite layers have been directly covered with indium oxide (In₂O₃) thin films as transparent electrodes. Both the Si nanocrystallite layers and In₂O₃ thin films have been synthesized by pulsed laser ablation in inert background gas (PLA-IBG) process. For the synthesis of Si nanocrystallites, a second harmonic Nd: YAG laser beam was focused onto a surface of p-type Si wafer target. A pure helium (He) gas was introduced into a vacuum chamber and was maintained at a constant pressure.

Subsequent thermal annealing was carried out at 825°C for 10 min in a nitrogen (N₂) gas. In order to form contacts with the Si nanocrystallite layers, In₂O₃ thin films (200 nm) were deposited as transparent electrodes using the PLA-IBG process. An argon-fluoride (ArF) excimer laser beam was focused onto a sintered In₂O₃ target in a pure He gas of 2.0 Torr, where transparent crystalline films were obtained at room temperature. This LED structure can suppress the decrease of luminescence intensity from the Si nanocrystallites by exposure to air under excited conditions. After the annealing of Si nanocrystallites, crystallinity was recovered and quantum confinement effects for both phonons and carriers remarkably appeared in Raman scattering and optical absorption measurements. Consequently, photoluminescence intensity was increased. For the LEDs, we realized a low onset voltage of 3.0 V for emission, which has great compatibility with the established Si large scale integrated (LSI) technology. Furthermore, we will discuss the optical properties of Si nanocrystallites with well-controlled size distribution.

4:15 PM F18.3

STABILIZATION OF POROUS SILICON ELECTROLUMINESCENCE BY SURFACE CAPPING WITH SILICON DIOXIDE FILMS. Nobuyoshi Koshida, Junichi Kadokura, Tokyo Univ. of A&T, Dept of Electrical and Electronic Engineering, Tokyo, JAPAN; Mitsutoshi Takahashi, Kazuo Imai, NTT Telecommunications Energy Laboratories, Atsugi, JAPAN.

For practical applications of electroluminescence (EL) from nanocrystalline porous silicon (PS), the external power efficiency (EPE) should be at least 1%, the operating voltage below 10 V and the stability longer than 10,000 h. We recently developed a PS-EL device which offers the red band emission performance with an EPE of 0.4%, an external quantum efficiency (EQE) exceeding 1%, and an operating voltage of about 5 V. The EL device is composed of an indium tin oxide (ITO) top contact, a PS layer treated by electrochemical oxidation (ECO), an n⁺-type Si substrate, and an ohmic back contact. It has been shown that in addition to a significant enhancement in the efficiency, the post-anodisation ECO treatment effectively improves the EL stability. Oxidation during operation and upon storage in air, however, still affects the EL efficiency due to an increase in nonradiative defects. To prevent this undesirable oxidation, surface capping with silicon dioxide films is proposed here: at the final stage of the device fabrication, high quality transparent SiO₂ layers with various thicknesses (50, 100, and 200 nm) were deposited by an ECR sputtering technique onto the ITO film. The top electrode was made by contact hole generation and subsequent tungsten deposition by in-situ focused ion beam processing. With increasing the SiO₂ film thickness, the EL operation was significantly prolonged. In the case of a 200 nm thickness, for instance, the EQE showed no degradation during a continuous dc operation of 3 h. This is quite different with the situation in the conventional device with no capping, where the EL deteriorates within only several min under the same condition. Obviously the ECR-deposited SiO₂ layers protect PS from oxygen penetration without affect the hydrogen termination of nanocrystalline silicon surface. This should become more effective for stabilizing the oxide-free green and blue EL emission.

4:30 PM F18.4

MODELING CARRIER TRANSPORT IN OXIDE-PASSIVATED NANOCRYSTALLINE SILICON LEDS. Karl D. Hirschman, Rochester Institute of Technology, Dept of Microelectronic Engineering, Rochester, NY; Philippe M. Fauchet, University of Rochester, Dept of Electrical and Computer Engineering, Rochester, NY.

Electroluminescence (EL) from porous silicon (PSi) was observed shortly after photoluminescence (PL) was discovered by Canham in 1990. A typical PSi-based LED consists of a transparent or semitransparent contact (Au, ITO or conducting polymers) and a PSi layer (thickness between 1-10 micron) fabricated on an n-type or p-type crystalline silicon substrate. These devices have typically been modeled as a type of Schottky junction device. The use of pn-junctions has also been implemented, with some results claiming improved electrical characteristics and EL efficiency. The oxide-passivated nanocrystalline silicon (OPNSi) LED is quite different from other porous-silicon based LEDs. The OPNSi material has been characterized as a porous glass with remaining embedded nanocrystals of silicon. The system is highly interconnected, and allows the transport of carriers through defect states. The device operation is explained by bipolar injection from an electron-injection cathode and a hole-injection anode into the OPNSi layer. This material facilitates tunneling transport of electrons and holes, some of which will participate in radiative recombination events. A thorough investigation on electrical properties of OPNSi LEDs has revealed fascinating details on transport behavior. The device is modeled as a "field effect diode", where untraditional concepts are needed to make sense out of the experimental observations. This study presents a consistent and comprehensive transport model which is well supported

by experimental evidence and sound arguments describing the device physics.

4:45 PM F18.5

BIPOLAR INJECTION DEVICES IN CMOS COMPATIBLE Si/SiO₂ SUPERLATTICES FOR LIGHT EMITTING DIODES. Zeno Gaburro, Georg Pucker, Lorenzo Pavesi, INFN and Department of Physics, University of Trento, Povo (Tn), ITALY; Pierluigi Bellutti, ITC-IRST, Povo (Tn), ITALY.

We have designed and tested novel bipolar injection devices for Si/SiO₂ superlattices, in order to obtain electroluminescence based on quantum confinement. Despite the specific target of the study, very general transport properties in Si/SiO₂ superlattices, of wider potential interest, have been characterized by conductance (dc and ac) and capacitance measurements. On the practical side, the devices are attractive since they combine potential optical functionality, low fabrication cost and integration with silicon technology. In fact, they are based on optically active Si/SiO₂ superlattices completely fabricated in a standard CMOS line. The single layer Si thickness can be tailored down to about 1.1 nm. In this study, to pursue quantum confinement effects, a dedicated design for the carrier injectors has been developed. In fact, both holes and electrons have to be injected into the active layer, whereas, on the other hand, carrier injection in simple gate-superlattice-substrate devices is essentially unipolar (due to the difference between the potential barrier for the holes and the one for the electrons). For this reason, we have fabricated special injection devices based on two and three contacts schemes. With such structures we have characterized the bipolar injection both *perpendicular* to the Si layers barriers and *parallel* to the Si layers. Results and specific advantages of the two different bipolar injection schemes will be presented and discussed.