SYMPOSIUM F
Nano- and Microcrystalline Semiconductor Materials and Structures

November 27 – 30, 2000

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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 Zitser
Semiconductor Research Corporation, Research Triangle Park, NC

Silicon CMOS technology, the engine of the microelectronics industry for the last 35 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 will in 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 sustain 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 future multielectron quantum electronics will be addressed. Examples will include physics and chemistry of interfaces, conductivity at low dimensions, determinist dopings effects etc. to fine tune the electrical, optical, mechanical, and sensing properties of nanostructures by precise compositional and size control.

9:00 AM F1.2
LAYERED TUNNEL BARRIERS FOR NANOCRYSTALLINE MEMORY APPLICATIONS. Andrew T. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA; 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 major gate oxide devices is the long program (~ us) 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 Si3N4/6 nm Al2O3/6 nm Si3N4 dielectric heterostructure with assumed conduction band offsets with respect to the Si conduction band of 2.0 eV and 3.4 eV for Si3N4 and Al2O3 respectively, the latter being calculated to be much more rapidly with applied bias than for a homogeneous Al2O3 or SiO2 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 Si3N4/6 nm Al2O3/6 nm Si3N4 as well as homogenous 6 nm Al2O3 barrier structures by reactive ion beam sputter deposition. A comparison of the current-voltage and capacitance-voltage properties of these structures with conventional SiO2 tunnel dielectric will be discussed.

9:15 AM F1.3
SILICON SINGLE ELECTRON TRANSDUCERS WITH SINGLE AND MULTI DOT CHARACTERISTICS. A. Swini; A. Mammen; J. Krammer; J. Pekola, Dept. of Physics, Univ. of Jyvaskyla, Jyvaskyla, FINLAND; M. Kumpiene, M. Eisma, A. Eckstein, Technische Physik, Univ Wurzburg, Wurzburg, GERMANY; M. Pramila, J. Aboukhel, VTT Microelectronics Centre, Espoo, FINLAND

Silicon single electron transducers (SET) with fixed 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 of the characteristics: some of them demonstrate multi dot array behaviour and one demonstrates single adatom behaviour in a wide temperature range. Nonetheless, all 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 100 K. 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 16-30 min at 4.2K. With increase of temperature the rate of the process increases (characteristic time decreases) and at T > 253K 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 switching of both the gate voltage and the gate coupling capacitance. Switching between two states at fixed drain-source and gate voltage. Current 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/SILICONE OXIDE 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 amorphous-thick tunnel saturable SiO2 layers exhibits at low temperature conductivity fluctuations. Analysis of the fluctuation spectra shows a tent-worse, 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 unusual signatures of phase coherent carrier transport, including a 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-photon 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 n-Si/SiO2 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 AEROSOLS SILICON NANOPARTICLE NONVOLATILE FLOATING GATE MEMORY. Michele L. Osterman1, Richard C. Flanagan1, Harry A. Atwater2, California Institute of Technology, Pasadena, CA; J. W. De Boer, Andrew Kerber, Gary Weber, Martin L. Green, Lucent Technologies, Murray Hill, NJ

Silicon nanoparticle-based floating gate MOS field effect devices have potential for terabit/cm$^2$ density nonvolatile memory applications. We have fabricated nanoparticle memory devices in a conventional MOS ULSI process with channel lengths from 0.5-10 microns with a Si nanoparticle floating gate fabricated by aerosol deposition. SiO2 passivated Si nanoparticle have been synthesized in an ultraclean two-stage aerosol reactor that is interfaced to a 200 mm wafer deposition chamber in a class 100 cleanroom. We synthesized silicon nanoparticle cores 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 1150°C. Particles are thermochromically deposited onto 200 mm wafers with densities from $10^{13}$ particles/cm$^2$ to the wafer center to $10^{17}$ particles/cm$^2$ at the wafer edge in tens of minutes. We have fabricated floating gate memory devices in which the dielectric layer contains a discontinuos 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 little further oxidation of the nanoparticle core occurs during control gate oxidation. Aerossol nanoparticle floating gate devices exhibit normal transistor behavior and have promising nonvolatile device performance. Aerosol nanoparticle devices with 0.2 microns channel length exhibit threshold voltages < 5V with large threshold voltage shifts (> 2 V), submicrometer program times and millisecond erase times. No degradation in program/erase threshold voltage swing was
11:00 A.M. E2.2
CHARGE STORAGE MECHANISM IN NANO-CRYSTAL-LINE Si BASED SINGLE-ELECTRON MEMORIES. Bruce J. Hindi, Takwaki Yamaha, Shigeo Hattori, Shunro Odia, 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 cell. The present trend towards smaller contact geometries is forcing the current transport to pass through a proximity conduction channel. In particular, it is of interest whether the electron is localized over n-Si dot or whether interfacial states with n-Si play a dominant role in retention time. Studies of storage lifetimes of single dots involving the variation of temperature and applied potential are reported in this work. Enhanced CVD is used to form thin diameter n-Si dots in the gas phase from pulsed SiH source. This easily scalable process is used to deposit dots over a decimicron scale transistor thus making a memory device. The 80 nm by 20 mm transistor channel is synthesized by Edemarih 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 n-dots is such that statistically 1.3 dots are in the active region of the transistor. This method allows a memory device that is sensitive to charge in a single n-Si dot. A stored electron is observed to stabilize a 20nm channel current shift. This shift is expected for a 50 nm diameter n-Si dot over 30nm wide channel as calculated by Coulombic shift in channel surface potential. Steplike increase in channel current shows the loss of several electrons from n-Si dot. Lifetimes are seen to be 80k-120 seconds at 100K in absence of any ambient atmosphere under the following 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 A.M. E2.3
A MEMORY DEVICE UTILIZING RESONANT TUNNELING IN NANOCRYSTALLINE SILICON SUPERLATTICES. L. Moses, G.F. Grom, R. Krashen, P.M. Pechet, and I. Tylczak, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY. H.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/erase cycle time if the level of impact ionization is associated with Fowler-Nordheim hot electron tunneling can be avoided. In this paper we present definitive experimental observations of resonant carrier tunneling in nano-structures of Si/SiO2/Si and its application in memory devices with artificially graded barriers between current channel and floating gate. The device properties and limitations including write/erase time, “on/off” voltage operation, endurance, retention time and leakage dynamic will be discussed.

11:30 A.M. E2.4

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, whereas 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 becomes possible, opening the door to broader applications. If these islands are further reduced to the point where Coulomb charging or electron recombination 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.

1:30 P.M. E3.1
ANALYSIS OF PHYSICAL PROPERTIES OF NANO-STRUCTURED SEMICONDUCTORS VIA NOISE SPECTROSCOPY. Vittal P. Parakhutik, 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-macroscopic 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 - fliker-noise spectroscopy - FNS) 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 nanostructured semiconductors. Morphological features of surfaces containing imperfections (dots or holes), their optical properties, etc. Degree of this memory depends on the properties of nanostructures.
- Studies of chaos-order transitions in a system of nanostructured semiconductors. The oscillations of physical properties of microsystems are due to a synchronization of elementary events involving their microscopical parts. Reproducibility of signals produced by micro-minisized devices containing an ensemble of nanostructured components.

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

2:00 P.M. E3.2
ELECTRICAL CONDUCTIVITY IN THE CRYSTALLITES OF POROUS SILICON DETERMINED BY AN IMPROVED COMPLEX IMPEDANCE ANALYSIS. Berndjan Breinle, Stephanie Perdich, Volodymyr Lyseiko, Daniel Biess, 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 element 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 mesoporous 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/Al structures. The samples were prepared on 0.02-0.2 cm p-type Silicon substrates. The SiO2 layers were used as a protecting mask to avoid metal 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 electrophoretically compensated crystallites with semi-insulating interconnections. Besides, the associated nanocage mobility values differ from that of the porous layer, suggesting a strong individuality of the crystallites in the nanostucture network.

2:15 P.M. E3.3
ANALYSIS OF BALLISTIC ELECTRON TRANSPORT IN NANOCRYSTALLINE POROUS SILICON. Akira Kojima, Xing Sheng, Nobuyoshi Koshiba, Tokyo Univ. of A&T, Dept of Electrical and Electronic Engineering, Tokyo, JAPAN.

Nano-crystalline porous silicon (PS) diodes, composed of thin Au films, structure controlled PS layers, n-type Si substrates, and ohmic contact contacts, efficiently emit ballistic electrons when positive bias voltage are applied to the Au electrode about the implantation to the substrate. The emission characteristic suggests that electrons injected into the PS from the substrate become ballistic under high electric field. To confirm this hypothesis, we have investigated the temperature dependence of energy distribution of emitted electrons.
electrons in a temperature range of 100 to 300 K. The energy distributions were measured by an x-ray scanning technique in an ultrahigh vacuum. The current-voltage characteristics of the silicon diode in PS were also investigated in terms of the temperature dependence of the diode current, the dynamic response, and the drift length. The energy distribution function emitted from PS diodes showed a behavior characteristic of ballistic electron emission that is quite different from 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 current-voltage characteristics are found directly from the emission source of a flat panel display. A 1.5 μm polysilicon layer is deposited on a metal substrate formed on a glass substrate and oxidized in an ethylene gas solution. The polysilicon (PPS) layer is treated by an electron-chemical oxidation (ECO) in an H₂SO₄ solution. The Co thin film is deposited onto the ECO-treated PPS layer and used as a top electrode. The emission current density Jₑ is measured as a function of the bias voltage Vₑ. Cold emission mechanism has been studied in terms of the dependence of the emission current density on the bias voltage and the structure of the PPS layer. Electron emission of which onset voltage is about 6 V quickly increases with increasing Vₑ. The Jₑ value reaches about 80 μA/cm² for Vₑ = 20 V at which the emission efficiency defined as Iₑ/Vₑ is about 1 %. The observed energy distribution curve of output electrons suggest that the PPS layer acts as a ballistic transport medium in 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 oxides. In the PPS sample with a low emission efficiency, in contrast, only a blue 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 ballistic emission model based on multiple-tunneling silicon nanocrystallites and provide an important suggestion for developing the efficient ballistic emitter.

3:30 PM   F4.1

**BALLISTIC ELECTRON SURFACE-EMITTING COLD CATHODE IN POROUS POLYSILICON AND POLYCRYSTALLINE SILICON FILM FORMED ON GLASS SUBSTRATE.** Takuaki Komaeda, Tsutomu Ichioka, Yoshihiko Honda, Koichi Aimura, 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 forms the electron emitting from the tip of a Si nanowire as a source of a flat panel display. A 1.5 μm polysilicon layer is deposited on a metal substrate formed on a glass substrate and oxidized in an ethylene gas solution. The polysilicon (PPS) layer is treated by an electron-chemical oxidation (ECO) in an H₂SO₄ solution. The Co thin film is deposited onto the ECO-treated PPS layer and used as a top electrode. The emission current density Jₑ is measured as a function of the bias voltage Vₑ. Cold emission mechanism has been studied in terms of the dependence of the emission current density on the bias voltage and the structure of the PPS layer. Electron emission of which onset voltage is about 6 V quickly increases with increasing Vₑ. The Jₑ value reaches about 80 μA/cm² for Vₑ = 20 V at which the emission efficiency defined as Iₑ/Vₑ is about 1 %.

**SESSION F4: POROUS SILICON II**

**Chair:** Leigh T. Canham

**Monday Afternoon, November 27, 2000**

**Constitution A (Sheraton)**

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**SESSION F4: POROUS SILICON II**

**Chair:** Leigh T. Canham

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**Constitution A (Sheraton)**
electronic. Optical parameters of principal interest for OPS WGs made in both p- and n-type silicon substrates are discussed. Possibilities for ion 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 simulations has been used for the WG elaboration. Consideration is being given to the possibilities of these WGs.

4:30 PM  F4.4
BRAGG GRATINGS ON POROUS SILICON WAVEGUIDES.
Phintrikha S. P., Massoud Sayyadi, D. N. Zmuidzinas, and C. G.是很抱歉，但是这个文档似乎包含大量难以理解的字符，可能是由于输入或者编码错误。我无法从这个文档中提取任何有意义的信息。
Silicon nanocrystals grown by controlled crystallization of amorphous Si/SiO$_2$ films hold 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/SiO$_2$ interfaces be atomically smooth, dense, and chemically and structurally abrupt. These requirements are achievable in Radio Frequency (RF) 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 atomic and electronic structure of these films. We demonstrate that amorphous Si/SiO$_2$ superlattices deposited at non-optimum conditions tend to have a columnar growth and a high void volume deposition condition, 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/SiO$_2$ interfaces within the superlattice remains chemically abrupt. After the controlled crystallization process, the resulting Si nanocrystals are uniformly distributed and clearly discernible in X-ray photoelectron micrographs. After X-ray analysis, the following results were obtained:

F5.5 CHARACTERIZATION OF Si NANOPARTICLES FOR MEMORY APPLICATIONS


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 in the floating gate for memory devices. In this case, the size 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 complementary 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 from the X-ray microspectroscopy performed, Raman spectroscopy will be discussed. Some novel results from SPAM-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 SiO$_2$ LAYERS AND FUSED SILICA


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-nanocrystals) formed by ion-beam synthesis have received considerable attention. However, the factors governing the formation, properties and stability of Si-nanocrystals remain to be better understood. We studied the formation and radiation stability of Si-nanocrystals synthesized in thin films and in bulk porous Si (PSi) by implantation of 25-150 keV Si ions to the doses of 10-20 nC cm$^{-2}$ followed by annealing at 250-1150°C in air. Fast electrons and -particles irradiations were used to introduce the defects. The samples were studied by Raman spectroscopy, electron microscopy, XPS, HREM, and photoemission (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 nanocrystalline Si in the Si thin layers. Then they transform to the Si phase, nanocrystals, remaining amorphous until the temperature reaches ~1000°C. Further annealing leads to the formation of Si nanocrystals 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 single atomic displacement may cause prompt crystallization of Si nanocrystals at room temperature. Raman spectroscopy gives evidence of the nanocrystals being present, depending on whether thin films or bulk substrates were used. Further increase in the irradiation dose amorphizes the Si-nanocrystals. The above results are discussed in terms of the balance between the volume and surface free energies in Si-nanocrystals.

F5.7 EFFECT OF AMORPHOUS Si/SiO$_2$ BOUNDARIES ON STABILITY OF NANOCRYSTALLINE/AMORPHOUS SiO$_2$ MIXED PHASE. Vladimir I. Gerasenko, Ruslan 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/SiO$_2$ 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/Si layers is necessary. In this work, we study stability of a model nanocrystalline/amorphous SiO$_2$ system with additional amorphous Si/SiO$_2$ boundary on each side. The silicon nitride layer is assumed to be 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 NANOCUSTERS IN Si-SiO$_2$ SYSTEM. Laura Diaz-Flores, Francisco Espinosa-Beltran, Jesus Gonzalez-Hernandez, Yuri Vorobiev, Laboratory of Investigation of Materials, CINVESTAV-IPN, Queretaro, MEXICO.

We investigated the optical properties of the Si-SiO$_2$ system prepared by thermal oxidation of the Si-powder in air at different temperatures, and by incorporation of the same powder into solgel SiO$_2$ 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 and absorption spectra of some samples were taken for the lines related to the Si nanoclusters, in particular, those related to the cluster Si$_2$ and Si$_4$. The detailed analysis was made of the spectra of SiO$_2$ phonon bands in the region 1000 - 1300 cm$^{-1}$ obtained in the samples of different origin and treatment. The well pronounced Bragg's 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 entraped within the SiO$_2$ 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 SiC QUANTUM DOTS. Katsuhiko Negashia and Shunji Odii, 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). nc-Si is an n-i-n layer doped with phosphorus and Ge, whose merits are high efficiency, high resolution, and easy fabrication process without requirement of high vacuum and high vacuum device operation. But with P, a wet process is required. On the other hand, we fabricate nc-Si dots in gas phase by using plasma enhanced chemical vapor deposition (PECVD). Using this method, we control the size the dots by applying pulsed gas of silane into argon plasma. For CEE, an nc-Si substrate is used as an electron source. On nc-Si substrate, the nc-Si dots are grown by placing the substrate at the substrate at the distance to the plasma source, and the size of the nc-Si dot 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 10⁻¹² Torr. The grounded and illuminated electrodecollector of electrons extracted into vacuum, is located in front of the sample and applied a constant positive potential. While a negative voltage is applied to the Si substrate, a diode current flows. When a negative voltage over 4V is applied, which results in 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 similar to the collector. An electric field is applied mainly to SiO₂ region covering the dots, so electrons from the wafer surface SiO₂ with 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 CHEST, JSI.

F5.10 SINGLE-ELECTRON MEMORY EFFECTS IN MOS STRUCTURES FABRICATED BY LPCVD DEPOSITION OF Si NANOCRYSsTALS Vulcic, G., Garelli, B., Fazio, G., Renna, S.M., Microelectronics, Catania, ITALY, S. Lombardo, I. Crupi, V. Lino, V. Raineri, CNR-METEM, Catania, ITALY.

Single electron devices, among which nanocrystal memories, are perceived as the successors of the present MOSFETs when future 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 time 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 spherical shaped nanocrystals are obtained with a quite uniform distribution peaked at a diameter of 4 nm. An interpoly 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 new 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 pair of side gates with keeping the other gates grounded. The side gate were formed by deep etching into the barried 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 4kA at zero magnetic field exhibit up to three-peak-plateaus with small interpair spacings and large interpair spacings. Three interpair spacings are found to be nearly a constant value, corresponding to the single charging energy U, whereas two interpair spacings are different which are associated with U and U/2, i.e., successively one and two level spacings are observed. The Coulomb blockade effects, alternating odd(\( \sin(1/2) \))even(\( \sin(0) \)) 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 non-linear current-voltage, and well explained by a simple model calculation.

F5.12 LATERAL CARRIER TRANSPORT IN ULTRA-THIN LAYERS OF SILICON NANOCRYSTALS H.B. Kim, L. Mettes, R. Krishnan, P.M. Fauchet and L. Tayleskov, Department of Electrical and Computer Engineering, University of Rochester, Rochester, NY, USA.

Low-dimensional Si/SiO₂ based structures have attracted strong attention due to their interesting physical properties and potential applications in the future. For electronic devices, layered structures 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 significant high density memory (Erasure) requires the understanding of Si nanocrystal “cross-talk”, which must be measured 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 SiO₂. The thermal and electrical properties of the Si layers was studied by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The measurements of nc 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.


Two-dimensional periodic arrays of inverted pyramid holes with nanometer scale have been patterned on the surface of a 100 nm 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 480 nm laser beams was used to exposure 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 pyramidal geometry was formed using 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 500 nanometer 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. Nee-Man Park, Sung-Hun Jeon, Hyeun-Soo Hong, Seong-Ju Park, Kwangju Institute of Science and Technology, Dept. of Materials Science and Technology, Kwangju, KOREA, Sung-Mo Cho, School of Materials and Information, College of the Advanced Institute of Materials Science and Technology, Kyung Hee University, Suwon, KOREA.

Recently some research groups have investigated the electrical properties of Si nanocrystals and reported on charge storage in these structures. The nanocrystal memories are very interesting in very large scale integrated circuits in the future because this nanocrystal memory has advantages such as long term charge storage, fast response, and quantum-lossless. 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 SOCS 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 electrical charging in a-Si QDs embedded in silicon nitride as an insulating layer in MIS structure which was grown by plasma enhanced chemical vapor deposition. This electrical 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 net 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 multistate memory devices.

F5.15 CRYSTALLIZATION AND INITIAL GROWTH STAGE OF MICROCRYSTALINE Si FILM DEPOSITED BY PHOTO-CVD AND ITS MEMORY DEVICE APPLICATION. Seung-Jae Baik, Koeng Su Lim,
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 that they have longer charging time constants. And they respond at lower temperature because higher capture rate of nanocrystals 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 growing clusters. With optimization procedure, we obtained the spatial density of microcrystals to be mid 10^14 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 case 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. Hironori Miyamoto, Yoshikazu Ohnaw, Hiroshi Naito, Osaka Pref University, Dept of Electronic and Electronics, Osaka, JAPAN; Yoshikiko Kanematsu, 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-carrying characteristics. Si nanocrystals with an 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 from 0 to 10% and varies essentially between 1.0 and 3.6 eV. Also, it is deduced that change carriers are photoexcited on nc-Si and transport through nc-Si. The I-V characteristics of Au/nc-Si-Polyester/Au exhibit I a) V in nc-Si concentration range from 0 to 10 wt% where 3 c) 5. Such variations 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 Deang Feng, National Laboratory of Solid State Micro-structures, and Center of Materials Analysis, Nanjing University, Nanjing, JINGOU, CHINA; Ji Cheng, Department of Materials Engineering, Jiaotong University, Shanghai, CHINA; Hua-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 absorption technique. We report the results obtained using Raman Scattering spectra, which is shown that Raman representative of optical gap is intimately related to the grain size of the nanometer silicon, whole change process can roughly be divided into three different steps, around 5.0 (nm) grain size, i.e., corresponding to the region which are 1.88~2.0(eV), the slope of the curve of log ε/ε_0 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/ 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 Ohshio in 1998, 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 the relationship between PL spectra and the properties of different samples. 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 to elucidate 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, the 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 enhance the irradia- tion recombination centers, which were introduced into the samples during the oxygen implantation; 2) the blue PL originates from luminescence centers in Si dioxide, 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 NANO SCALE Si IN a-SiO2 MATRIX. Kuros Umezuy, Ken-ichi Yoshida, Akira Sugimura, Konan Univ, Dept of Applied Physics, Kobe, JAPAN; Mitsuhiro Inada, Konan Univ, High Technology Research Center, Kobe, JAPAN.

We prepared a-SiO2 (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-SiO2 matrix. The optical absorption and photoluminescence (PL) spectrum of the films are discussed. The structure of the films was evaluated by X-ray photoelectron spectroscopy (XPS) and infrared absorption. The XPS spectrum of the a-SiO2 films showed two 2p peaks at 95.6 and 106.0 eV. This indicates that the a-SiO2 films are not homogenous but are comprised of clusters in 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 spectrum 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 ANOMALY OF SILICON USING A PREFORMED NANO SCALE TEMPLATE. S.P. McGinnis, P. Sines, C. Garman, and B. Drs., 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 modified 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 control over 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 PHOTOLUMINESCENCE IN POROUS Si investigated BY EVAPORATION INDUCED PORE COLLAPSE. Donald J. Sirbuly, Michael D. Mace, Steven K. Burrage, 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
silicon/p-$\alpha$-Si/metal configuration and another with Eu-doped silicon-silicon dioxide/n-type silicon/p-type silicon /p-$\alpha$-Si/metal configuration are discussed in detail.

F5.25

Metal/pPS/p-$\alpha$-Si and metal/pSPS/p-$\alpha$-Si PHOTO-DETECTORS BASED ON POROUS SILICON: Leonid A. Balagurov, Sergey Ya. Andrushin, Vladimir S. Krastochvik, Dmitriy G. Yurkin, State Institute of Rare Metals, Moscow, RUSSIA; Sue C. Bayliss, Bayramunal, Solid State Research Centre, Faculty of Applied Sciences, De Montfort University, Leicester, UNITED KINGDOM.

Metal/pPS/p-$\alpha$-Si and metal/pSPS/p-$\alpha$-Si photodetector structures were fabricated and investigated. Metal/pPS/p-$\alpha$-Si porous silicon (PS) based photodiodes with top grid metal contact demonstrate quantum efficiency of photosensitivity up to 70.8 in visible range of spectra, detection up to $6 \times 10^4$ cm$^2$/V$^2$/W and response time less than 2 ms. Three types of metal/pPS/pPS/p-$\alpha$-Si detector structures were found: with ring metal contact, mean structure and device structures with two guard rings. For fabrication of these device structures the silicon dioxide and silicon nitride layers were deposited on the top of p-type c-Si substrates. Photocurrent was measured for 250 nm Si$_2$O$_3$ and Si$_3$N$_4$ layers formed on the Au n-anode by using a laser semiconductor laser and on-wafer pads. Finally, upper metal contact was formed by using sputter deposition method. It was obtained that such device structures with guard rings have sufficiently low reverse currents of (5-10$^{-9}$ A/cm$^2$) at a quantum efficiency of 0.7 for such type of structures, detection value of 6 x 10$^4$ cm$^2$/V$^2$/W and response time less than 2 ms.

F5.26

TRANSPORT OF CARRIERS IN THIN METAL/pPS/p-$\alpha$-Si STRUCTURES BASED ON POROUS SILICON. Leonid A. Balagurov, Elena A. Petrova, Dimitriy G. Yurkin, State Institute of Rare Metals, Moscow, RUSSIA; Sue C. Bayliss, Bayramunal, Solid State Research Centre, Faculty of Applied Sciences, De Montfort University, Leicester, UNITED KINGDOM.

Metal/pPS/p-$\alpha$-Si structures with relatively thin (1 $\mu$m) and high porosity porous silicon (PS) layers were made on moderately and highly resistive substrates. Current-voltage (LV) and impedance measurements at different temperatures were used for investigation of transport in thin change carriers in the metal/pPS/p-$\alpha$-Si structure. Low current, $LV$ dependencies for both types of structures spread over several orders of magnitude with low value of ideality factor (close to 2) and high activation temperature dependence 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-recombination of carriers in the depletion region of the structure determines the reverse and forward currents. Thin $p$-doped device structures by the analogy to metal/pPS/p-$\alpha$-Si structures made on moderately doped substrates constant rectification for device structures made on highly resistive substrates is found to be caused by the potential barrier in the substrate at $p$-Si/p-$\alpha$-Si heterojunction. 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 $p$-Si/$\alpha$-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; Chuanmin Wang, TIFUNAM, Mexico City, MEXICO; Yuri Rodin, Julio Tagliabue Martinez, CHOUCAM, MEXICO.

A detailed study of the dielectric function of porous silicon by using a superradiant-tight-binding sp$^3$ 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 hydrogen on the surface and in the bulk of 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-
LUMINESCECE OF POROUS SILICON. Shunsaku Ogura, Nobutomo Ueno, Osamu Ohmura, Tomoaki Tsuchi, Masa-ichi Ueda, Kusatsu College of Technology, Kobe, JAPAN.

We studied the effect of surface roughness of Si wafers on porous silicon by means of photoluminescence (PL) and infrared (FTIR) absorption and Raman spectroscopy. We prepared several kinds of Si wafers with a different surface roughness, and then the modification was performed at a single 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 SILICON PREPARED BY PHOTOELECTROCHEMICAL ETCHING OF N-TYPE SINGLE-
CRYSTALLINE SILICON AT VARIOUS CONDITIONS. Chik-Woo Lee, Bum-Suck Kim, Dong-II Kim, Nam-Ki Min, College of Science and Technology, Korea University, Jondhon, Choongnam, KOREA.

Since the visible photoluminescence from photoelectrochemically anodized porous silicon material was reported at room temperature in 1990, it has been the subject of considerable interest to develop the materials as silicon-based optoelectronic media. A porous silicon optical-electronic circuit in which a silicon bipolar transistor drives a porous silicon light-emitting diode integrated on the same wafer has been demonstrated. The electroluminescence observed 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 microstructures would be required to fabricate possible well-behaved silicon-based opto-
electronic 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 investi-
gated 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 chromophotometric curves strongly depend on the experimental factors involved. Photoluminescence spectra depend 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 spectrum changed little. Multiply-perked 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 LUMINESCECE CENTER OF POROUS SILICON UNDER LOW TEMPERATURE THERMAL-
OXIDATION. Kazuo Gomi, Meisei Univ, Dept of Physics, Tokyo, JAPAN. Takayuki Hidai, Electro-Communication Univ, Yamanashi, JAPAN; Yukako Honda, Kurehashi 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 the occurrence process of the PS because the PL properties are influenced by the process. In this paper, the relationship between structure and PL spectral photoionization of porous silicon at low temperatures (150, 200, 250°C) in air was investigated using an infrared (IR) spectroscopy and PL measurements. IR measurements show that the IR absorption peaks for Si-H stretching band (2 100~2 150 cm^-1) shift to the higher energy side due to Si-O-Si bonding (2 1000~2 1050 cm^-1) associated with the increasing 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.

F5.31 COMPARATIVE SEM AND CATHODOLUMINESCECE-
MICROANALYSIS OF POROUS SILICON STRUCTURES. M. Stevens Kellef, Univ of Technology, Microstructural Analysis Unit, Sydney, Australia; S. Longa, I. Ming, Tignini, Technical Univ of Moldova, Laboratory of Low-Dimensional Semiconductor Structures, Chisinau, Moldova, J. Christensen, M. Christiansen, H. Frili, Christian-Albrechts-Universitats, 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 n-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 forms 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 (~100 mA/cm²) the formation of the so-called circular pores orientated were observed. These pores have no specific crystallographic orientation and their morphology reflect the current flow during the anodization process.

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 porous silicon membrane has been fabricated. The sensitive membrane has been bonded to a 1 cm² Al₂O₃ substrate [1], where electrical contacts have been previously deposited by sputtering procedures. In this work we present the 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 biology operating range for both humidity and temperature. Many materials have been used. Like ceramics, polymers, porous Al₂O₃ 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 response time, t < 16 s, is limited by experimental conditions and is, anyway, much shorter than a commercial device, t = 122 s, obtained in the same conditions. Moreover, the new fabrication process used to realize the device merges the advantages of CMOS technology with high sensitivity compared to the typical gas sensors of the above-mentioned 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 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. Vezziello, F. Rocc, D. Nino, V. La Ferrara, G. Iaconisi, L. Lancellotti, G. Sberveglieri, P. Maddalena: "Metodo per la fabbricazione di dispositivi a stato solido" patent No GE094000146 deposited at Italian Patent Office on December 29th 1998. [2] Z. M. Ritterman Ph.D Thesis: "Microsensors application of porous silicon", Shaker Publishing B.V., Munster (1999).

F5.33 NANOCRYSTALLINE & VOID-COLUMN NETWORK THIN FILMS DEPOSITED BY HIGH DENSITY PLASMA.
APPLICATION TO HIGH SENSITIVITY AND ULTRA-FAST HUMIDITY MONITORING. A. Kumar, Koiken, Hongou Li, Stephen J. Fonash, and Paul M. Laskin. The Pennsylvania State University, University Park, PA.

Deposited high porosity nanocrystalline Si films have been obtained by the combination of two extreme range 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). These conditions, in combination with results of nanometer-sized rodlike columns oriented normal to the substrate surface and situated in a void matrix. Sensitivity can be varied up to ~90% by varying the plasma power, which controls the nucleation 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 charge injection 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 NANOPISTLES ON FLAT GERMANIUM (100) SURFACES. Jon A. Porter, Jr., Hee Cheul Choi, Jillian M. Burrack, Purdue University, Dept. of Chemistry, West Lafayette, IN.

Monolayer films of gold, platinum, and palladium nanoparticles have been prepared as a result of the immersion of nanoporous and thin germanium (100) substrates into dilute, aqueous solutions of tetrachloroaurate (III), tetrachloroplatinum (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 area, 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; Rosella Piaggio, Siemens, Settimo M. e, ITALY; Monica Bollini, Consorzio Milano Ricerche, Milano, ITALY, Istituto Nazionale per la Fisica della Materia and Edifa, 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 (HJGSs). HJGSs 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 (100) substrate. The film was structurally characterized by High-Resolution Transmission Electron Microscopy and by Nanodiffraction. It is known as a "quasi polycrystalline, 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, CPA-Marseille, FRANCE; Monna Bollini, Consorzio Milano Ricerche, Milano, ITALY, and the sensitivity of the sensor, defined as 0 ln I/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 by the standard theory of surface barrier modulation. Instead, a model based on the modulation of the heterojunction between the sensing film and the substrate must be advanced. The adsorption of CO onto the oxide grains (either specifically or nonspecifically) 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 (100). Dario Narducci, Istituto Nazionale per la Fisica della Materia and Dept. of Materials Science, University of Milano Bicocca, Milano, ITALY; Ahmed Charrar, FRANCE; Dario Narducci, Cons. Milano Ricerche, Milano, ITALY, Istituto Nazionale per la Fisica della Materia, ITALY, and Edifa, University of Aix-Marseille III, Marseille, FRANCE; Rosella Piaggio, Siemens, Settimo M. e, ITALY; Pier Maria Berruti, Cons. Milano Ricerche, Milano, ITALY, and Edifa, University of Aix-Marseille III, Marseille, FRANCE.

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 bonds under mild conditions. These systems were found to act as chemiresistive sensors for gases. These new sensors are based on the 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 300 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 molecule with the gas molecules. A correlation between gas composition and surface conductance was found. Based upon computer simulations could be advanced. We hope to 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 experienced. The results obtained pave the way to the development of new generation of sensing devices, capable of sensing the flexibility of organic chemistry with the structural order 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 Baym, IPCES-UMR 6038 CNRS, University of Limoges, Limoges, FRANCE; Liandi Merheri, Ceramic R&D, Limoges, FRANCE.

It is well-known that surface chemistry is a critical parameter to be controlled during the processing of nanoparticle films 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 in band bending properties. Therefore, any tailoring of semiconductor surface chemistry should 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) spectroscopy. Then, it will be demonstrated that FTIR spectroscopy allows the simultaneous investigation of 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 BRUTE EuraM III program (contract number BRPR-CT95-0039).

F5.38 TUNGSTEN OXIDE NANOCOMPONENTS FOR GAS SENSOR APPLICATIONS. Justin T. McCue, Jackie G. 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 the industrial process control have been made with these 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 to a wide range of gases, 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 this work. Novel tin oxide titanium oxide (SnO2-TiO2) semiconductor nanocomposites have been designed and synthesized via wet chemical approaches. They display superior thermal stability and sensitivity to ppm levels of CO and NOx. By controlling the SnO2-TiO2 microstructure and composition, and by introducing active dopants, sensors with excellent selectivity for CO and NOx have been successfully attained and optimized.

**F5.30**

**NANOSTRUCTURED TiO2 AND W-TiO2 THIN FILMS BY A NOVEL SOL-GEL PROCESSING FOR ALCOHOL SENSING DEVICES.**

G. Cerreli, E. Comini, E. Piretti, S. Frigeri, F. Filippetti, G. Cerreli, G. Szelebiger, IFM and Brescia Univ, Dept of Chemistry and Physics for Engineering and Materials, Brescia, ITALY; Cesare Frigeri, CNR-MASPEC Inst, Pavia, ITALY.

TiO2 and W-TiO2 thin films have been prepared by a chemically modified sol-gel technique, that implies hydrolysis and condensation of tetrachloroethane in the presence of a polymer dissolved in ethanol. The technique results in an effective method for preparing nanocrystallized 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 TiO2. To our knowledge this dopant has never been studied for sol-gel titanium dioxide in the gas sensor field. TiO2-polymer nanocomposites thus were deposited by dip-coating and 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 1/3, and the morphology and structural characteristics of thin films were studied through micro-Raman, XRD, SEM and TEM analyses. The W contents were obtained by Microprobe analysis. Both doped and undoped oxide resulted in amorphous form and no evidence of W-O oxides resulted. The morphological comparison between doped and undoped TiO2 layers highlights that a finer nanostructure can be obtained by doping. Regarding the alcohol sensing properties, the response toward alcohols is always enhanced with the doping content. The behavior could be ascribed to the finer granularity obtained, that implies a higher surface area to volume ratio. W-TiO2 sensors can detect very well ethanol concentration required for breath analyses. [1] C. Gavi, E. Comini, E. Tempesti, C. Frigeri and G. Szelebiger

**F5.40**

**NANOIZED MO-W-O THIN FILM GAS SENSOR FOR ENVIRONMENTAL MONITORING.**

E. Cerreli, E. Comini, G. Szelebiger, INFM and Dept. of Chemistry and Physics, Brescia University, Brescia, ITALY; Vincenzo Guidi, Matrix Ferro, Locandro Cairoto, IFM 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. WO3 was recently recognized as a sensor for NOx, with fairly good response owing to exaggerated green snow-cover growth of nanostructured layer. Moreover, the presence of the thin layer of molybdenum oxide was chosen because it exhibits excellent sensing capability [2] and has similar ionic radius to Tungsten. We have deposited thin films of Mo-W-O by rf 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 film and in turn the sensing behavior: we have comparatively studied the electrical performance of the layers towards either oxidizing or reducing gases such as NOx 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 between 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 the oxidized and reduced response in the range to 90 s. The response of these sensors is high and fast enough to be applied for environmental monitoring [1]. G. Szelebiger et al., WO3: dotted thin films for NOx monitoring, Sensors & Actuators B 26-27, 89, 1995 [2] M. Ferroni et al. Characterization of 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 TiO2 STUDIED BY HIGH RESOLUTION ELECTRON MICROSCOPY.**

Jordi Arbiol, Anna Ruiz, Albert Grema, Francisco Pena, Albert Corom, Jose Ramirez Morante, Barcelona Univ, Dept of Electronics, Barcelona, SPAIN; Abdelali Alimou, Maria-Jose Casanova, CEMES/CNRS, Toulouse, FRANCE.

In this work, we studied the Pt particles embedded on crystalline TiO2 nanoparticles used as a semiconductor gas sensor. As it is well known, metal nanoparticles distributed on TiO2 surface can improve dramatically the reaction rate and selectivity of reaction in gas sensing. We prepared a wide set of TiO2 samples grown at different temperatures and with different nominal Pt concentration. The aim of this study was to analyze the Pt distribution on TiO2 surface (density of Pt particle size distribution), as well as the different Pt phases (metallic Pt, PtO and PtO2) 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/TiO2 sample for gas sensing applications and discard those that presented the worst characteristics.

**F5.42**

**A NEW METHOD TO CONTROL PARTICLE SIZE OF SnO2 NANOPARTICLES FOR GAS SENSOR APPLICATION.**

Edison R. Leitz, I.T. Weber, E. Longo, LIEC-DQ-UFSCar- Sao Paulo, BRAZIL; J.A. Vazelas I.Q. UNESP-Assuncao, Sao Paulo, BRAZIL.

This work described the synthesis of a nanostructured material with good potential for gas sensor applications. Nb2O5-doped SnO2 particles with a narrow particle size distribution and an average Sn particle size were obtained by a new approach to control the particle size during the synthesis of SnO2 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 Nb2O5. This work involves the synthesis of a nanostructured material prepared by the polymeric precursor method. The addition of Nb2O5 can modify the rate of nucleation during the SnO2 crystallization process, promoting a high rate of nucleation. After nucleation, Nb2O5 can inhibit particle growth, thus preventing the formation of necks between particles and the process of condensation. Preliminary gas sensing measurements are performed and it is demonstrated that the response time of the Nb2O5-doped SnO2 is faster than that of the undoped material.

**F5.43**

**THE GAS RESPONSE TO OXIDIZING GASES OF WO3 THIN FILMS SENSORS PREPARED BY THERMAL EVAPORATION TECHNIQUES.**

Carlo Carlini, L'Aquila Univ, Dept. of Chemistry and Materials, L'Aquila, ITALY; S. Santucci, M. Passarutto, L'Aquila Univ, Dept. of Physics, L'Aquila, ITALY.

W03 thin films have been deposited on Si/SiN4 substrates provided with platinum interdigital electrodes by Vacuum Thermal Evaporation (VTE) technique and annealed at temperatures between 800°C and 500°C for 1 to 240 hours at static air. The morphology, crystalline phase and chemical composition of the films have been characterized using SEM, glancing XRD, XPS and SAM techniques. The evolution of the microstructure (surface roughness, crystallite size and chemical composition) has been related to the annealing time at different temperature and temperature. The thermal annealing process has been optimized in order to obtain the smoothest 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 NO2 (0.2 - 2 ppm), Cl2 (0.1 to 1 ppm) NOx (27 ppm NO and 1 ppm NO2) at different operating temperatures ranging between 180 and 250°C and different humid air conditions between 20% and 90% Relative Humidity. The gas response to NO2 and Cl2 has been found to be at maximum at 180°C. At this temperature and 1 ppm NO2 or 1 ppm Cl2 the measured gas response S = 0.2 and 0.15 respectively. The gas response S, has been related to be influenced by the annealing time. No cross sensitivity has been found by exposing the WO3 films to CO and CH4. Negligible H2O cross to NO2 and Cl2 response has resulted in the 205 - 405°C RH range.

**SESSION 6: SILICON QUANTUM DOTS PREPARATION**

Chair: David J. Lockwood

Tuesday Morning, November 28, 2000

Constitution A (Shattuck)

8:30 AM FE.1

**RAMAN SPECTROSCOPY OF Si NANOCRYSTALS IN NANO.**

Precise control over structural parameters such as size, shape, and crystallographic orientation of Si nanostructures and their optical properties is central for reliable modeling and fabrication of nanoscale Si-based devies. In this work, Raman spectroscopy is used to study these structural parameters of Si nanocrystals formed by solid phase crystallization of amorphous Si/SiO₂ networks (Si₅N₅) 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 interface). The nanocrystallinity of the amorphous Si/SiO₂ layers strongly influence the Si/SiO₂ interface roughness, which is inferred from the folded acoustical 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 *FE.2* NUCLEATION AND CRYSTALLIZATION OF ULTRA THIN FILMS - A NEW CRYSTALLIZATION MODEL, Murti Zacharias, Peter Streitenberger, Institute of Experimental Physics, Osnabrueck University, Magdeburg, GERMANY.

We study the exponential scaling of the crystallization temperature and the layer thickness for various superlattices with oxide interfaces. Using an empirical model this behavior could be reduced to basic material properties like the bulk amorphous crystallization temperature and the melting point. A new crystallization model is presented which correctly accounts for 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 question in agreement with our experimental observations. The evidence of a critical crystallization radius and the influence of a non stoichiometric interface are discussed.

9:00 AM *FE.3* OXIDATION OF SILICON NANO CRYSTALS, S. Keaten C. Smith, J.M. White. The University of Texas at Austin, Department of Chemistry, Austin, TX and Digital DNA Labs, Motorola, IPS, Austin, TX; Suchith Malukkar, Ramachandran Muradhir, Michael Sall, David O'Meara, Bruce White, Bob Jones, Materials and Structures Laboratory, Digital DNA Labs, Motorola, IPS, Austin, TX.

Silicon nanostructures are of interest due to their potential importance in microelectronics [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 memory 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 the 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 viscous-toelastic transition of SiO₂ (550°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 tied 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 nanocrystals. The 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. Mann, H.R. Pinchard. The Electrochemical Society, Pennington, NJ, 1996, 250. [2] A.G. Nkamboupolous and S. Grigoropoulos, Appl. Phys. Lett. 69, 1996, 2927.

9:15 AM *FE.4* FABRICATION OF SILICON NANO CRYSTAL DOTS ON SiO₂ BY ULTRAHIGH VACUUM CHEMICAL VAPOR DEPOSITION, Takayuki Kusumoto, Masato Oishi, Susumu Mashino, Junro Sakai, Semiconductor Equipment Div, Aneba, Tokyo, JAPAN; Suchith Malukkar, Bich-Yen Nguyen, Bruce E. White, Motorola, Materials and Structures Laboratory, Austin, TX.

In this work, fabrication of nano-scale hemispherical shaped Si crystal dots on SiO₂ in a Coldwall Ultra-high-Vacuum Chemical Vapor Deposition (UHV-CVD) system is demonstrated. Si₅N₅ gas was used as pre-cursor for this work. In our system, nucleation, growth, and coalescence phases of nanocrystal dots on SiO₂ layers were found to be related with the optical pyrometer read-out curve. Thus, optimum irradiation time to obtain highest dot density without coalescence were decided by using the optical pyrometer, for every gas irradiation condition. Dependence of the optimal 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 Si₅N₅ 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 some 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 3nm in diameter with density of 6×10¹¹ dots/cm² were obtained. Typical process time to get such dot formation characteristics was about 2×10⁴ s, which were long enough for ensuring precise repeate process.

9:30 AM *FE.5* THE NOVEL SYNTHESIS OF SILICON AND GERMANIUM NANOCRYSTALITES, Sasan M. Kashefi, Qi Liu, Department of Chemistry, University of California at Davis, Davis, CA; Howard W.H. Lee, Robert Taylor, Lawrence Livermore National Laboratory, Livermore, CA.

Interest in the synthesis of semiconductor nanomaterials has been generated by their unique optical and electronic properties arising from quantum confinement effects. We have synthesized Silicon and Germanium nanocrystals 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 MgBr₂ (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 nanocrystals will be presented.

SESSION F7: SILICON QUANTUM DOT DEVICES

Chair: Leonid Tayshesov

Tuesday Morning, November 28, 2000

10:30 AM *F7.1* THEORY OF ELECTRONIC TRANSPORT IN SILICON NANO STRUCTURES, Y.M. Nguep, C. Delaere, G. Allan, IEMN, Dept. ISEN, Lille, FRANCE; M. Laroze, 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. Theoretical 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 behind this. 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 1/V characteristics. Finally we will discuss
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.H. Bronsgaard, H.A. Atwater, Caltech, Thomas J. Watson Laboratory of Applied Physics, Stanford, CA; M. Ostran, 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 ±0.15% control of size in the 5-30 nm size range. We have used conductive tip manipulation microscopy to apply, and electronically manipulate single silicon nanocrystals on an insulating substrate (a 100 nm thermally grown SiO2 layer on silicon). By applying voltages of 0-400 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 1000-10,000 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 the charge detection method to be on the order of ±5 electrons.

11:15 AM F7.3
ELECTRON TRANSPORT THROUGH ULTRASMALL Si NANOPARTICLES USING SCANNING TUNNELING MICROSCOPY: ZERO BIAS CONDUCTANCE. J. Thieren, G. Beloezin, S. Bou, and M.H. Nafie, Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL.

Ultrasmall, uniform size (~1 nm), ultrathin Si nanoparticles are reconstituted on p-type, n-type Si, and on aluminum-grown 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 CV spectra at a biasing of ±0.45 eV. However, under light irradiation, we observe a highly visible regular staircase structure, for negative tip biasing at ~1.0 eV spacing. The second series is discussed in terms of light-induced hole states that 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 zero bias response that is more complicated. The peaks observed on the staircase of the tunneling tip is first biased at a voltage larger than 3.1 eV. We discuss the zero-bias conductance in terms of metal-semiconductor coupling in a quantum dot coupled to leads, as in a Kondo effect.

11:30 AM F7.4

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 mm thick SiO2 grown on Si (001) wafers. The combination of ultrathin 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 1015/cm2. Spectroscopic studies of single dots are made by recording the L curves on the Si nanocrystals 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 L-curves of single dots with Coulomb blockade response and tunneling effect through quantum confined states. The first step like structures appear on the L-curves 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 peak pseudo-ECVs may be observed below 0.25 eV and ±0.5 eV for different dots. From the width ~60 meV and height ~40 PA of the staircase observed at bias greater than 0.5 eV, capacitance of 0.5 to 1 fF and tunnel resistance of 3.5 E8 and 5.7 E9 Ohms are measured within the ‘orthodox’ approximation for charge storage, similar to nonvolatile devices. In the nanocrystal based NMV devices, 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 0.25μm n-MOSFETs 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 x 1014 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 oxide ≈ 40-70Å), and were encapsulated by a deposited high temperature oxide (t oxide ≈80-120Å, 800°C) via a SiH4/N2O chemical vapor deposition process. The devices were 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 2-6 V have been obtained for typical program/erase voltages and times, while only limited window closure is observed after 10 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 Kodama
Tuesday, November 28, 2000
Constitution A (Sheraton)

1:30 PM F8.1
SILICON-BASED PHOTONIC BAND GAP 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 microcavity 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 optoelectronic applications.
2:00 PM F8.2
A NEW WAY TO FORM THREE-DIMENSIONAL MICRO-STRUCTURE BY ELECTROCHEMICAL ETCHING OF SILICON
P. Kleemann, R. Juhasset and J. Linnenk, 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 been used in many other applications. It has been shown that the width of pores and trenches cannot 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 micro-etching of silicon by electrochemical dissolution of silicon based on etch-patterning an n-type silicon sample in a HF containing electrolyte except where vertical walls or pillars are needed. This patterning is achieved by preetching 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 enable 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 NO INJECTION-INDUCED POROUS SILICON INDUCED BY CARRIER INJECTION
Yusuke Terumitsu, 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-FP). The experimental devices consist of a transparent ITO top contact, an active PS layer sandwiched with upper and lower PS-FP mirrors, a n-type Si substrate and an ohmic back contact. The resonator was prepared by modulating p-type PS wafers in an anodic 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-FP 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 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 recombinations rate of accumulated carriers. [1] M. Takahashi, Y. Terumitsu, T. Ito, Matsudome, Y. Matsuokoo and N. Koshida, Proc. IEEE Symp. Adv. Lumin. Mat. and Quantum Conf., PV86-22, 35 (ECs, Pennington, 1989). [2] M. Takahashi, Y. Terumitsu and N. Koshida, Phys. Status Solidi (in press).

3:30 PM F9.1
LASER DESORPTION MASS SPECTROSCOPY USING THIN FILM DEPOSITED NANO-POOROUS SILICON
Joseph D. Cuijff, Daniel Hayes, Stephen Fennah, 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 mass spectrometry by desorption ionization on silicon (DOS). These methods overcome 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 DOS. Our deposited Si offers several advantages over conventional porous silicon including its absence of electrochemical etching and its capability to be deposited on glass and plastics. With our film, we successfully detected molecular detection of molecules in the mass range of 0 to 6000amu along with specific molecular detection at concentrations in the femtomole range. To further understand the DOS process, we characterized molecular detection versus laser intensity and film reflectivity, and we studied the effect of various chemical and thermal modifications on 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
PHOTO-LUMINESCENCE FROM N- (P-) TYPE IMPURITY-DOPE SILICON NANOCRYSTALS
Minoru Fujii, Atsushi Mizuma, Shinji Hayashi, Department of Electrical and Electronic Engineering, Faculty of Engineering, Kobe University; Kokkaido, Nada, Kobe, JAPAN; Dmitri Kovalenkov, Frederick Koch, Technische Universitat Munchen, Physik-Department, Garching, GERMANY.
Since the discovery of visible photoluminescence (PL) from porous-Si, optical properties of Si nanoparticles (nc-Si) have been intensively studied, but the subject of impurity doping has not yet been clarified. It has not been fully understood how dopant atom works in such a confined and dielectrically disordered medium. In this work, the effect of F-atom type impurity doping on the PL properties of nc-Si was studied. Impurity doped nc-Si were prepared by the coaggregation of Si and phosphosilicate (borosilicate) glass, and post-annealing. In the case of P-doping, the PL intensity first increased and then decreased with increase in P concentration. A possible explanation for the observed P concentration dependence is as follows. At low concentration, P-doping electrophotically passivates P centers, which are donors in Si. At high concentration, however, P centers act as nonradiative recombination centers. This passivation results in the improvement of the PL efficiency. At high concentration, after completing the passivation of P centers, electrically active P atoms supply free electrons in nc-Si, which makes the nonradiative Auger recombination of free-carrier holes possible, leading to the quenching of the PL. The decrease in the number of P centers at low P concentration and the existence of free electrons at high concentration were confirmed by electron spin resonance and optical absorption spectroscopy. In the case of B-doping, the PL intensity decreased monotonously. This suggests that holes supplied by B-doping are not trapped by P centers and always act as free holes. The quenching of the PL may be due to the Auger recombination between the hole and a photoexcited exciton. The present results imply that P 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

Nanocrystalline silicon superlattice (nc-Si/SiO2) is a structure consisting of highly crystalline Si nanocrystals 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 the nc-Si/SiO2 interface with a roughness of ca 5A. Photoluminescence (PL) of 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. Recently excited PL spectra show phonon steps proving that the PL originate from Si nanocrystals. The PL intensity temperature and lifetime dependences are in a good agreement with the spin-orbit interaction model. The PL lifetime and PL intensity under applied magnetic field of 0.01T. 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 increases as a function of the excitation intensity, and the PL spectra show a blue shift decreasing in 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 nanoparticles.

4:15 PM F9.4
Abstract Withdrawn.

4:30 PM F9.5
STIMULATED BLUE EMISSION AND SECOND HARMONIC GENERATION FILMS OF ULTRASMALL SILICON NANO PARTICLES. M.H. Naveh, N. Barry, J. Therrien, O. Alcikir, E. Gratton, G. Beloson, University of Illinois at Urbana-Champaign, Department of Physics, Urbana, ILL.

We dispersed electrochemical etched Si into a colloid of ultrahigh, blue emitting, ultrasmall (1 nm in diameter) nanoparticles, and reconstituted it into microcrystals or uniform films on device grade Si wafers. The emission spectra of 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 directed blue emission is observed. We attempt to speculate on the direction of this history between faces of the microcrystals. 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 microcrystals. Under certain waveguide/doping conditions, Si-Si dimer phase is suggested as a basic mechanism for inducing non-resonant emission of free electrons at the centrosymmetric.

SESSION F10: BIOLOGY WITH NANOSCALE MATERIALS

8:30 AM F10.1
NA NOBRAHICATED 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 developed nanoconstructions 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 silicon substrates. The differential electrophoretic mobility of large DNA fragments (>5,000,000 base pairs) and electronically 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 confirm the detection and selectively permit their motion in a microfabricated medium. Other applications of narrow fluidic channels in molecular analysis will be considered.

9:00 AM F10.2
SIZING OF PROTEINS WITH ELECTROCHEMICALY MACHINED POROUS GRADIENTS IN SILICON. Bayce E. Collins, Keiki-Pun Dascil, Gurair Abhi, Michael J. Ssnor, Univ of California at San Diego, Dept of Chemistry and Biochemistry, La Jolla, CA.

Porous silicon films displaying a distribution of pore sizes ranging from microns to nanometers can be generated by electrochemically etching silicon in an aqueous ethanolic HF solution using an asymmetric electrode configuration. The medium 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 microscopy and atomic force microscopy are used to characterize the pore size gradients. It is demonstrated that films with pore gradients in the few nanometer range can be used in size exclusion matrices to perform on-chip determination of macromolecule dimensions. Optical and, in particular, porous silicon films thin film photovoltaic devices are produced, the photovoltaic properties of which are studied in the Fabry-Perot fringes of 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
MICRONUTRITION AND THERAPEUTIC ELEMENT DELIVERY FROM A BIODEGRADABLE SEMICONDUCTOR: MESOPOROUS SILICON. L.T. Cunliffe, C.L. Reehl, W.J. Wright, T.J. Cho, Sensors and Electronics Division, DERA Malvern, UNITED KINGDOM.

The introduction of porosity on the nm scale into silicon renders the semiconductor biocactive 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 (e.g. Se, Cr, Mn, Mo) are needed by the body at extremely low levels ("trace elements" or "microminutrients") 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 micronutrients are absorbed. Other elements (e.g. Li, Au, Ag) have widespread use clinically for therapeutic purposes. We have started to investigate the use of micromachined silicon tablets, doped with a range of such elements via a recently developed technique of pore impregnation and high temperature annealing. By tailoring 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. Cunliffe Adv. Mater. 7, 1033 (1995)
9:30 AM F10.4

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 etching 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. These results are obtained when a biological object is attached to the internal surface of porous silicon. We demonstrate the usefulness of this microcavity resonator structure as a DNA optical biosensor which displays appropriate selectivity, sensitivity, 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 shift confirms successful recognition and binding of the DNA molecules within the porous structure. Detailed device fabrication procedures and the results of current work will be presented. This 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 an "smart bandage", where the detection of bacteria or viruses can be diagnosed and an antibiotic treatment can be recommended.

SESSION F11: S PASSIVATION AND FUNCTIONALIZATION
Chair: Philippe M. Fauchet
Wednesday, November 19, 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 becomes increasingly important. Organic modification is one means of providing new functionality to the silicon surfaces, imparting properties useful for passivation, molecular recognition, lubrication, or biocompatibility. This talk will focus on organic functionalization of silicon surfaces. Bipolar 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 characterize the bonding and reactivity of the organic layers at the silicon surface. On the Si(100)-2x1 surface, unsaturated molecules such as alkenes or alkenes react by cyclodition chemistry across the Si-Si surface dimers. We show that the [4+2] cyclodition (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 in a potential means of surface modification. Studies of a series of pyrroles provide insight into the relative reactivities of cyclodition, N-H bond dissociation, and nitrogen lone pair interaction. At the Si(100)-2x1 surface, the possibilities 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
REACTONS OF ORGANIC MOLECULES FOR CONTROLLED MODIFICATION OF GROUP IV SEMICONDUCTOR SURFACES: THEORETICAL AND EXPERIMENTAL. Douglas J. Durig, 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. Cyclodition reactions of alkenes and alkenes 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-dipolar which are also undergoing cyclodition. 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, leading to 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 these rearrangements resulting from different reactions, will be discussed. Finally, a new reaction that attaches an organic molecule to the surface by dissociation (as opposed to cyclodition) will be described.

11:00 AM F11.3
REACTIVITY PATTERNS AND MECHANISM OF A WHITE LIGHT PROMOTED HYDROSILATION REACTION WITH ALKENES AND ALKynes AT THE SURFACE OF PHOTOLUMINESCENT POROUS SILICON. Michael Stewart and Jillian Burik, 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) hydrosilation (H2Si(g) + R=CH2SiH3(g) in a mixture of 80:20 air:argon) 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 sites consistent with the quantum of light emission are thought to mediate the hydrosilation. The reactivity pattern of substrates suggests nucleophilic attack of surface-localized holes and electrons from excitation pairs. The LP derivatization reaction is unprecedented in that it requires a long-exposed excimer-photolysis by light fluence. Experimental evidence for a mechanism involving excited-mediated nucleophilic attack, along with alternative explanations for the LP hydrosilation reaction will be discussed.

11:15 AM F11.4

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 on handling 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 surface 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 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 the PSi surface 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, ethylenebisdimethylsilylene, 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 hydrogen-terminated 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 stored at 70°C 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 "packaging" process is thus highly effective in retaining the optical and optoelectronic properties of hydrogen-terminated 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 INTERFERO METERS. Sonja E. Leflar, Hongmei Sun, William C. Trotman, Michael J. Sule, and Computer Sciences Corporation 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
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, GaN, ZnO, and GaN) using wet
processes and/or by physical vapor deposition (PVD) approach.
A typical example is the synthesis of real freestanding 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
HRTEM. The unidirectional growth mechanism of nanowires was
investigated based on TEM features. In the third part the quantum
confinement effects were evaluated via the measurements of
photoluminescence and Ramans 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.R. 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, 1362 (1999)). The oxide of the silicon
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-standing and oriented in parallel direction.
Atomic resolution images showed that the silicon nanowires had
Si(111) surfaces, which assumed the Si(111)- (x1x) structure.
A structural model was proposed which accounts for the observed STM
features. STM measurement showed that the electronic properties of
the silicon nanowires depended on diameter and morphology.

2:30 PM F12.4
PSEUDO-MOS OPERATION OF ULTRA-NARROW POLYSILICON
WIRES: ELECTRICAL CHARACTERIZATION AND MEMORY
EFFECTS. Costin Angel, Naser Hefyane, Adrián M. Ionescu.
LEGEPHEL, Lausanne, SWITZERLAND, J-Trage, 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, similar to that of a MOSFET, is biased as a MOSGate and, in addition to the
ac current being imposed at the polysilicon-oxide interface, MOS-like DC characteristics are observed, 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 1/f 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 LV DC characteristics, when high
voltage is applied on the substrate acting as 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 SiH 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.
SESSION F13: ALTERNATIVE Si NANOSTRUCTURE SYNTHESIS
Chair: Jim Linros
Wednesday Afternoon, November 29, 2000
Constitution A (Sheraton)

3:30 PM F13.1
FORMATION OF NANOSTRUCTURES IN SILICON BY PULSED-LASER ABLATION. J.D. Fosket, A.J. Pedram, 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.

Nanostructures of silicon and silicon oxide are formed during UV-pulsed laser ablation of silicon substrates. It is shown that the nanotubes’ size is controlled by the initial micro-topography of the substrate and the wavelength of the laser beam. The generation of nanotubes is strongly enhanced if the initial silicon substrates are laser treated. This treatment is performed by multiple irradiations in a reactive atmosphere where the films are combined by the laser plasma during irradiation. The generated nanotubes are strongly enhanced if the initial silicon substrates are laser treated. This treatment is performed by multiple irradiations in a reactive atmosphere where the films are combined by the laser plasma during irradiation.

3:45 PM F13.2
SIZE CONTROL AND OPTICAL PROPERTIES OF SILICON NANOPARTICLES FORMED BY PIEZOSECOND PULSED LASER ABLATION. M.H. We, W.J. Yost, R. Mox, 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 nanoparticles produced by picosecond pulsed laser ablation. Results observed for nanocrystals produced by picosecond pulse widths are compared to those reported earlier for femtosecond pulse widths, where energy densities of 10-100 J/m^2 and background 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 nm^-2 observed on a microsubstrate 1 cm^2 from the target. Higher background gas pressures, such as those used for femtosecond experiments, result in formation of particles larger than 100 nm.

4:00 PM F13.3
GROWTH MECHANISM OF CHAINS OF SILICON NANOCRYSTALLITES. Hideo Kohno, Seiji Takeda, Osaka University, Department of Physics, Osaka, JAPAN; Koji Tsuchiya, Osaka National Research Institute, Department of Material Physics, Osaka, Japan.

We have reported growth of self-organized chains of silicon nanocrystals with detection of silicon nanocrystals of about 1.0 nm in diameter 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 in 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 has been attributed to the periodic instability of the catalyst at the tip of a growing chain and controlled growth of silicon nanocrystals. The growth mechanism has been controversial. In this study, these chains were examined with energy-filtered transmission electron microscopy (EFTEM) to reveal the growth mechanism of the chains. Energy-filtered TEM images showed tails of silicon of 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 reduces the core, while at a known the core remains unoxidized. Additionally, we have performed simple numerical simulations of the periodic instability in the chain growth. We would be able to 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. Toshiba Makoto, Nobuyasu Suzuki, Yuka Yamasu, Takeshi Yoshida, Yamada Electrical Industry Co., Ltd., Advanced Technology Research Laboratories, Kawasaki, Japan; Takafumi Seto, AIST, MIJ, Mechanical Electronics Laboratory, Tsukuba, JAPAN.

We have synthesized monodisperse, nonagglomerated silicon (Si) nanocrystals 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 monocrystals by pulsed laser ablation in inert background gas (PLA-IG), 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-IG were introduced into LP-DMA with an inert background gas (a carrier gas) through a conization 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, biases 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 classified the crystallinity of the deposited Si nanoparticles were 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 diodes (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 nanocrystallites increased at the whole range of monodisperse (3-10 nm).

4:30 PM F13.5
ENLARGEMENT OF CRYSTALLINE SILICON SIZE AND SIGNIFICANT INCLUSION OF HEXAGONAL DIAMOND PHASE IN ULTRA PURE MICROCRYSTALLINE SILICON. Teshiko Kamai, CIS, Dept of Electrical Engineering, Stanford, CA.

Hydrogenated microcrystalline silicon (μc-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 SiH₄ and H₂. 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 μc-Si:H enlarges crystalline grain size at higher substrate temperatures than 250°C. While grain size of (111) and (311) oriented crystallites increases almost independently 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 $\text{SiH}_{3}$ to $\text{SiH}$, for $\text{SH}$ may favor $\text{SiH}_{3}$ surface. Another interesting feature is the significant inclusion of diamond hexagonal phase which is accompanied by the enhancement of crystalline grain size. X-ray diffraction pattern shows that the Ge grown at 100°C shows additional peaks which are clearly observed in the lower diffraction angle (26.9° for Cu-Kα line) than that of (111) diffraction peak. We believe that this stems from (10-10) crystalline phase 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 NITRITE. Nae-Hui Park, The-Soo Kim, Cheol-Jong Choe, The-Young Seong, Seong-Ju Park, Kwangju Institute of Science and Technology, Dept of MSE, 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 by changing the measurement condition was demonstrated for the first time. a-Si QDs were grown on 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 blue-green-light emitting doped QDs layer with blue-light emitting one. Light-emitting devices (LEDs) with metal-insulator-semiconductor (MIS) structure were also fabricated and 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. Cho, 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-deposited Ge SiO2 samples synthesized by rapid thermal annealing (RTA) has been presented. The samples were prepared by co-sputtering a SiO2 target with six pieces of Ge target. 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 nanocrystalline size distribution. PL results showed a peak at ~2.3eV and the peak intensity increased 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 show 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 SiO2 to the PL results.


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 spatially and thermally characterized 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 nm. The parameters for making the Ga-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-structure 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 IHP-program.

F14.3 PREPARATION AND FUNCTIONALIZATION OF HYDRIDE TERMINATED POROUS GERMANIUM BY BIPOLAR ELECTROCHEMICAL ETCHING (BEE). Hee-Chul Chai, Jillian M. Burink.

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 77K in a darkened room upon illumination with 365 nm UV irradiation. In contrast to the 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 method for the formation of PG. Artificial color changes of the samples during BEE due to Fabry-Perot fringes, also indication 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 hydrogennation by thermal reactions with alkynes 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. Nosaki 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 surfaces are often 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 bath of SiGe alloy as a source, by taking advantage of a lower melting point of Ge. The other is to use two baths with Si and Ge each as source material. 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 bolt with a SiGe alloy surface, Ge nanocrystals are found to be oxidized and appear to be a SiGe alloy. In the case of a single bolt, the XRD pattern shows presence of Ge nanocrystallites 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 can be concluded that the surface of Ge nanocrystallites 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.

P14.5 STRUCTURAL, COMPOSITIONAL AND OPTICAL PROPERTIES OF SELF-ASSEMBLED QUANTUM DOTS ON Si [001]. Matthew Haakali, Alan Dunbar, Phillip Dawson, Ushi Bangert, Department of Physics, UMIST, Manchester, UNITED KINGDOM.

The structure of the Ge quantum dots, grown by gas source molecular beam epitaxy grown 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 bimodal size distribution: doped quantum dots, of approximately 100 nm base width and 12 nm in height, occurring alongside smaller pyramidal quantum dots of approximately 50 nm base width and 6 nm in height. Cross-sectional TEM measurements show that capping the quantum dots with Si causes them to flatten such that their base widths and domes are much more alike in conical 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 20 and 30 microseconds.

Timo-resolved photoluminescence spectroscopy suggest that the 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.

P14.6 ON THE STRUCTURE AND STABILITY OF SMALL Ge DOTS. Laurent Pizzagalli, Gianluca Galli, John K. Kepert, Francois Gygi, Lawrence Livermore National Laboratory, CA.

Understanding the influence of surface reconstruction and passivation on the growth and properties of semiconductor quantum dots is 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 relevant to the subject of controversy. Using first principles calculations, we have studied the influence of both He- and core-beam-reconstructed surfaces on the relative stability of diamond and tetragonal, STI1-2-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 STI1-2-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 STI12 clusters in vapor deposition experiments, by cold quenching of amorphous nanoparticles that have unreacted, reconstructed surfaces. Our results suggest that the pressure exerted on the inner core of the dot by an unwanted helium can induce a transition to STI12 transition in clusters with diameters smaller than 2.5±0.0 nm. In conclusion, our results indicate that by tuning the surface properties of nanodots, the pressure exerted on the dot core can be modified and used to tailor the optical and electronic properties of Ge 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-88.


Combining different scanning electron 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 (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 at the base to x = 1 at the top, in conjunction with an almost planar strain gradient along growth direction from z = 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.

P14.8 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 optoelectronic properties of Si based materials. The idea is to overcome the limitation of the indirect band gap of Si by a strong localization of the carrier 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 on top of the buffer layers were deposited on planar as well as on patterned substrates by molecular beam epitaxy. The structural and optical properties of the samples were analyzed 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 mean 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.

P14.9 Abstract Withdrawn.

P14.10 Si/Ge INTERMIXING AND ISLAND-IsLAND INTERACTION INFLUENCE ON THE Ge/Si(100) ISLAND SIZES. G. Cingolani, M. De Seta, and F. Evangelisti Istituto Nazionale per la Fisica della Materia Dipartimento di Fisica Universita 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 microscopy (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 find that the deposition temperature of 850°C strongly influences the island density of the Ge islands as a function of deposition temperature. We found that the intermixing is present above Tdep = 600°C. The Ge content x in the alloyed epilayer decreases upon increasing the deposition temperature. This scaling relationship connecting the alloying parameter and the effective mismatch with the Si substrate has been determined. By changing the growth rate at fixed deposition temperature we are able to modify the island density. The influence of the island density on the island size has been investigated. We found that the island density from 10^8 to 2×10^15 cm^-2 at Tdep = 600°C, the mean
island size changes from 90 to 60 nm. Island-island interaction effects on the growth dynamics will be discussed.

F14.11
MICROSTRUCTURE OF STRAIN-RELAXED SiGe LAYERS.
P.M. Mooney, J.L. Jordan-Street, IBM T.J. Watson Research Center, Yorktown Heights, NY; B. Suggs, B. Mooney, James Franke, Frank Inst.; University of Chicago, Chicago, IL; B. Lay, Z. Chu, Advanced Photon Source, Argonne National Lab, Argonne, IL.

Strain-related $Si_{1-x}Ge_x$ alloy films on (001) Si substrates serve as buffer layers for field-effect transistors containing strained Si or $Si_{1-x}Ge_x$ ($y > x$) 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 $Si_{1-x}Ge_x$ ($x=0.15$) layer of varying thickness. Measurements of the internal friction and TEM (X200) capillary-focused beam ($0.1 \times 0.5 \mu m$) show that all regions of the top $Si_{1-x}Ge_x$ layer have the same lattice parameter ($\Delta d/d_n=0.01 \pm 0.001$) but different average tilt angles whose variation depends on the misfit dislocation density. High angular resolution x-ray rocking curves measured at the APS (31-D3) from a $\theta$-3$\phi$ stage $Si_{1-x}Ge_x$ layer show many discrete tilt angles with sharp lines ($\theta=0.1 \pm 0.02^\circ$) that correspond to individual tilted regions (“micro-prints”) illuminated by the $0.1 \times 0.5 \mu m$ beam with complex and varying rocking curve line shapes. Using a model in which the local tilted regions are considered to be columnar “micro-prints” extending from the misfit dislocation network up to the surface, we have found that some illuminated regions show a few “micro-prints” with the largest size $\theta=0.5 \mu m$ while others show $1.5 \times 1.5 \mu m$-“micro-prints” with an average size $\theta=0.5 \mu m$. The dimensions are smaller than previously estimated with cross-section TEM images and with measurements of the surface morphology.

Partially supported by DOE contracts DE-AC03-76CH00016 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 gate of FET, channels of TFT). The reports on the effect of SiGe heterostructures on the size and shape of crystallites and on crystallization properties on $SiO_2$. We have measured SiGe heterostructures ($Si/5\%Ge/SiO_2$; $x=0-1$) 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 in $x$. The incubation time, however, is not simply a linear function of $x$. The composition of SiGe crystallites have larger grain size than that of $Si/SiO_2$. We have used patterned ($\mu$-mask) $SiO_2$ to modulate the surface geometry and found that the nucleation-site of SiGe crystallites strongly relates to the local geometry of 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 SI0.85Ga0.15GERMANIUM REACTIVE THERMAL CHEMICAL VAPOR DEPOSITION.
Kosaku Shimizu, Jin-ann Zhang, Jeong-won Lee, Jun-ichi Hama, 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 gas mixture. This material is expected to have a lower thermal expansion coefficient and a higher thermal conductivity than silicon. 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 other materials. However, a high current density is decomposed to afford the films. The films are composed of the $SiO_2$ matrix. The films consists of silicon-rich monocrystalline (2-10nm in diameter) and elongated twinned dendritic grains. The area proportion of these dendritic grains increases with an increase of $H2$. High resolution transmission electron microscopy (HREM) shows an obvious defect structure at grain boundaries, which are typically one or two atomic layer thick (0.2-0.4nm). Cross-section view reveals mixed columnar structure of the films. The internal nucleation of diamond occurs on $Si$ matrix directly when $H2$ is present in a gas mixture from a reactant layer which is about 16-18nm thick above the matrix $Si$. This distinction is observed in the enhancement of diamond nucleation by $H2$. The relation between diamond nuclei and $Si$ is primarily random and occasionally epitaxial.
NOVEL BULK NANODIAMOND/PYROCARBON SEMICONDUCTOR MATERIALS. Sergey K. Geodev, Central Research Inst of Materials, St. Petersburg, RUSSIA; Peter I. Belobrov, Nikolai K. Kiselev, Eleonora A. Petrowkova, Kirensky Inst of Phys. & Inst of Biophysics, SB RAS, Krasnoyarsk, RUSSIA; Tommy C. Ekstrom, Royal Institute of Technology, Stockholm, SWEDEN.

Novel semiconductor materials from nanodiamond/pyrocarbon composites (NDC) consisting carbon γ > 99 mass % were produced using a synthesis method. NDC and nanodiamond particles of 4.6 nm are connected into a bulk solid composite by pyrocarbon matrix. The high-porous NDC has the narrow pore-size distribution and effective pore size of 8±1 nm. Main features of NDC are controlled by γ = mass ratio of sp²/sp³ graphites. 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 varied from 3 to 2 nm and resistance to 1 kΩ is ranging from 30 to 600 Ω. The physical nature of cooperative structure 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 invariance with g = 2.0027(1), ΔH = 0.8(2) mT which conserves in NDC. Both g-factor and line width are not depending on γ and temperature. Concentration of unpaired electrons is $3.5\times10^{19}$ spin/cm$^3$ in equimolar conducting high-porous NDC. 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 ratio for variable-range hopping conduction is to observe a T$^{2/3}$ dependence at low T. A strong positive temperature dependence of electrical power is observed in NDC with narrow gap. The considerations of NDC should take into account. None of the levels of surface electrons. Observed zero values of magnetoresistance and the absence of Hall potential for all NDC are assigned for by the ionic conductivity mechanism within one-dimensional band of surface states.

MOLECULAR DYNAMICS SIMULATION OF N IMPURITIES IN ULTRANANOCRYSTALLINE DIAMOND GRAIN BOUNDARIES. Peter Zappl, Larry A. Curtiss, Dieter M. Gruen, Materials Science and Chemistry Division, Argonne National Laboratory, Argonne, IL; Michael J. Stillinger, Theoretical Chemistry Department of Physics, University of Paderborn, Paderborn, GERMANY.

Ultrananocrystalline diamond films grown from hydrogen-poor plasma 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 at the grain boundaries. High-angle twist grain boundaries in diamond have been shown to have a large fraction of three-coordinated carbon atoms in sp$^3$ 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 N-immersed high-energy high-angle (100) twist grain boundaries with N. It is shown by simulation that the ionic contribution 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.)

CHARACTERIZATION OF DEFECTS IN BORON DOPED CVD DIAMOND FILMS. Y.L. Paul, A.B. Fruchtman, Rukhovitchko, N.A. Rousk, N.I. Goltz, E.Z. Korovin, Institute of Radio Engineering and Electronics, RAS, Moscow, RUSSIA; V. Rakhlenko, General Physics Institute, RAS, Moscow, RUSSIA; V.P. Varin, I.G. Temtretinsk, 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 study electrical properties of the semiconductor boron doped p-type CVD diamond films were studied. Isothermal Charge-based Deep Level Transient Spectroscopy (QDLTS) was applied to explore the density, activation energies, and capture cross-sections of trapping centers (TC) - electronic 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 QDLTS spectra for all samples, measured in different conditions, was shown that discrete levels have the same activation energies about 0.3 eV with strongly different in capture cross-sections and are induced by boron. The obtained defects levels are of 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 compensations and concentration of compensating donors (nitrogen) in growing diamond films. The results are discussed in comparison with data available in literature. This work was supported by Grants No of the RFBR (03-02-16750) and of the Russian Foundation of Fundamental Research.

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

Thermally carbonized porous silicon (TCPs) films have been prepared by exploiting a disassociation of an acetone. 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, sensor 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 behavior indicates that the TCPs samples are more stable then the thermal oxidized PS samples. Also, the reaction of TCPs aqueous solution is smaller in TCPs than, for example, in dodecane treated sample. Several other promising results will be presented and future prospects of TCPs in applications will be discussed.

INTERBAND TRANSITIONS IN Si QUANTUM WIRES GROWN IN (100) PLANE. X. Zhang and A. Naumov, Institute of Microelectronics, NSCS, "Demokritos", Atiki, 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-photon assisted transitions both F-A electron-photon and hole-photon 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). For electrons, the six anisotropic valleys near the X point in bulk Si are taken into account. The position of the minimum of 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 electron wavefunctions depend on the direction of growth. The overlap integrals for interband and intraband transitions exhibit strong directional dependence. These effects explain the dependence of the calculated emission rates of Si quantum wires on the growth direction and the number of the quantum wires.

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

We describe the synthesis and characterization of nanocrystalline Si ( ncSi) prepared by the reaction of ZnI2 phase silicon MSe (Me = Na, Mg, K) with different oxidants, such as I2, Br2 in solution. Glyme, diglyme, tetrahydrofuran, and hydrocarbon have been investigated as solvents. Different reaction conditions have been explored. These reactions produce crystals Berc-Si. This method offers an easy, useful way to prepare silicon particles that can be chemically modified (R=alkyl, H), along with amorphous material. The resultant nanoparticles can be suspended in organic solvent, and be 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 MSe with SiCl4.

MICROSCALE DIAMOND FILMS: APPLICATIONS TO THIN-FILM TRANSISTORS AND OTHER ELECTRONIC DEVICES. J. Sung, Huk-Gyu Lee, Lihong Tong 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, in situ mass spectrometer (MS) records the plasma conditions during the process 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⁻¹ with position at 522 cm⁻¹ as desired for crystalline Si. Typical film thickness is 100 nm with grain size of 2630 nm, using standard deposition, and 51.80 nm when the substrate is intensively optically illuminated during deposition, called photon assist (PA). Hydrogen dilution serves to increase the crystallinity of the film. The ratio of hydrogen to Si in the dark conductivity exceeds 10⁴ with dark conductivity as low as 1.5 x 10⁻¹⁰ S/cm. Thin film transistors have been fabricated using amorphous Si/nc-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.


general drawbacks of microcrystalline silicon (μc-Si) films prepared by rfglow 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 rfglow discharge on the properties of μc-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 μc-Si was determined from Raman backscattering spectra and the formation of hydrogen bonding was obtained from Si-H stretching local vibrational modes (LVM) at 2080 and 2100 cm⁻¹ and from He evolution measurements. With decreasing pulse frequency the deposition rate increases by up to 60%. The crystalline fraction Xc is independent of pulse frequency and duty cycle. A decrease of the duty cycle to 0.4 to 1.0 mbar did not affect Xc at a given frequency and duty cycle. However, pulsed deposition has a significant impact on the hydrogen microstructure. The H microstructure parameter R(H2) = 1000/1000 (12000/12000) 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 1686 cm⁻¹ that is common observed in μc-Si films. The H evolution spectra of μc-Si films are distinctively different from those measured on amorphous silicon. They show a low temperature peak at T = 620°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.


Rutherford Backscattering Spectrometry (RBS) and channeling studies with 1.4 MeV ²He ions as well as He-Lyon Elastic Recoil Detection Analysis (ERDA) with 200 MeV ¹²C²⁺ 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 H-ERDA without any need of calibration. The analytical potential of the ion-beam technique is demonstrated by two examples: (1) μc-Si films prepared by dc magnetron sputtering in a pure Ar plasma and (2) transition from oriented to disoriented growth in homoepitaxial Si films deposited by electron cyclotron resonance CVD at low temperatures. In case (1) we compare the atomic area density Nd obtained by RBS and the optical thickness n-d [naread index] derived from the interference structure of IR reflection spectra and use the ratio n/Ns 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/Ns 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 is not aligned with a perpendicular bias. In case (2) we evaluate disorder profiles from the ion channeling spectra. Comparing these with the impurity profiles determined by H-ERDA we observe that hydrogen and also oxygen are accumulated in the disoriented 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 corroborated by low energy electron microscopy. The H-ERDA results suggest that with increasing film growth oxygen is increasingly involved in the evolution of disorder.


A new method of silicon multilayer 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 the high pressure (105 Pa) majority 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 amorphous silicon film. This film consists of the nanocrystalline silicon in SiO₂Ny matrix. Several samples were strain etched, and porous silicon (PS) layers formed on the conical surface. These PS layers present the composite structure which contains nanocrystalline silicon in porous SiO₂Ny matrix. Northern surface voltage characteristics were usually observed on unetched samples. Recently, high emission parameters: effective emission area = 1.88 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 EREHBIUM-DOPED SILICON-RICH SILICON OXIDE. Se-Young Seo and Jung H. Shin.

A great interest has been aroused in doping silicon-rich silicon oxide (SiRSO), which consists of Si nanocrystals embedded in a SiO₂ matrix, with erbium to obtain a Si-compatible photonic material operating at the present telecom transmission wavelength of 1.56 μm. Recently, there have been reports that by tailoring the quantum effects and taking advantage of the strong coupling between the Er³⁺ ions and the nanocrystals, 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 SiRSO, however, the trapped-exciton-mediated excitation model of Er-doped bulk Si is often used with little modification. But unlike bulk Si, SiRSO is an inhomogeneous material with diverse Er locations and electronic states. Thus, the excitation mechanism of Er in SiRSO 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 SiRSO. The time evolution of Er³⁺ luminescence from erbium-doped SiRSO with 0.1 % at Er and nan-sized Si nanocrystals under pulse 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 excitation is the limiting step in the Er excitation mechanism, and that the excitation 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 SPOTTERING ON THE LUMINESCENCE OF Er-DOPED NANOCRYSTALLINE Si/SiO₂. Guillermo A. Nery, Luis F. Fonseca, Oscar Resto, S. Zvi Weiz, Dept of Physics, University of Puerto Rico, San Juan, PR; Himun Liu, and A. M. Mishina, Dept of Physics, University of Puerto Rico, Mayaguez, PR.

We co-sputtered Er₂O₃, Si and SiO₂ for different substrate temperatures and with the gases H₂ and He of Sputtering. The gases were then annealed. The photoluminescence intensity versus substrate temperature and versus presence or absence of H₂ is presented, with a focus on Er(H). The effects of annealing are also presented.

F14.28 RESONANT EXCITATION OF Er³⁺ BY THE ENERGY TRANSFER FROM Si NANOCRYSTALS. Kola Nanotechnology, Minoru Funabashi and Shinji Hayashi* - Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodani, Nada, Kobe, JAPAN.

Er-doped Si nanostructures such as porous Si and Si nanocrystals (nc-Si) have recently been attracting much interest, because Er⁺⁺ incorporated into these materials emits light at 0.81 eV, which corresponds to the absorption maximum in silicon optical fibers. In our
previous work, we have studied photoluminescence (PL) from SiO$_2$ films containing nc-Si and Er and discussed the excitation mechanism of Er in nc-Si. The samples exhibited strong 0.8 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 0.8 eV peak becomes strong as the Er concentration increases, while the 1.5 eV peak becomes weak. These results suggest that the excitation of Er$^{3+}$ 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 Er$^{3+}$ are discrete and the bandgap of nc-Si with some specific sizes can resonantly excite Er$^{3+}$, however, such specific sizes are not known.

In this work, we studied PL and PL excitation dynamics of SiO$_2$ films containing nc-Si and Er. The average size of nc-Si was changed in order to tune the excitation energy of nc-Si to the energy separations between the discrete electronic states of Er$^{3+}$. This wide tunability provides valuable information to understand the energy transfer mechanism. We will demonstrate that phonon-relaxed related features in the PL excitation spectra and the PL spectra of the features implies the existence of a resonant energy transfer process. We will also show that the 4f shell PL of Er$^{3+}$ exhibits a delay after the pulsed excitation of nc-Si, and the risetime depends strongly on the size of nc-Si.

**F14.31** IMPACT OF ERBIUM-DOPED SILICON NANOCRYSTALS ON THE PROPERTIES OF POLYVINYLENENE VINYLENE (PPV)

**FILMS.** Jeffrey L. Coffin 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 studies of Er-doped discrete silicon nanomaterials, in particular relevance since its observed luminescence band at 1540 nm lies at an absorption minimum for silicon-based waveguides. This type of silicon-based light emitter, when coupled to a suitable waveguide, would enable 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 processable and cost-effective conducting/polymer/nanocomposite materials such as poly(phenylenevinylene). Compared to conventional inorganic/organic light-emitting materials, there are 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[phenylenevinylene] (PPV) composites. Preliminary results have focused on the characterization of these materials via atomic force microscopy (AFM), profilometry, absorption/fluorescence spectroscopy, 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 ELECTRUMINISCENCE DEVICE USING SILICON NANOCRYSTALS. Keisuke Satc and Tomio Inami, Department of Electrical Engineering, Tokyo University, Hirasaka, Kanagawa, JAPAN; Mitsuo Inami, Department of Electrical Engineering, Tokai University, Hiramatsu, Kanagawa, JAPAN; Yoshihiko Shio, Shinji Nonaka and Hiroshi Morikani, 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 properties (PL) from silicon nanocrystals with high-dose X-ray 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 SiO$_2$ films were deposited by RF sputtering method. A sputtering target was 16 pieces of 5 mm$^2$ Si chips on a silicon dioxide (SiO$_2$) 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 hydrolytic (HF) acid solution treatment. The indium tin oxide (ITO), deposited by sputtering method, was used for the top electrode of the EL devices. The ultraviolet (UV) Al electrode was formed by the evaporation method on the back side. EL spectrum was not observed from EL device using unannealed Si nanocrystals because the resistance of the EL device was high (10$^9$Ω) and the electrons were not injected into its device. On the other hand, the EL spectrum of the 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 devices during the forward bias EL 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 Testa, ENEA Canecina, Roma, ITALY.

A paper recently published has introduced a 3D model to simulate the surface microstructure resulting after pulsed laser processing of Si. The influence of thermal effects on the surface microstructure 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 from the local critical radii corresponding to the respective interface growth rates at any point of the undercooled liquid. 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 radius corresponds 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** ATOMIC SIMULATION OF LASER-INDUCED RECRYSTALLIZATION OF AMORPHOUS SILICON. Luigi Brindilla, Dip. to Scienze dei Materiali, Universita di Milano “Bicocca”, Milano, ITALY; Luciano Colombo, Dip. to Scienze dei Materiali, Universita di Cagliari and INFN, Cagliari, ITALY; Fabrizio Cleri and Gregorio D'Aguanno, ENEA Division Materials, Centro Ricerche Canecina, Roma, ITALY and INFN; Vittorio Romano and Massimo Celino, ENEA, High-Performance Computing and Networking Project, Centro Ricerche Canecina, Roma, ITALY and INFN; Mario Romi, 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 these two melting temperatures plays a key role in the production of microcrystalline Si film from a-Si precursor, upon laser melting and recrystallization. Classical MD simulations using the EDF potential have been performed with a system with a number of atoms of the order of 10$^9$ 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 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 also been 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 MEDIUM. J K. Berling, Department of Physics, University of Oslo, NORWAY.

By molecular dynamics simulations we have performed rapid quenching of melt germanium and silicon. The quenching is sufficiently slow to provide the molecular distribution function (PDF) 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 modulation and photonic crystal behavior of the modified amorphous material, we examined crystallites of different diameters in the amorphous matrix at different temperatures. Crystals anneal in or grow depending on their size. At a temperature about midway between absolute zero and the melting temperature the critical size for growth is 2 nm. At lower temperatures the evolution of the crystals slows down dramatically and so they appear to be stable. We observe that small crystals can comprise at least 20% of the total volume without significant difference from the RDF from the original material. Due to the high spatial and temporal resolution of molecular dynamics simulations we were able to study the crystalline/amorphous boundary at the 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. J.K. Boring, Phys. Rev. B (scheduled to be published June 15 2000).

F14.34  DEPOSITION OF SILICON CLUSTERS ON SILICON. A MOLECULAR DYNAMICS STUDY, A. M. Massone, C.N.R.-Istituto LA-MEL, 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 interest in 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 a two-dimensional nanocluster lattice on a silicon substrate. The purpose is to gain insight into cluster-cluster coalescence, cluster fragmentation and cluster-substrate 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 evolution 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 A MОРPHOUS 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. Ridgeway, J. Conway, Department of Electronic Materials Engineering, Research School of Physical Science and Engineering, Australian National University, Canberra, AUSTRALIA; F. Fortun, M.O. Ruselt, H. Bernas, Centre de Spectrometré Nucléaire et de Spectrometré de Masse, Centre National de Recherche Scientifique, Orsay, FRANCE; B. Roberton, 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. Nanocrystals have recently been produced in crystalline silicon and these small voids exhibit intriguing properties, such as providing efficient sinks for diffusing interstitials, especially first diffusion, and for trapping positrons. Although the electronic properties of nanocrystals have been extensively studied in terms of their monoatomic effects, such properties of their counterparts i.e. nanocrystallites have not been studied. In this paper, we show experimentally that nanocrystals 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 Characterize 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 gain the mechanism is dependent on the irradiation conditions. A steady increase in the average size of cavities in 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 behavior is also observed in terms of nanocrystallite properties, i.e. such open-volume, nanometer-sized cavities surrounded by defective silicon. Some implications for silicon technology are also discussed.


We have found the new method to introduce various kinds of diphenyl and non-periodic arrays of nanoholes, about 6 nm in diameter, in dense, on (100), (110) and (111) 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 non-periodically were formed at higher temperature 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 vacancies introduced by electron irradiation. We have found that the nanohole array was doped non-periodically suggesting an amorphous 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 diffusion 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 effects.

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 of the modern silicon technology. The growth of complex three-dimensional structures is an important problem in nanotechnology. A new approach worldwide to construct nanosized arrangements is a recent publication, where 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 present the irradiation of clean Si(100) with Ar ion irradiation 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 stored in random doped arrangements at the irradiation site but in spatially extended structures at predetermined locations. These artificially reoriented structures consist of random Si atoms, placed atomically sharp next to the single-crystalline lattice. The structures are stable (11 00 K) and are characterized by modified bond gaps and Si-Si distances. Scaling of the size structure with temperature and primary ion energy loss was presented. P. Sen, G. Agarwal and U. Tiwari, Phys. Rev. Letters, 80, 97 (1998).

F14.38  HIGHLY STABLE 1D NANOSTRUCTURES ON 3C-SC: FROM A SINGLE ATOMIC CHAIN TO A LARGE SUPERLATTICE OF MASSIVELY PARALLEL ATOMIC LINES, V. Dey龑ce, P. Fonteneau, Nga Phuong Pham, V. Yu. Aristov, P. Subkis, 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 in the 3C-SiC(100) surface by means of low-energy scanned 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 diamantization including, at the initial step, Si removal “dimer row by dimer row” knowing 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 the reduced lateral interaction between atomic lines when the spacing between them is increased. Through a simple 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.

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 pulses-laser irradiation in an SF₆ 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-induced microstructures in solid cells and sensors are discussed. Laser irradiation conditions leading to nanostructure formation are briefly mentioned. This research was sponsored by NSF Grant DMR-9681238 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.
Xiong 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, 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 re-deposited amorphous silicon, we identified a five-gram polycrystalline structure, which will be released into the lower-energy continuous random network structure after thermal annealing. With the same fluctuation microscopy technique, we have 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 IL-V CAVITY SURFACE-Emitting LASERS ONTO SILICON WAFERS.
Jie Zhong, Univ. of Almelo, SUNY, Dep. of Physics, NY; Mengfei Huang, Univ. of Albany, SUNY, Dep. 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 used as an important optical material. In our work, we investigate the possibility of transferring GaAs-based vertical cavity surface-emitting lasers (VCSELs) onto silicon wafers. The VCSELs structures with sizes of 5 X 5 μm and 10 X 10 μm have been fabricated. The samples were transferred into a silicon wafer via ion beam induced layer splitting and wafer bonding techniques. The VCSEL structures on the silicon wafer are evaluated with various analysis methods (e.g. scanning transmission electron microscopy, photoluminescence measurement). The study suggests a promising method for integrating IL-V CAVITIES with the silicon technology.

F14.43

PROFILEDIMAGING OF SEMICONDUCTOR TRANSISTOR STRUCTURE BY ELECTRON HOLOGRAPHY.

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 affect the amplitude of the incident electron wave to be efficiently useful to depict dopant atom in conventional TEM (Transmission Electron Microscopy) mode. However, electric field 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 the 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 developed and proven to be a promising candidate for dopant profiling. In this work, TEM samples were prepared by FIB (Focused Ion Beam) with a thickness ranging from 250 to 400 μm. The use of the FIB will provide site-specific capabilities for feature sizes as well as sufficient thickness of the sample and the electrically inactive layers. Dopant profiling of different channel length n- and p-type oxide-semiconductor transistors will be discussed in the presentation.

F14.44

DIFFUSION LENGTH MEASUREMENTS OF MINORITY CARRIERS IN SiO₂.
Y. Paszak, L.P. Fonseca, O. Resto, S.Z. Weiss, 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 SiO₂ has raised the necessity of study its photo-transport properties. Five measurements of transport properties were made in SiO₂ at room temperature using the Photo-reading Technique. The SiO₂ films were prepared by R.F. Co-sputtering on quartz substrates. The measurements were made for different concentrations and sizes of Si nanoparticles, starting from a barely luminescent site to non-luminescent sites. Diffusion length measurements, minority and majority carriers were found for each site including their photovoltaic properties.

F14.45

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

We have prepared 3D arrays of silicon nanostructures using artificial opal as matrices. Both “direct” silicon optical composites and silicon inverted opal structures have been fabricated. An amorphous-nanocrystalline silica film was deposited on the inner surface of opal cavities by SiH₄ 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 film factor, the nanocrystallite size and phase composition of substances in the pores. The inverted structure was obtained by etching out substances of the opal matrix (silica spheres) in aqueous solution of hydrofluoric acid. The prepared nanostructured 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 10⁴ cm⁻², 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 optical matrixes on the light wavelength scale. The inverse opal structure is found to be a photonic crystal with effective index contrast ~3.5, 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 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 Krauss

Thursday, November 30, 2000

Constitution A (Seronor)

8:30 AM F15.1

SCHOTTKY SYNTHESIS OF NANOCRYSTALLINE HIGH PRESSURE PHASES IN Si, Ge, AND GeTe BY HIGH VELOCITY THERMAL SPRAY.
J. Pace et al. \(^2\), R. Goswami et al., S. Sampath et al., G. Ambi et al., H. Hermann et al., Z. Zhu et al., and D. Welch et al. \(^3\), Center for Thermal Spray Research, SUNY at Stony Brook, Center for High Pressure Research, SUNY at Stony Brook, Brookhaven National Laboratory, Energy Sciences and Technology Department, Upton, NY.

Shock synthesis of high-pressure phases of Si, Ge and GeTe 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 phases. Thermal spray can be treated as a "dynamic-pressure anvil"
allowing synthesis of high-pressure metastable forms of nano-
crystalline Si and diamond, where it is estimated shock pressures of 0
to 40 GPa can be 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 form including nano-
crystalline [2-3 nm] SiC, Si, SiC, 4H-SiC, 6H-SiC, and B-C-S phases.
This is consistent with results of strictly high pressure experiments, which
shows cubic Si (Si) transforms to SiCII, which
passes a beta-SiC type structure at 6 GPa and forms metastable phases
upon decompression. In Ge, a metastable phase, ST-12, was observed.
The ST-12 is a decomposition product of GeII with a beta-SiC type
structure. The transformation pressure of Ge-II is slightly lower than
that of Si II (30 GPa). The nano-
crystalline GeC particles (Warzutz)
with an average size of 10 nm was obtained. The paper presents the synthesis and characterization of these
nano-crystalline semiconductor materials. This work was supported by the
MRLC program of the National Science Foundation under Award No. 96-32570 through the Center for Thermal Spray Research
and the U.S. Department of Energy, Office of Basic Energy
Sciences under Contract No. DE-AC03-92CH10789.

S45 AM F15.2
OPTICAL PROPERTIES OF Si AND Ge QUANTUM DOTS
STUDIED BY LIQUID CHROMATOGRAPHY, J.P. Wilcoxen,
G.A. Samara, and P.N. Provenco, Nanotechnology 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 nanometer indirect semiconductors are formed when the melting point of the material is lower than its decomposition temperature in inert oils in the complete absence of water and oxygen
and in a 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
gain 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, 1-1.5 nm clusters and had an efficiency of about ~23% 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

Acknowledgment
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Basic Energy Sciences, U.S. Department of Energy under contract
deAC04-94AL85000. 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. 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.
Kaufman, Chung-Sang 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
been defined as major 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 simple method, i.e., growth at high temperatures; (ii) the energy gap can widen considerably from QD (~80 eV with our
smallest QDs), and (iii) the experiment size-dependent energy gap agrees
with pseudopotential and tight binding calculations but not with
effective masses. Growth at high temperatures 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
QD size on the thermal quenching of the emission. Further single
dot experiments verify these conclusions. Our results generalize earlier
results by showing that QD effects optical and electronic properties
much more extensively and over a much broader range than previously
realized, providing the QD surface is appropriately terminated. We
show that this can be achieved for a variety of surfactants and
organic solvents (oxides and organic groups). Red to UV light emission
can also result from non-QD such as traps. This underscores the
canonical light emission from nanocrystalline Si and Ge. With the
appropriate surface terminations, trapping can be mitigated or eliminated and the full range of QD effects can be observed that might otherwise be obscured by non-QD effects. Organic termination with solvent films results in mainly
quantum confined light emission. We show for the first time that
the oxide termination can also be made stable in ambient and essentially
transparent as to display a similar strong range of QD effects and thus becomes a viable surface engineering technique. We will
demonstrate 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-NOANOCLUSTER FILMS
PROBED WITH SYNCHROTRON RADIATION. C. Bosetti,
T. van Buuren, N. Franco, L.J. Terminello, Lawrence Livermore National Lab T. Miller, Heidelberg, EST, 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 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 5nm. Characterization of the nanoclusters in size and shape was done by non-contact atomic force microscopy. X-ray absorption spectroscopy at the Ge K-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 2nm and 2nm. Photoemission data shows a
erelatively small shift of around 0.1eV of the valence band in clusters of
around 1nm in size. Measurements of the Ge clusters show a
strong increase of the surface plasmon compared to the bulk plasmons 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. Bosetti 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 Materials 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).
Makuii Sakiyama, Yoshih Nitta, Mototsi Shibukawa, and Ken Fujita,
Joint Research Center for Atom Technology, Bunkyo, JAPAN.
Selective growth of nanometer-scale is an important technique for fabricating well-defined nanostructured materials in given areas. Previously we reported that the 20nm scale islands with pyramidal shaped top 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 20nm 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 865 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 but island with (1, 0, 5) facets. This
enabled us to form an array of nanometer-scale Ge but islands by the
selective growth in the window performed by the STM tip. We also
grew Ge nanoislands on pyramidal Si islands in the windows using
their stability at high temperature. During GeH4 supply at 708 K, pyramidal Si nanoislands with (1, 1, 13) facets gradually changed to high index islands with [100] facets due to Ge overgrowth on 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. Shibukawa, Y. Nitta, K. Fujita, M. Sakiyama, Phys. Rev. B61, 7499 (2000).
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. Gugan, B.R. Weiner, B.L. Weiss and G. Moll, 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-sulphur gas mixtures respectively. For the intrinsic nanocrystalline diamond 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 field emission properties (turn-on fields and emitted current). Low-field electron emission for the best samples was observed at 6.8 V/µm. The continuous bias also causes microstructuration as characterized by in 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 films under no bias. We have found a correlation of the EVE characteristics with the nanocrystalline diamond layer observed at around 1.180 cm⁻¹ in the Raman spectra of these films, suggesting a significant role of the tetrahedral-honored bond (tn-C) in the electron emission. Films grown under electron bombardment show smoother surface morphology than the films grown without it, and ion bombardment. These studies are performed to understand low-field emission mechanisms and the role of tn-C towards improving the emission from the nanocrystalline carbon thin films.

This research work is supported from the Department of Defense (DoD ONR, Grant No. N00014-88-1-0570), the Department of Energy (DoE Grant No. DE-FG02-89ER45796), and the University of Puerto Rico (UPR IFIPI Grant No. 880244).

11:15 AM F16.3
N-TYPE DOPING OF NaNOCRYSTALLINE DIAMOND FILMS WITH NITROGEN. Sumith Bhatnacharya, John Schheter, Dieter M. Gruen, and Alan R. Krauss, Materials Science and Chemistry Division, Argonne National Laboratory, Argonne, IL.

Nanocrystalline diamond (NCD) films were prepared in a microwave chemical vapor deposition plasma from ammonia and methane [1%] using up to 20% nitrogen in the gas phase. Films prepared without nitrogen doping exhibit polycrystalline diamond films surrounded by 3-4 A wide grain boundaries. Such films were good insulators, the conductivity of the films is found to increase rapidly when nitrogen is introduced into the plasma. From measurements of the bulk 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 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 onset voltage from the n-doped NCVD 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-38.

11:30 AM F16.4
EFFECT OF SF⁶/SP³ 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, NIIH, Ibaraki, JAPAN; J. Koh, ETH, Ibaraki, JAPAN; T. Kusum and K. Okano, Dept of Physics, ICU, Tokyo, JAPAN.

The low-threshold electron emission from CVD-grown polycrystalline diamond films doped with N was reported in our previous study. 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, Sp³/SF⁶ 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 Sp³-rich emitter has been confirmed to be much higher than that of the Sp³-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 NANOCUSTERS. T. van Baum, C. Bostedt, L. Chase, L. Terenzi, 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 Struas chemical corporation and are synthesized in a high vacuum system 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 Cls core electrons are more clearly observed in the K-edge absorption spectrum 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 was observed 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 the x-ray emission TEM. We compare our results to the published measurements on this compound. The differences in 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 Sn and Ge nanoclusters and the effects of reduced size in the electronic structure of group IV semiconductors will be discussed. [2] The work...
Erbium doping of silicon has been identified as one of the most promising methods for developing silicon-based optoelectronics, yet it is 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 Er^{3+}

luminescence at room temperature can be obtained and population inervation of Er may be achieved. However, with silicon having the size and the number of the clusters and the location of Er, which all play a significant role in determining the Er^{3+} luminescence, are difficult to control. One possible way of obtaining such control is using Si/SiO_{2} superlattices instead. In this paper, we report on Er^{3+}

photoluminescent properties of erbium-doped Si/SiO_{2} superlattices with sub-nm thin Si layers. The superlattices were deposited by UHV beam-sputter deposition method at room temperature and subsequently annealed at 950°C. Erbium was doped only into the SiO_{2} 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 scattering. First, the Er^{3+} luminescence increases very strongly as the film thickness decreases, and then one monolayer of silicon is sufficient for carrier-mediated excitation of Er to dominate. The temperature dependence of Er^{3+} luminescence, however, is nearly independent of the Si layer thickness, indicating that quantum confinement effect is not a major factor controlling the Er^{3+} luminescence. The differences between Si nanoclusters and superlattices will be discussed, and photonic application (e.g. waveguides) demonstrated.

2:15 PM F17.4

STUDIES OF EXCITON-ERBIUM COUPLING IN Si NANOCRYSTAL DOPED SiO_{2} OPTICAL WAVEGUIDES. P.G. Kik and A. Polman, FOM-Institute AMOLF, Amsterdam, THE NETHERLANDS.

We have observed strong coupling between optically generated excitation states in Si nanocrystals and intra-4 electronic states of erbium ions implanted into the nanocrystal-doped SiO_{2} matrix. The energy transfer rate is larger than 10^{7} 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 SiO_{2} using Si ion implantation and thermal annealing. The nanocrystal-doped SiO_{2} layer was implanted with different doses of Er, resulting in Er peak concentrations in the range 0.015 at 1.8 at % of Er. Some 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, 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 of carrier-induced quenching, that can both occur at high pump power. We also find that the excitonic Er ions are most likely located in an SiO_{2}-like environment.

Channel waveguides based on index guiding though the high-index nanocrystal doped region show excellent mode confinement. At a typical nanocrystal concentration of 10^{18} cm^{-3}, the maximum optical gain at 1.54 μm of an Er doped waveguide amplifier based on Si nanocrystal doped SiO_{2} is estimated to be 0.6. These waveguides 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. Jeffrey L. Coffer, Robert Senter and John St. John, Texas Christian University, Fort Worth, TX.

Studies of the preparation and fundamental properties of three dimensionally-confined Si nanocrystals 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 nanocrystals; excitation and power dependency measurements of this luminescence suggest a two photon excitation 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 nanocrystals. For crystalline Si, pressure alters the conduction band minima of the nanocrystal host and subsequently should affect the extent of energy transfer to the Er center(s) (and its resultant PL intensity).
optical absorption measurements, the emphasis here is with respect to
the effect of particle size on pressure dependence of the bandgap,
as well as (b) an indirect estimation of the structural impact of the
erbium dopant on the pressure-induced phase transition(s).

2:45 PM F17.6
SUPERFINE STRUCTURE OF PHOTOLUMINESCENCE
SPECTRA FROM ERBIUM CO-INCORPORATED WITH IRON IN
POROUS SILICON. Nikolay Kuznich, Belarusian State Univ.,
Minsk, BELARUS; Svetlana Volchk, Vladimir Petroukov, Leonid
Dolgyi, Nikolay Vorozov, Valentin Yakovenko, Vasily Bondarenko,
Belarusian State Univ of Informatics and Radioelectronics, Dep.
of Microelectronics, Minsk, BELARUS.

We report for the first time the observation of the highly defined
Sralk 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 treatment. The observed more than 11 super sharp emission
bands related to highly resolved transitions between split d
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 more than times less than that for Er
incorporated by ion implantation in silica glasses (4.5-13 meV FWHM
at 77K), crystalline silica (53 meV FWHM at 77K), and GaN (1.1
meV FWHM at 8K). To explain the experimental results we proposed
that electronic energy levels of Er and Fe can form a donor-acceptor
pair. This conclusion is in agreement with the high temperature
treatment well organized nanoclusters in porous silicon matrix.

SESSION F18: LIGHT-EMITTING DEVICES
Chair: Howard W.H. Lee
Thursday, November 30, 2000
Constitution A (Sheraton)

3:30 PM F18.1
ION BEAM SYNTHESIS BASED FORMATION OF GALV-THERMALLY GROWN SILICON DIOXIDE LAYERS: A
PROMISING APPROACH FOR A SILICON-BASED LIGHT
EMITTER. L. Rebholz 1, T. Gebel 1, J. Zhao 1, D. Bordetzky 2, J. V.
Borany 3, and W. Schrenk 4. 1 Institute of Ion Beam Physics and
Materials Research, Forschungsunumsamt Rosendorf, Dresden,
GERMANY; 2Department of Electrical Engineering, Fermananun
University, 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 has been ion beam synthesis. In this paper we will report
on our recent progress in enhancing the blue-violet (~400 nm)
photoluminescence (EL) from an Er-doped silica 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 6.3x10^14 - 1.2x10^16 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 EL was measured in the range 10-25% (%) one of the best values ever reported. The EL duration time without special measures of stabilizing
the EL-active layer against ion or other contamination can reach several
hours. Moreover, results are reported dedicated to the investigation of the
influence of the i-line photolithography process on the EL-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 ABATION PROCESS.
Yuka Yamada, Toshikazu Makino, Nobuyuki Suzuki, Tadahito
Yoshizaki, Matsushita Electric Industrial Co., Ltd., Advanced
Technology Research Lab, Kawasaki, JAPAN; Seisouke Onari, Univ.
of Tsukuba, Inst of Materials Science, Ibaraki, JAPAN; Kousuke
Urano, 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 hydrogenated oxide (InOx) thin films as transparent
electrodes. Both the Si nanocrystallite layers and InOx thin films
have been synthesized by pulsed laser ablation in inert background-gas
(3A-BG) process. The synthesis of Si nanocrystals, a second harmonic Nd:YAG laser beam was focused onto a surface of p-type Si wafer
at a 45° tilt angle. 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 (200 nm), we used AlAg (100 Å) metal electrodes
placed on the pressure-induced phase transition (a).

4:15 PM F18.3
STABILIZATION OF POROUS SILICON ELECTRO-
LUMINESCENCE BY SURFACE CAPPING WITH SILICON
DIOXIDE FILMS. Nobuyuki Kashima, Junichi Konokura, Tokyo
Univ. of A&T, Dept of Electrical and Electronic Engineering, Tokyo,
JAPAN; Mitsuo Takahashi, Kansai U, NTI, Telecommunications Energy
Laboratories, Atsugi, JAPAN.

For practical applications of electroluminescence (EL) from
nanocrystallite 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 base emission with an external quantum
efficiency 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) anode, a PS layer, and an ITO cathode.
It has been shown that in addition to an enhancement in the efficiency, the post-modification EC 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 sputter 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 EC deposited SiO2 layers protect PS
from oxygen penetration without affecting the hydrogen termination
of nanocrystallite silicon surface. This should become more effective for
utilizing 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 (PS) was observed
shortly after photoluminescence (PL) was discovered by Carraim in
1990. A typical PS-based LED consists of a transparent or semitransparent contact (Au, ITO or conducting polymers) and a P shitty 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 (OPNS) LED is quite different from other porous silicon based LEDs. The OPNS material has been characterized in 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
contact and hole-injection mode in the OPNS layer. This
material facilitates tunneling transport of electrons and holes, some of
which will participate in radiative recombination events. As a result, investigation on electrical properties of OPNS LEDs has revealed
facinating detail on transport behavior. The device is modeled as a
"field effect diode", where undirectional 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 P.M. F18.5

BIPOLAR INJECTION DEVICES IN CMOS COMPATIBLE Si/SiO₂ SUPERLATTICES FOR LIGHT EMITTING DIODES: Zeno Gabarro, Georg Parker, Lorenzo Pavesi, INFN and Department of Physics, University of Trento, Povo (TN), ITALY; Piergiorgio Belletti, ITC-IRST, Povo (TN), ITALY.

We have designed and tested novel bipolar injection devices for Si/SiO₂ superlattices, in order to obtain electro luminescence 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-superlattices-substrate devices is essentially unipolar (due to the difference between the potential barriers 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.