SYMPOSIUM H

Hydrogen in Semiconductors

April 13 - 14, 2004

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Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 813
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

SESSION H1/A1: Joint Session: Hydrogen in Silicon
Tuesday Morning, April 13, 2004
Room 2001 (Moscone West)

8:25 AM
OPENING REMARKS

8:30 AM *H1.1/A1.1
Hydrogen in Silicon and Germanium: Dopant Activation and Passivation. Eugene E. Haller, [1]MS&E, UC Berkeley, Berkeley, California; [2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

In an attempt to fulfill the predictions of Moores Law, the silicon device community is turning increasingly to SiGe alloys and to elemental Ge. The inherently higher electron and hole mobilities in Germanium and certain strain induced bandstructure changes both contribute to spectacular device performance increases.* It is timely to revisit the role of hydrogen in the elemental semiconductors Si and Ge and their alloys. Discussion of dopant passivation and activation by hydrogen will be emphasized.
See for example: J. S. Rieh et al., IEDM Technical Digest, IEEE 2002, pp. 771-4 and H. Shang et al., IEEE Electron Device Lett. 24(4), 242-4 (2003).

9:00 AM *H1.2/A1.2
The Role of Hydrogen in the Creation of Metastable Defects in Hydrogenated Amorphous Silicon. P Craig Taylor[1], T Su[1], G Ganguly[2] and D E Carlson[2]; [1]Physics, University of Utah, Salt Lake City, Utah; [2]PB Solar, Toano, Virginia.

The Staebler-Wronski effect, which is a decrease in the photo- and dark conductivities in hydrogenated amorphous silicon (a-Si:H) after irradiation with light of band gap energy, has been known for over 25 years [1]. From electron spin resonance (ESR) measurements [2], the defects responsible for the decreases in conductivity are thought to be silicon dangling bonds. Hydrogen has long been invoked as important in stabilizing these dangling-bond defects, but the experimental proof of this conjecture has been elusive. We have reported an 1H nuclear magnetic resonance (NMR) signal in a-Si:H that occurs only after light soaking for 600 hours [3]. This signal, which is attributed to a pair of hydrogen atoms, exhibits similar annealing kinetics to that of the defects created during light-soaking, and the concentration of these sites is comparable to that of the defects measured by electron spin resonance (ESR). The inescapable conclusion is that these paired hydrogen sites stabilize the silicon dangling bond defects that cause the Staebler-Wronski effect. The distance between the two hydrogen atoms in the pair is about 2.3 angstroms. The temperature dependence of the lineshape suggests that the pair may undergo some form of local motion as the temperature increases [4], but the evidence is not compelling. Recently, we have seen similar effects in samples of a-Si:H made by a technique (hydrogen dilution of silane in a PECVD reactor) that reduces the saturated densities of these defects. Some possible microscopic models for the paired hydrogen sites will be discussed. 1. D. Staebler and C. R. Wronski, Appl. Phys. Lett. 31, 292 (1977). 2. H. Dersch, J. Stuke and J. Beichler, Appl. Phys. Lett. 38, 456 (1980). 3. T. Su, P. C. Taylor, G. Ganguly, and D. E. Carlson, Phys. Rev. Lett. 89, 015502-1 (2002). 4. T. Su, P. C. Taylor, G. Ganguly, and D. E. Carlson, Symposium A, this meeting.

9:30 AM *H1.3/A1.3
Hydrogen in amorphous Silicon: A simple Atom in a complex Environment. Martin Stutzmann, Walter Schottky Institute, Technische Universitaet Muenchen, Garching, Germany.

Historically, the scientific interest concerning hydrogen in semiconductors to a large extent has been triggered by the beneficial role which hydrogen plays in hydrogenated amorphous silicon (a-Si:H)as a chemical terminator of silicon dangling bonds. However, it was almost immediately realized that the hydrogen content in device quality a-Si:H is much larger than what would be necessary to just saturate dangling bonds. Ever since, the influence of the excess hydrogen in a-Si:H on the overall structural and electronic properties of a-Si:H has been the subject of many investigations, with very different conclusions. In the meantime, much of what we believe to know today about hydrogen in silicon has emerged from detailed studies of hydrogen in crystalline rather than amorphous silicon. Yet, a direct transfer of this knowledge back to amorphous silicon has basically failed due to the inherent disorder of the amorphous matrix. The purpose of this contribution is emphasize the role which a-Si:H has played in our present understanding of hydrogen in silicon, and to point out some central unresolved questions concerning fundamental effects of
hydrogen in a-Si:H (defect passivation, doping efficiency, metastability).

SESSION H2: General Properties of H in Semiconductors
Tuesday Morning, April 13, 2004
Room 2020 (Moscone West)

10:30 AM *H2.1
Hydrogen as a Shallow Center in Semiconductors.
Chris G. Van de Walle, Palo Alto Research Center, Palo Alto, California.

In most semiconductors hydrogen can passivate both acceptors and donors, establishing its character as an amphoteric impurity. Hydrogen acts as a donor (H^+) in p-type material, and as an acceptor (H^-) in n-type material, always counteracting the prevailing conductivity. Experiments and first-principles calculations for silicon and other semiconductors (including wide-band-gap materials such as GaN) seemed to confirm this behavior as a general feature of hydrogen's interactions with semiconductors. It therefore came as a surprise when calculations showed that hydrogen behaves exclusively as a donor in ZnO [1]. Only the positive charge state is stable in ZnO, and therefore hydrogen can act as a source of doping, rather than merely reducing the conductivity introduced by other dopants. This unexpected result has prompted us to investigate the fundamental mechanisms for hydrogen's electronic behavior. The resulting "universal alignment" [2] has allowed us to predict that hydrogen will act as a shallow donor in other materials, such as InN, and as a shallow acceptor in GaSb. I will discuss the physics underlying this universal rule, as well as details of the atomic and electronic configurations associated with interstitial and substitutional hydrogen in these semiconductors. Formation energies determine the solubility and stability of hydrogen centers, and migration barriers control diffusion. Vibrational properties, which constitute one of the prime methods for experimental identification, will also be presented. [1] C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000). [2] C. G. Van de Walle and J. Neugebauer, Nature 423, 626 (2003).

11:00 AM H2.2
Determination of Hydrogen in Semiconductors and Related Materials by Cold Neutron Prompt Gamma-ray Activation Analysis. Rick L. Paul, Analytical Chemistry Division, NIST, Gaithersburg, Maryland.

An instrument for prompt gamma-ray activation analysis (PGAA) at the NIST Center for Neutron Research has proven useful for the measurement of hydrogen and other elements in a variety of materials. The sample is irradiated by a beam of low energy neutrons. Gamma rays emitted by atomic nuclei upon neutron capture are measured using a high purity germanium detector. Because both neutrons and gamma rays penetrate the sample, the entire sample is analyzed. The presence of hydrogen is indicated by a 2223 keV gamma ray. Recent improvements to the instrument have resulted in improved detection limits. The detection limit for hydrogen is $<$ 5 mg/kg in most materials, and 2 mg/kg for hydrogen measured in silicon. The instrument has been used to measure hydrogen mass fractions of $<$ 100 mg/kg in high purity germanium, and $<$ 10 mg/kg in quartz. The PGAA measurements for quartz were in agreement with concentrations measured by IR. More recently PGAA was used to measure the hydrogen content of 1 μm porous thin films on a silicon substrate. The results were in agreement with data obtained by RBS and FRES. The method is currently being used to measure hydrogen in silicon carbide crystals.

11:15 AM H2.3
The role of hydrogen in H-induced exfoliation and layer transfer of InP. Anna Fontcuberta i Morral[1], James M Zahler[2], Harry A Atwater[2], Martin M Frank[4] and Yves J Chabal[3]; [1]LPICM, C.N.R.S-Ecole Polytechnique, Palaiseau, France; [2]Applied Physics, California Institute of Technology, Pasadena, California; [3]Chemistry and Biomedical Engineering, Rutgers University, Piscataway, New Jersey; [4]IBM, Yorktown Heights, New York.

We present Fourier Transformed Infrared Spectroscopy (FTIR) and Elastic Recoil Detection Analysis (ERDA) studies of the role of hydrogen in the process of hydrogen-induced exfoliation and layer transfer. Undoped, semi-insulating InP substrates were implanted at an energy of 80KeV to doses of 1x1017, 1.5x1017 and 2x1017 H+ on a passively cooled stage. FTIR spectra of the samples were measured with both multiple internal reflection and transmission geometries to detect P-H as well as In-H stretching. Absorption peaks at 2198.5, 2275 and 2306cm-1corresponding to the mono and di-hydride P-H species in (100) planes are clearly evident in the as-implanted samples. After annealing for 10 minutes for each temperature in a range from 200 to 350oC, hydrogen is seen to evolve from mono to di-hydride configurations at the low temperature range. Just prior to the formation of blisters (T=350oC), the di-hydrides peak area decreases by 65%. The total amount of hydrogen in InP as a function of the temperature annealing was measured by both Elastic Recoil

Detection Analysis and by thermal desorption. These experiments indicate that the quantity of implanted hydrogen remains inside the InP up to a temperature of 300oC (just below the blistering temperature) and is lost by the dramatic release of hydrogen during the blister rupture process (T=350oC) and subsequent out-diffusion at higher temperatures. Based on these observations our mechanistic view of the process is the following: As the temperature of annealing is increased, hydrogen evolves partially from a configuration of mono-hydride to di-hydride and finally to molecular hydrogen trapped at internal surfaces. Blistering and layer transfer occur when the H2 pressure in the internal surfaces is high enough to initiate the cleavage of InP. Detailed analysis of Atomic Force Microscopy of the surface of the as-split layers complement this picture, indicating that the cleavage takes place in the (100) planes following <110> directions.

11:30 AM H2.4
On the Role of Hydrogen in the Hydrogen-Induced Exfoliation and Layer Transfer of Germanium.
James M. Zahler[1], Anna Fontcuberta i Morral[2], Harry A Atwater[1], Martin M. Frank[3] and Yves J. Chabal[4]; [1]Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California; [2]LPICM, C.N.R.S.-Ecole Polytechnique, Palaisseau, France; [3]IBM, Yorktown Heights, New York; [4]Chemistry and Biomedical Engineering, Rutgers University, Piscataway, New Jersey.

We present a study of the role of hydrogen in the process of hydrogen-induced exfoliation and layer transfer from single crystal Ge(001). Undoped Ge substrates were implanted with H^+ at 80 keV to a dose of $1x10^{17}$ cm^{-2} under passive cooling conditions at a power density of 1000 W m^{-2}. FTIR spectra of the samples were measured in transmission mode at 10°, 45°, and 60°. Following implantation there is a broad absorption peak centered at 2013 cm^{-1} attributed to a combination of the vibrational modes of internal, interacting (001) and (111) monohydride surfaces as verified by transmission mode TEM. Annealing to 200°C makes no quantitative change in the absorption spectrum, but annealing to 300 and 350°C causes the overall peak size to decrease while simultaneously revealing a shoulder at 1975 cm^{-1}. This latter band confirms the presence of (111) internal surfaces as free internal monohydride (001) and (111) surfaces are reported in the literature to have modes of 1988 and 1976 cm^{-1} respectively.[1] However, TEM results indicate that internally fractured surfaces lie dominantly on the (001) planes. These surfaces coalesce into a large area fracture by way of crack jumping along differing crystallographic planes. The mechanistic interpretation of these results is that upon annealing H is released from Ge-H defect structures. The mobile H then diffuses to and is trapped in (001) and (111) platelet structures where it forms trapped H_2 and builds sufficient pressure to cause a fracture to be driven in the plane of the implanted layer. 1) Myers, S. *etal.* (1995) "Hydrogen interactions with cavities in helium-implanted germanium." Physical Review B **51**(15): 9742-9752.

11:45 AM H2.5
Non-metastable Recombination Induced Reactions Involving Hydrogen in SiC. Yaroslav Koshka, Michael S. Mazzola, Bharat Krishnan and Andrei Los; Mississippi State University, Mississippi State, Mississippi.

A variety of non-metastable recombination-induced defect reactions involving hydrogen can take place in hydrogenated 4H and 6H-SiC polytypes under optical excitation at reduced temperature. Photoluminescence (PL) spectroscopy revealed recombination-induced formation of different non-metastable hydrogen-defect complexes (e.g., hydrogen complexes with Al and B acceptors, hydrogen complex with Si vacancy, as well as some other non-identified complexes) [1,2,3]. Electrical measurements indicated strong recombination-induced passivation of electrical activity of aluminum and boron acceptors in SiC. This passivation results in reduction of the net free hole concentration and even inversion of the conductivity type in the hydrogenated p-type samples subjected to low temperature optical excitation. Further insight in the formation of specific complexes as a result of recombination-induced defect reactions is provided by thermal capacitance spectroscopy. The effect is strong in a wide temperature range from as low as 4K up to about 250K. It disappears at higher temperature. This form of the temperature dependence suggests that trapping of the optically generated non-equilibrium electrons and holes by a hydrogen-related band gap level and the resulting change in the charge state of the hydrogen defect is likely to be responsible for the defect reactions. The activation energy of the temperature dependence of the defect reaction rate is used to estimate the position of the corresponding level in the SiC band gap. The nature of the hydrogen state contributing to the formation of the new complexes is investigated. The variety of different centers that can be formed suggests that the origin of the defect reactions is not only an interaction between hydrogen and trapping centers located at the neighboring lattice sites but also a long range recombination-induced migration of hydrogen before it gets captured by one or another kind of trapping centers. The extent of the proposed athermal migration of hydrogen is investigated. 1. Y. Koshka, M. S. Mazzola, Appl. Phys. Lett. 79(6), 752-754 (2001). 2. Y. Koshka, M.S. Mazzola, Appl. Phys. Lett. 80, 4762-4764 (2002). 3. Y. Koshka, Appl. Phys. Lett. 82, 3260 (2003).

SESSION H3: Hydrogen in Oxides
Tuesday Afternoon, April 13, 2004
Room 2020 (Moscone West)

1:30 PM *H3.1
Hydrogen in ZnO. Bruno Meyer, I. Physics Institute, University Giessen, Giessen, Hessen, Germany.

In order to realize controlled p-type doping in ZnO the role of extrinsic and intrinsic donors have to be clarified. Among the extrinsic n-type dopants Al, Ga and In commonly found in bulk ZnO crystals also hydrogen appears in relevant concentrations thus controlling the residual n-type carrier concentrations in nominally undoped ZnO. We will report on multiple magnetic resonance experiments which allowed to identify hydrogen as a shallow donor. Combined with Halleffect and luminescence experiments we will present evidence that a bound exciton recombination is caused by the shallow donor H. In ZnO quantum dots we find that hydrogen is only present on the shell of the dots but not in the core contrary to the bevaviour of Li which is incorporated as shallow donor and deep acceptor. The role of H with respect to incorporation of nitrogen as shallow acceptor in bulk and epitaxial ZnO will be discussed.

2:00 PM H3.2
Infrared spectroscopy of hydrogen in ZnO. M. D. McCluskey and S. J. Jokela; Dept. of Physics, Washinton State University, Pullman, Washington.

Zinc oxide (ZnO) has shown great promise as a wide band gap semiconductor with optical, electronic, and mechanical applications. Recent first-principles calculations and experimental studies have shown that hydrogen acts as a shallow donor in ZnO, in contrast to hydrogen's usual role as a passivating impurity. The structures of such hydrogen complexes, however, have not been determined. To address this question, we performed vibrational spectroscopy on bulk, single-crystal ZnO samples annealed in hydrogen (H_2) or deuterium (D_2) gas. Using infrared (IR) spectroscopy, we have observed O-H and O-D stretch modes at 3326.3 cm^{-1} and 2470.3 cm^{-1} respectively, at a sample temperature of 14 K. These frequencies are in good agreement with the theoretical predictions for hydrogen and deuterium in an antibonding configuration, although the bond-centered configuration cannot be ruled out. The IR-active hydrogen complexes are unstable, however, with a dissocation barrier on the order of 1 eV. The complexes can be reformed by rapid thermal annealing. The hydrogen apparently goes into a complex that does not have an IR signature. One possibility is the formation of hydrogen-decorated oxygen vacancies, which would have a vibrational frequency below the spectral range of our experiments. We have also performed polarized IR spectroscopy at room temperature. These measurements indicate that the dipole of the O-H complex lies at an angle of approximately 110 degrees to the c axis of wurtzite ZnO. No dipoles were oriented parallel to the c axis, contradicting theoretical studies that show the parallel orientation to be energetically favorable. This work was supported by the National Science Foundation (DMR-0203832).

2:15 PM H3.3
Hydrogen Bonding in ZnO. N. H. Nickel and K. Brendel; SE1, Hahn-Meitner-Institut Berlin, Berlin, Germany.

In the past ZnO has attracted a great deal of interest because of its optical and electrical properties for a variety of applications ranging from UV light emitting diodes to piezoelectric devices. However, a major drawback is the fact that ZnO almost always shows n-type conductivity. Recently, based on first-principles calucations it has been suggested that the observed n-type conductivity is due to H atoms that act as shallow donors [1]. In order to elucidate the role of hydrogen in ZnO single crystal and sputter deposited polycrystalline Zno samples were characterized with Raman backscattering spectroscopy and hydrogen effusion measurements. In state-of-the art nominally undoped ZnO single crystals six local vibrational modes were observed at 2854, 2890, 2918, 2948, 2988, and 3096 cm^{-1}. While the local vibrational modes between 2854 and 2988 cm^{-1} are due to symmetric and antisymmetric stretching modes of C-H_X (X=1, 2, 3) the mode at 3096 cm^{-1} is indicative of the stretching vibration of N-H. An anneal up to 950 °C removes hydrogen from the samples and the local vibrational modes disappear. This establishes that the local vibrational modes are caused by the presence of H in ZnO. H effusion measurements reveal that the H concentrations range from $5.2x10^{16}$ for single crystal ZnO to $3x10^{21}$ cm^{-3} for polycrystalline ZnO. From

the H effusion spectra the H chemical-potential is determined as a function of the H concentration that can be related to the H density-of-states (DOS) distribution. State-of-the-art single crystal ZnO reveals six peaks in the H DOS located between 0.59 and 1.4 eV below the H transport site. With increasing H concentration the amount of hydrogen accommodated with binding energies larger than 1.0 eV increases to about 75%. [1] C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000).

2:30 PM H3.4
Hydrogen in sputter deposited ZnO films. Christian Pettenkofer and Ulrich Meier; SE6, Hahn-Meitner-Institut, Berlin, Germany.

ZnO contains a considerable amount of Hydrogen. Beside the intrinsic defect chemistry Hydrogen is considered as a doping agent in thin films. We will report on the chemical nature of Hydrogen in ZnO films deposited by magnetron sputtering on Si. The complicated interface chemistry will be explained as deduced from spectroscopic data. About 0.1 of the Oxygen signal measured by XPS of an UHV deposited film is obtained from OH-groups at the surface, the bulk and at grain boundaries. Annealing of films results in a conversion of Zn(OH)2 to ZnO and water. Time dependent binding energy shifts in Photoemission data are used to determine the role of Hydrogen. Different bonding sites and surface terminations will be discussed with respect to the energetics in the interface and the surface of the TCO.

2:45 PM H3.5
Highly Stable Hydrogenated Ga Doped ZnO Films.
Satoshi Takeda and Makoto Fukawa; Asahi Glass Company, Yokohama, Japan.

We have developed highly stable hydrogenated Ga doped ZnO films grown by DC magnetron sputtering using hydrogen gas. In the presentation, we will report the characteristics of the films and the role of hydrogen. Transparent and conductive oxide (TCO) films, which are degenerate wide band-gap semiconductors with low resistance and high transparency in the visible wavelength range, have been used extensively in optoelectronic devices such as transparent electrodes in flat panel displays and solar cells. The electrical and optical properties of TCO films must be stable to obtain high quality devices. In this study, we investigated the effects of water partial pressure (P_{H2O}) on electrical and optical properties of Ga-doped ZnO (GZO) films grown by DC magnetron sputtering. With increasing P_{H2O}, the resistivity of the films grown in pure Ar gas (Ar-films) significantly increased due to the decrease in both free carrier density and Hall mobility. The transmittance in the wavelength region of 300-400 nm for the films also increased with increasing P_{H2O}. However, no significant P_{H2O} dependence of the electrical and optical properties was observed for the films grown in H_2/Ar gas mixture (H2/Ar-films). Secondary ion mass spectrometry and X-ray diffraction analysis revealed that hydrogen concentration in the Ar-films increased with increasing P_{H2O} and grain size of the films decreases with increasing the hydrogen concentration. These results indicate that the origin of the incorporated hydrogen is attributed to the residual water vapor in the coating chamber, and that the variation of resistivity and transmittance along with P_{H2O} of the films resulted from the change in the grain size. On the contrary, the hydrogen concentration in H_2/Ar-films was almost constant irrespective of P_{H2O} and the degree of change in the grain size of the films versus P_{H2O} was much smaller than that of Ar-films. Based on these analyses, we will discuss the difference in stability of the electrical and optical properties of GZO films versus PH2O between Ar and H_2/Ar-films.

3:30 PM *H3.6
Vibrational Signatures of Hydrogen in Semiconductors.
Sukit Limpijumnong, School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

Vibrational spectroscopy is a powerful technique for experimental identification of hydrogen in semiconductors. In principle, when used in conjunction with *abinitio* calculations the microscopic configurations can be identified. In practice, the usual approach of calculating vibrational frequencies in the harmonic approximation is rarely accurate enough to allow a direct comparison with experiment. Anharmonic contributions are particularly important in the case of a light impurity such as hydrogen. I will discuss the magnitude of these contributions and a practical method of calculating them. Often, there is more than one microscopic configuration of H in the semiconductor with similar formation energy as well as vibrational frequency. For these cases, the absolute value of the vibrational frequency alone is not sufficient to provide a reliable identification of the microscopic structure. The changes in the frequency under lattice compression offer an additional means of identifying the microscopic structure. In the case of atomic H in ZnO, our calculations show that the two configurations in question (the so-called antibonding and bond center) have very distinct pressure dependences. An experimental measurement of this property, although challenging, could add a significant degree of confidence in identifying the structure. I will also present our version of calculated vibrational signatures of atomic H in ZnO and our recently determined diffusion barrier for atomic H in ZnO. Supported by the Thai Research Fund under contract No. BRG4680003.

4:00 PM H3.7
Effect of hydrogen doping on the properties of zinc oxide and its related alloys. Naoki Ohashi[1], Takamasa Ishigaki[1], Takashi Sekiguchi[2], Hiroyuki Taguchi[1], Yuguang Wang[1], Isao Sakaguchi[1] and Hajime Haneda[1]; [1]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Effect of hydrogen doping to zinc oxide (ZnO) was investigated by using inductively coupled thermal plasma under pulse-modulated-operation mode. In order to realize the detailed nature of hydrogen in ZnO, hydrogen doping was carried out to various kind of ZnO samples, i.e., high purity single crystals, poly crystals and ZnO phsohors with native or extrinsic luminescence centers. Some of the sammples were prepared by irradiation of deuterium instead of hydrogen, so that concentration of hydrogen (deuterium) by ion mass spectroscopy could be enabled. It was clearly indicated that the non-structured green emission of ZnO was not passivated by doping with hydrogen, while the structured green emission originated in substitutional Cu was suppressed by hydrogen doping. For ZnO powder giveing yellow luminescence originated in D-A pair transition, the effect of hydrogen doping was complecated. Namely, the profile of the yellow band strongly depended on the concentration of hydrogen introduced by the plasma treatments. Deteild result will be discussed at the conference site.

4:15 PM H3.8
Electronic Conduction in a Nanoporous Crystal, $12CaO{\cdot}7Al_2O_3$ Doped with H^- ion. Katsuro Hayashi[1], Masahiro Hirano[1] and Hideo Hosono[1,2]; [1]ERATO, Japan Science and Technology Agency, Kawasaki, Japan; [2]Materials and Structure Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Light metal oxides, as represented by alkaline-earth oxides, alumina, and silica, have been have been believed to be unexceptionally good insulators. However one of this class of material, $12CaO{\cdot}7Al_2O_3$ (C12A7), have been converted into an electronic conductor by utilizing its inherent nanoporous structure [1,2]. Crystal structure of C12A7 is characterized by sub-nanometer sized cage. Hydride (H^-) ion was incorporated by a thermal treatment in hydrogen atmosphere. The product (C12A7:H) was colorless transparent and insulating ($< 10^{-10}$ $S{\cdot}cm^{-1}$). Upon a illumination of ultraviolet light (4 eV), the C12A7:H was converted into an electronic conductor with 0.3 $S{\cdot}cm^{-1}$ at 300 K. The conductive state remained persistently after the illumination stops. These properties are attributed to that F^+-like centers are created at empty cages by capturing photo-released electrons from H^- ions, and then the captured electrons hop among cages [3]. Restoration to the insulator occurred when the conductive sample was heated at more than 320°C. Electronic conduction with an activation energy of 0.75-0.9 eV also appeared at high temperature range up to 550°C, above which H^- effuses from the crystal. By accounting the electron hopping energy of 0.1-0.2 eV, the carrier electrons are thermally excited from H^- ions with an energy of 0.7 eV. [1] K. Hayashi *etal.Nature* **419**, 462 (2002); [2] Matsuishi *etal.Science* **301**, 626 (2003); [3] P. V. Sushko *etal.Phys.Rev.Lett.* **91**, 126401 (2003).

4:30 PM H3.9
First principles predictions of H sites in rutile.
Simon W deLeeuw[1], Marina V Koudriachova[1] and Nicholas M. Harrison[2]; [1]DCT, Delft University of Technology, Delft, Netherlands; [2]Chemistry, Imperial College of Science Technology and Medicine, London, United Kingdom.

Most oxides contain hydrogen impurities which affect the properties of both bulk and surface. The strong charge transfer from the H-ions modifies the electronic structure of the host material and, at elevated temperatures, proton diffusion makes a significant contribution to the ionic conductivity. The large and growing use of oxide materials, and nanostructured oxides in particular, as solid state devices such as solar cells, battery cathodes and recording materials has lead to a great deal of interest in the influence of H-ions on their properties. The intercalation of H into oxide materials may also be a promising approach to hydrogen storage for fuel cells. Rutile TiO_2 is a technologically important material with applications in ferroelectrics, heterogeneous catalysis and pigment industry. The effect of H on various properties of rutile has been studied with avariety of experimental techniques. Of particular interest is thebehaviour of rutile on electrochemical insertion of H. A sizeable amount of H can

be accommodated in rutile electrochemically, on further cycling (after withdrawal of protons) the structure of rutile becomes brittle. Based on experimental findings different models for H-sites in rutile have been proposed. However, none of the existing models is entirely satisfactory. Here H-site in rutile structured titania has been considered in an ab initio study. High quality first principle calculations were used to determine the structures adopted on H-insertion in pure TiO_2 and doped with tri-valent-ions. Ab initio calculations allow us to resolve the contradiction in experimental data and explain the electrochemical behaviour of rutile on H-insertion.

SESSION H4: Poster Session
Tuesday Evening, April 13, 2004
8:00 PM
Salons 8-9 (Marriott)

H4.1
Hydrogen induced degradation in GaInP/GaAS HBTs revealed by low frequency noise measurements.
Jean-Guy Tartarin[1,2], Laurent Escotte[1,2], Mattia Borgarino[3], Robert Plana[1,2] and Jacques Graffueil[1,2]; [1]CISHT Team, LAAS-CNRS, Toulouse, France; [2]Paul Sabatier University, Toulouse, France; [3]University of Modena, Modena, Italy.

One of today's challenges to enable the improved electrical performances and reliability of microelectronic devices consists in controlling impurities contamination : hydrogen appears to be present in most (if not all) the processes steps of the device making (ambiant atmosphere, or associated with AsH3 -VPE, AsCl3 -VPE for example in GaAs based devices). Hydrogen induced reliability has already been investigated for many technologies Si or GaAs based (CMOS, FET, HEMT, PHEMT as well as HBT devices). These effects of hydrogen on electrical behavior and long term reliability are very difficult to understand because of the different nature and ionic association of hydrogen (H, H+, H-, H2, or associated with impurities (Ge-H, Be-H, C-H, ...). Most of these studies make use of IR, SIMS, Hall measurements : in this paper, we use low frequency noise measurements, associated with static as well as dynamic characterization to identify the degradation process in GaInP/GaAs Heterojunction Bipolar Transistors (HBT provided by Thomson LCR). Firstable, we will present the influence of passivation (SiN and GaInP ledge) on the reliability associated with hydrogen : low frequency noise measurements will be performed in the range of 250 Hz to 100 kHz. The noise spectra evolutions (current and voltage noise sources at the input of the device, and their correlation) will allow us to identify the activation process responsible of the static and dynamic rise and fall of the HBT's current gain when the device is biased at high current density level on the collector. This phenomena has been correlated with a doping change in the base layer, induced by the presence of C-H complexes before the stress application. Additive reliability tests have been performed on two devices sets (featuring different emitter length) under two distinct stocking conditions (temperature and biasing of the devices) leading to different junction temperatures : low frequency and high frequency noise measurements, associated with static and dynamic S parameters measurements will lead to the same conclusions about the hydrogen chemical reaction. C-H complexes breaking, and diffusion of H+ towards the extrinsic surface of the device have been observed. Sealed devices have exhibit the same degradation signature than on wafer devices : hydrogen is assumed to be present in high concentration levels in the device layers, and reacts under thermal and electrical stress. This study will also present the emitter orientation effects on the reliability, i.e. of the piezoelectric contribution both to electrical performances and reliability level of the device.

H4.2
Impact of Hydrogen Plasma Treatment on Getering by He Implantation-Induced Cavities in Silicon.
Daniel Alquier[1], Esidor Ntsoenzok[2], Chang Long Liu[1,2], A Vengurlekar[3] and S. Ashok[3]; [1]Laboratoire de Microelectronique de Puissance (LMP), Tours, France; [2]CERI-CNRS, Orleans, France; [3]Department of Engineering Science and Mechanics, Pennsylvania State University, Pennsylvania.

Plasma hydrogenation is widely encountered in semiconductor technology during various etching, deposition and passivation steps. It is well known that both defects and hydrogen atoms are injected into the subsurface layer under these conditions. Moreover, hydrogen exhibits an extraordinary chemical activity in silicon, reacting with point and extended defects, surfaces and impurities. He implantation followed by thermal anneal results in a buried layer of nm-size cavities, whose large internal surfaces act as excellent gettering sites for fast-diffusing metallic impurities. In previous work, we have demonstrated that additional H plasma treatment greatly impacts the morphology and size distribution of the He induced cavities. It is then crucial to figure out the impact of the plasma stage on the gettering efficiency of the cavities. P type, <111>, CZ silicon wafers doped at 1x1015 and 1x1018 cm-3 were used for this study. Helium implantation was performed at room temperature at an energy of 160 keV and a dose of 5x1016 He+/cm2. Half of the samples were then subjected to an electron cyclotron resonance (ECR) high-density hydrogen (deuterium) plasma treatment. Furnace Annealing (FA) was performed at 800C for 1h to form the cavity band. During the FA step, one set of the samples was contaminated by Cupper. Cross-sectional transmission electron microscopy (XTEM) and Secondary Ion Mass Spectrometry (SIMS) measurements were performed to analyze the samples. XTEM results clearly shows the modification of He-induced cavities due to additional plasma hydrogenation. SIMS measurements evidence a large segregation of both the B dopant and Cu contamination in the vicinity of the buried layer. In each case, the fraction of gettered specie was evaluated from the SIMS profiles. These results quantify the impact of H plasma step on gettering efficiency and are of high interest for future development of the He cavity gettering technique.

H4.3
Effect of Hydrogen Treatment on Room-Temperature Electric Field-Induced Properties in Narrow-Gap ZnCdHgTe Thin Films.
Halyna M. Khlyap and Petro G. Sydorchuk; General Physics, State Pedagogical University, Drohobych, Ukraine, Kaiserslautern, Germany.

Narrow-gap semiconductor compound ZnxCdyHg1-x-yTe is discussed as a material alternative to world-wide known HgCdTe due to improved structural and photosensitive characteristics. The abstract reports for the first time data of pulse-laser deposition growth of the films on amorphous substrates and effect of hydrogen treatment on electric field-indused properties of the samples. H-ray diffractometry and SEM investigations demonstrated the as-grown films were of monocrystalline structure with thickness of 2 - 8 mkm. Measurements of current-voltage characteristics carried out at the room temperature exhibited exponential form typical for barrier-like structures with large series resistance under both forward and reverse directions of applied electric field. The films demonstrated no sufficient photosensitivity. The hydrogen treatment was reformed during 24 hours in flow of molecular H2 under 573 K and gas pressure 3000 Pa. Similar studies revealed considerable decrease of the resistance of the samples (two orders of magnitude) and appearance of photosensitivity in visible and near-IR spectral ranges. Data of numerical analysis and simulation of experimental results are also available

H4.4
Hydrogen Density-of-States Distribution in Compensated Polycrystalline Silicon Thin Films.
Rosari Saleh[1], Norbert H Nickel[2] and Karsten Brendel[2]; [1]Department of Physics, Universitas Indonesia, Depok, Indonesia; [2]Department of Photovoltaic, Hahn-Meitner Institut, Berlin, Germany.

Excimer laser crystallization is a well established method to produced large-grained polycrystalline silicon (poly-Si) through the crystallization of hydrogenated amorphous silicon (a-Si:H). Since a-Si:H contain considerable amount of hydrogen laser crystallization has to be performed in a step-by-step procedure to avoid explosive out-diffusion of hydrogen and, thus destruction of the film. In this paper we investigate hydrogen bonding and diffusion during step-by-step crystallization procedure in compensated polycrystalline silicon. a-Si:H films as starting materials were prepared by rf glow discharge decomposition of silane. The dopant gasses were phosphine and diborane. The nominal gas phase doping was varied from 1000 to 2000 ppm. The samples were crystallized at room temperature with a shot density of 100 up to the desired laser fluence. Information on hydrogen bonding and diffusion in the starting material and in completely crystallized poly-Si were obtained from hydrogen effusion measurements. From the effusion spectra, the hydrogen density-of-states distribution is derived for samples prior to and after laser crystallization. In dependent of the doping concentrations of the starting amorphous silicon laser crystallization results in a shift of the hydrogen density-of-states distribution to larger binding energies. When the diborane and phosphine is at equal levels, hydrogen density-of-states reveals three prominent peaks at binding energy between -2.0 and -3.0 eV. This result is also observed in undoped sample. However, when the doping levels are different, the hydrogen density-of-states is close to that found for single majority doping. The data will be discussed in terms of models developed to describe hydrogen complex formation.

H4.5
Hydrogen Passivation of Bulk and Surface Defects in Multicrystalline Silicon.
Santo Martinuzzi and Olivier Palais; Physics, University of Marseille, Marseille, France.

Hydrogen Passivation of Bulk and Surface Defects in Multicrystalline

Silicon By Santo Martinuzzi and Olivier Palais Laboratory TECSEN - University of Marseilles, 13397 Marseille Cedex 20,France Tel. (33)491288349; Fax: (33)491288852; e-mail: santo.martinuzzi@univ.u-3mrs.fr The knowledge of how hydrogen interacts with defects and impurities in silicon is crucial for the understanding of solar cell performances made with multicrystalline silicon wafers. The present work is focused on hydrogenation by means of plasma enhanced chemical vapour deposition of hydrogen rich silicon nitride (SiN-H). Passivation effects are evaluated after annealing using minority carrier diffusion length (L) and lifetime values and also light beam induced current scan maps (LBIC) at various temperatures (T). Investigated wafers were P type multicrystalline silicon, boron doped to 1016 cm-3, and whose the mean grain size and dislocation density were 5 mm and 104cm-2, respectively. Companion samples presenting the same kind, density and features of defects were phosphorus diffused from a POCl3 source at 1150 K for 20 min to make a collecting structure for minority carriers. An Al layer was deposited on the back surface, a Ag grid was formed on the front side and a TiOx antireflection coating (ARC), or a SiN-H one, was deposited. Then the structures were fired at 1100 K. The SiN-H layers were obtained by a direct plasma reactor, with SiH4 and NH3 precursors at 650 K while TiOx layer were deposited at 750 K by atmospheric pressure CVD. During the firing, hydrogen in-diffuses in the wafer and this penetration is enhanced by a synergetic effect due to the injection of vacancies from the Al-Si alloy. TiOx samples were considered as raw samples. Other companion samples received the same ARC but without the phosphorus diffusion and are used for lifetime measurements by the phase shift technique, which evaluates also the surface recombination velocity. Comparing the samples covered by both ARC, it is found that the mean value of L increases by 80% in the SiN-H covered samples (i.e. from 0.14 to 0.26 mm). LBIC scan maps show that there is a marked contrast (C) at T=300K at grain boundaries and dislocation lineages or clusters in TiOx samples, while C is neatly attenuated in SiN-H ones, due to the passivation of these defects. When T decreases below 150 K, C decreases in TiOx samples and increases in SiN-H ones. Lifetime of minority carrier measurements confirm the improvement of the bulk by hydrogenation. The front surfaces are also passivated and the recombination velocity decreases below 100 cm.s-1. These results suggest that at defects, deep energy levels of TiOx samples are transformed in shallow ones (about 0.1 eV) in hydrogenated samples. Such transformations result probably from the formation of complexes between hydrogen and impurities (oxygen precipitates; metallic atoms) segregated at extended crystallographic defects.

SESSION H5: H in Dilute Nitride Semiconductors
Wednesday Morning, April 14, 2004
Room 2020 (Moscone West)

8:30 AM *H5.1
Hydrogen and nitrogen bonds and bands in diluted nitrides. Mario Capizzi, Physics, University of Rome "La Sapienza", Roma, Italy.

Hydrogen is present in the plasmas, etchants, precursors and transport gases of most growth processes and device mass-production steps. It diffuses easily in semiconductors where it neutralizes dangling bonds and forms strong bonds with impurities, as evidentiated by infrared absorption spectroscopy, thus cleaning up the band gap from defect energy levels. In (InGa)(AsN) alloys, post-growth hydrogen treatment gives rise to the passivation of the N isoelectronic impurity whose effective concentration vanishes at high H doses together with all effects N introduction has on the optical, transport, and morphological properties of the (InGa)As host alloy. The band-gap increases, the electron effective mass decreases, the exciton wavefunction size increases, and the lattice parameter changes for increasing H irradiation and the (InGa)As values are recovered finally. In the meantime, the optical quality of the alloys improves upon hydrogenation because of a strong suppression of the alloy fluctuations and passivation of competing non-radiative defects. Similar results have been obtained in Ga(PN), whose emission monotonously blue shifts and weakens upon hydrogenation until the indirect gap of GaP is fully recovered. Thermal annealing fully reverses the effects induced by H in (InGa)(AsN) and (GaP)N and restores the properties of the as-grown material. These results have been explained in terms of the formation of H-N complexes, whose detailed nature has been investigated by first principle density functional calculations. Infrared absorption measurements support the formation of di-hydrogen complexes in both hydrogenated (InGa)(AsN) and Ga(PN), as predicted by the theory. However, these measurements seem to exclude that this H-N complex could be the N-H2* complex predicted by theory.

9:00 AM *H5.2
Hydrogen-nitrogen tailors semiconductor optoelectronics: The case of dilute nitride III-V alloys. Anderson Janotti, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Hydrogen is an omnipresent impurity in semiconductors, often associated with other impurities and native defects, strongly affecting their electronic properties by passivating deep and shallow levels, or activating isoelectronic centers, and can be intentionally or unintentionally incorporated. On the other hand, nitrogen has profound effects on the electronic structure of conventional III-V compounds: just a few percent of N can drastically lower the band gap of GaAs making it suitable for long-wavelength optical devices; isovalent doping of GaP by N leads to a quasidirect band gap with enhanced optical functionality. The large difference in electronegativity between N and other group V elements is expected to couple with the high chemical activity of H, raising crucial questions about the behavior of H in dilute nitride alloys that theories of hydrogen in conventional semiconductors or in commom-anion nitrides are unable to answer. Here we show that N can qualitatively alter the electronic behavior of hydrogen: In GaAsN, an H atom bonds to N and can act as a donor in its own right, whereas in GaAs and GaN, H is amphoteric; Nitrogen also stabilizes the H2* complex, that is otherwise unstable against the formation of interstitial H2 molecules, reversing the effect of N on the band gap of GaAs. Moreover, the interaction between nitrogen and hydrogen significantly lower the formation of Ga vacancy in GaAs allowing us to interpret several recent experiments.

9:30 AM H5.3
Lattice-constant, effective-mass, and gap recovery in hydrogenated GaAsN. Simone Sanna and Vincenzo Fiorentini; Dept. of Physics, University of Cagliari, Monserrato, Italy.

Upon weak N alloying, GaAs exhibits a giant photoluminescence red-shift, a reduction of the lattice constant, and an increase of the electron effective mass. Post-growth hydrogenation was experimentally observed to restore the band gap, lattice constant, and effective mass to values close to those of pure GaAs. We present ab initio density-functional calculations on pristine and hydrogenated $GaAs_{1-x}N_x$ showing that the formation of N-H_2* complexes explains all three effects. We also discuss the large, composition-dependent gap bowing (with at least a linear dependence b(x)=8.3 - 37 x eV) and some of the structural properties of GaAsN (e.g. the bimodal distribution of Ga-As bond-length distribution as function of x).

SESSION H6: Hydrogen in Silicon
Wednesday Morning, April 14, 2004
Room 2020 (Moscone West)

10:15 AM *H6.1
Deciphering the Vibrational Spectrum of Interstitial H_2 in Si. Michael Stavola, W Beall Fowler, E Elinor Chen and G Alvin Shi; Dept of Physics, Lehigh University, Bethlehem, Pennsylvania.

H_2 is a fascinating molecule whose properties revealed the influence of nuclear spin on the molecular wave function in the 1920s. As an interstitial defect in Si, the H_2 molecule has given rise to a number of perplexing puzzles since the discovery of its vibrational spectrum. The absence of an ortho-para splitting for the H_2 vibrational line and an apparent low symmetry found in stress experiments misled several researchers into thinking that interstitial H_2 in Si must have a barrier to rotation. Our discovery of a new vibrational line for HD in Si and the recognition that certain transitions are possible for HD, but not for H_2 or D_2, establish that H_2 in Si is a nearly free rotator after all. The insights provided by these results lead to simple, in retrospect, explanations of the properties of interstitial H_2 in Si [1-3]. The vibrational lines of both ortho and para H_2 in Si were observed in a subsequent Raman study, confirming that H_2 in Si is a free rotator [4]. However, these studies also suggest the surprising result that the diffusivity of para H_2 is much greater than that of ortho H_2. While most of the properties of H_2 in Si are now understood, such puzzling experimental results continue to challenge us. 1. E E. Chen et al., Phys. Rev. Lett. 88, 105507 (2002); 88, 245503 (2002). 2. W.B. Fowler et al., Phys. Rev. B 66, 075216 (2002). 3. B. Hourahine and R. Jones, Phys. Rev. 67, 121205 (2003). 4. E.V. Lavrov and J. Weber, Phys. Rev. Lett. 89, 215501 (2002).

10:45 AM H6.2
On the Mechanism of Hydrogen Diffusion in Si Solar Cells Using PECVD SiN:H. Bhushan Sopori, Yi Zhang and Robert Reedy; National Renewable Energy Laboratory, Golden, Colorado.

In recent years, SiN:H has been adopted by almost all solar cell manufacturers as the favored antireflection (AR) coating material. Although SiN offers a good match of optical properties to be an effective AR coating on Si, the major reason for this use is that its

deposition and subsequent processing also allows H to be introduced into the bulk of the solar cell, where it passivates defects and impurities to improve the solar cell performance. In a typical commercial solar cell processing sequence, a thin layer of SiN:H is deposited by a PECVD process on the front side of an N/P junction. Next, a Ag-based contact metallization pattern is screen-printed and then fired through the nitride using a RTP step (at about 800 °C). In this step, the metal penetrates through the nitride to form a low-resistance ohmic contact, while the H diffuses into the bulk of the cell to passivate impurities and defects. It is generally believed that the H that diffuses into Si is released from SiN:H during RTP. Although this view is in agreement with the observed depletion of H from SiN:H film after RTP, our modeling of H diffusion in Si, which takes into account trapping and detrapping mechanisms, suggests that H is retained under the Si surface by the process-induced defects during deposition itself. This "stored" H is then released during high-temperature RTP and diffuses deep into Si. We have also performed SIMS measurements of H profiles in Si ribbons for two cases: (i) as-deposited with PECVD SiN:H and (ii) after the RTP step. This paper will present both theoretical and experimental results that verify the proposed mechanism of H diffusion.

11:00 AM H6.3
How much hydrogen and voids are energetically stable in non-crystalline silicon? Anna Fontcuberta i Morral, Holger Vach and Pere Roca i Cabarrocas; LPICM, C.N.R.S, Palaiseau, France.

We have developed a model to account for the effects of hydrogen and voids on the structural stability of amorphous silicon films. Density Functional Theory (DFT) calculations were performed to determine the energy of formation for four types of hydrogenated silicon tetrahedra of the form Si-SinH4-n (n=1, 2, 3, 4). In our model, these tetrahedral units are considered as the building blocks of hydrogenated amorphous silicon. Considering a homogeneous distribution of hydrogen in the solid, the proportion of the different Si-SinH4-n tetrahedra as a function of the hydrogen concentration was calculated. According to this distribution, the formation energy of hydrogenated amorphous silicon (a-Si:H) was calculated as a function of the hydrogen content. The role of the porosity in the formation energy of a-Si:H was also studied. The model predicts that hydrogen does not render the a-Si:H structure unstable for concentrations below 25%, provided that the presence of hydrogen is not associated with the incorporation of porosity in the film. Moreover, our DFT simulations were compared with new experimental results: a-Si:H thin films with different hydrogen contents were obtained by Plasma Enhanced Chemical Vapour Deposition. The corresponding hydrogen and void fractions were measured by Elastic Recoil Detection Analysis and Spectroscopic Ellipsometry. A linear correlation between hydrogen content and void fraction was found. Films with large hydrogen and void fractions (20%) were structurally unstable, and a phase transition from amorphous to microcrystalline silicon was observed during deposition. By tuning the deposition conditions, films with hydrogen contents up to 20% and very small void fractions (2%) were obtained without any phase transition to microcrystalline silicon. These films can also be characterized by excellent electronic properties. In conclusion, we show that the structural stability of amorphous silicon can be maintained up to a hydrogen concentration of 25% and that material unstabilities are caused by the film porosity.

11:15 AM H6.4
Comparative Study of Electronically Controlled Motion of Hydrogen around Carbon and Platinum Atoms in Silicon. Yoichi Kamiura[1], Namura Bao[1], Kimihiro Sato[1], Kazuhisa Fukuda[2], Yasuyuki Iwagami[1], Yoshifumi Yamashita[1] and Takeshi Ishiyama[1]; [1]Faculty of Engineering, Okayama University, Okayama, Japan; [2]NEC Laboratories, Otsu, Japan.

The characterization and control of hydrogen motion in semiconductors is one of the important issues in semiconductor technologies. Recently, we have studied the electronic states of two H-related (H-C and Pt-H_2) complexes in Si by deep-level transient spectroscopy (DLTS) under uniaxial compressive stress. We have also studied the local motion of hydrogen in the neighborhood of carbon and platinum impurities by observing the stress-induced alignment due to defect reorientation and subsequent recovery. We present the results of comparative study of these complexes, concerning their electronic states and atomic configurations and the local motion of hydrogen around the nearby impurities. If we compare hydrogen motion around the carbon atom with that around the platinum atom, we notice two interesting differences. The first one is a difference in the temperature where stress-induced alignment occurs. That of the H-C complex occurs at high temperatures above 250 K, while it occurs at temperatures as low as 80 K for the Pt-H_2 complex. The second difference is the effect of charge state of the complexes on their stress-induced alignment. It occurs preferentially when the level of the H-C complex is occupied by an electron, but the Pt-H_2 complex has the reverse effect of level occupancy. The activation energy for the hydrogen motion is 1.33 eV and 0.55 eV in the electron-empty and electron-occupied charge states of the H-C complex, respectively, and 0.27 eV in the electron-empty charge states of the Pt-H_2 complex. These differences may result from different atomic configurations and electronic states of two H-related complexes. In the H-C complex, hydrogen is located at the bond-centered site between carbon and silicon atoms. In the electron-occupied charge state, the complex captures an electron from the conduction band at its gap state with antibonding character, lowering the barrier for hydrogen motion. In the Pt-H_2 complex, the two hydrogen atoms are directly bonded to the platinum atom, and therefore defect reorientation needs no bond switching but only the rotation of the whole Pt-H_2 entity. A possible mechanism of the charge-state-dependent reorientation may be that if the electronic state with antibonding character is occupied by an electron, the two hydrogen atoms may be displaced outward, probably retarding their motion for the reorientation.

SESSION H7: Hydrogen in Silicon II
Wednesday Afternoon, April 14, 2004
Room 2020 (Moscone West)

1:30 PM *H7.1
Vibrational Lifetimes of Hydrogen in Silicon. Gunter Luepke, Department of Applied Science, College of William and Mary, Williamsburg, Virginia.

Recently, the dynamics of hydrogen-related defects in silicon has attracted much attention [1]. The lifetimes of the Si-H vibrational stretch modes of the H2* (2062 cm-1) and HV—VH(110) (2072.5 cm-1) defects in crystalline Si have been measured directly by transient bleaching spectroscopy from 10 K to room temperature. The interstitial-type defect H2* has a lifetime of 4.2 ps at 10 K, whereas the lifetime of the vacancy-type complex HV—VH(110) is two orders of magnitude longer, 295 ps. The temperature dependence of the lifetime of H2* is governed by TA phonons, while HV—VH(110) is governed by LA phonons. The observed large disparity in measured lifetimes is unexpected based on simple theories and is as yet unexplained. These initial results indicate that local defect structure plays a crucial role in the coupling mechanism. To elucidate the nature of the decay mechanism, it is necessary to study the Si-H bend modes. One of the best-characterized Si-H bend mode in silicon belongs to H2*, which has C3v symmetry with one hydrogen close to the bond-center site and the other at an antibonding site. This complex gives rise to vibrational modes with frequencies 817, 1599, 1838, and 2062 cm-1. The 817 cm-1 mode was identified experimentally and theoretically as the bend mode of H at the antibonding site [2]. We have investigated the vibrational dynamics of the 817 cm-1 bend mode of H2* as a function of temperature by infrared transient bleaching spectroscopy. The phase relaxation of the bend mode is dominated by low energy excitation of 270?9 cm-1 modes. This work was supported in part by DOE through grant DE-FG02-99ER45781 (C.W.M. and V.U.), ONR (C.W.M. and V.U.), NSF through grants DMR-00-76027, DMR-02-42316 (C.W.M.), and the Thomas F. and Kate Miller Jeffress Memorial Trust through grant J-545 (C.W.M.). 1. Luepke G., Tolk N. H., and Feldman L. C. (2003) J. Appl. Phys. 93, 2316-2335 2. Holbech J. D. et al. (1993) Phys. Rev. Lett. 71, 875-878

2:00 PM H7.2
Origin of the Hydrogen/Deuterium (H/D) Isotope Effect of Hot-Electron Degradation of MOS Devices. Zhi Chen and Jun Guo; Electrical & Computer Engr, University of Kentucky, Lexington, Kentucky.

The study on the desorption of hydrogen (H) and deuterium (D) on silicon in ultra high vacuum (UHV) by Scanning Tunneling Microscopy (STM) led to the discovery of the giant H/D isotope effect. It was later used in passivation of the SiO2/Si interface, leading to large improvement of the hot-carrier lifetime of MOS transistors [1]. Van de Walle et al [2] proposed a theory to explain this isotope effect, i.e. the Si-D bond is more resistant to hot-electron excitation than the Si-H bond. The Si-H/D bond-breaking at the SiO2/Si interface is caused by two competing processes. One is that the energy of the bonds is accumulated through excitation by energetic hot electrons. The other process is de-excitation where the bond energy is taken away by coupling between the Si-H/D vibrational modes and substrate phonons. It is suggested that the vibrational frequency of Si-D bending mode is close to the Si-Si TO phonon mode (460 cm-1), resulting in energy coupling between Si-D bond and the Si-Si phonon mode. This de-excitation efficiently strengthens the Si-D bond. On the other hand, the vibrational frequency of the Si-H bond is far away from the Si-Si phonon mode such that the Si-H bond is more vulnerable to hot-electron excitation. However, there are not any direct experimental data supporting the above theory and even no experimental data exist regarding vibrational frequency of the Si-D bond at the SiO2/Si interface. In

this paper, we present experimental results of vibrational modes at the SiO2/Si interface measured by Fourier Transform Infrared (FTIR) spectrometry and will show the direct correlation between the vibrational modes and energy dissipation of the Si-D bond. Fig. 1 shows the FTIR spectra of a SiO2/Si sample with oxide thickness of 32 nm before and after hydrogen anneal. The two curves (before and after hydrogen anneal) are very similar. The peak (592 cm-1) appears uniquely in the H-annealed sample, which is determined to be Si-H bending mode. Fig. 2 shows the FTIR spectra of a SiO2/Si sample with oxide thickness of 32 nm before and after deuterium anneal. The peak at 490 cm-1 uniquely appears in the D-annealed SiO2/Si sample, which should be the Si-D bending mode. Of the most importance, it is found in Fig. 2 that the absorbance (magnitude) of the Si-Si TO phonon mode and the Si-O TO rocking mode are all enhanced significantly (>25%) after deuterium anneal. There is not much difference for absorbance of the Si-Si TO mode and Si-O TO rocking mode after hydrogen anneal (See Fig. 1). This exclusively suggests that there is energy coupling from the Si-D vibrational mode to the Si-Si TO phonon mode and the Si-O TO rocking mode. Van de Walle only pointed out Si-Si TO phonon mode. Therefore, the oxide may play a crucial role in energy dissipation of the Si-D bond in MOS devices. 1 J. W. Lyding, K. Hess, and I. C. Kizilyalli, Appl. Phys. Lett., 68, 2526 (1996). 2 C. G. Van de Walle and W. B. Jackson, Appl. Phys. Lett., 69, 2441 (1996).

2:15 PM H7.3
Donor Behaviour of Implanted Hydrogen Ions in Silicon Wafers. Santo Martinuzzi and Damien Barakel; Physics, University of Marseille, Marseille, France.

Donor Behaviour of Implanted Hydrogen Ions in Silicon Wafers By Damien Barakel and Santo Martinuzzi Laboratory TECSEN, University of Marseille, 13397 Marseille Cedex 20 France Tel. (33)491288349 ; Fax: (33)491288852 ; e-mail: santo.martinuzzi@univ.u-3mrs.fr It was suggested that highly concentrated hydrogen behave as a shallow donor in crystalline silicon. It was also reported that hydrogen nanobubbles can be formed,which are transformed in nanocavities by exodiffusion of the gas. In the present paper we demonstrate that p type wafers are counterdoped in a region close to the projected range Rp. P type Czochralski (Cz) and float-zone (FZ) grown silicon wafers were investigated with doping levels of 5x1014 and 2x1015 cm-3, respectively. Hydrogen ions H+ are implanted at a dose of 2x1016 cm-2, at energies in the range 20 to 250 KeV. Hydrogen ions are accumulated at depth Rp of 200 to 2300 nm. After implantation the wafers were annealed between 650 and 850 K for 30 min, under argon flow. It is found that a n-p junction is formed, the n region is located below the implanted surface around Rp. After metallisation, i.e. by aluminium layer deposition on the backside and of by an aluminium grid on the front side, a photovoltaic device is obtained, which works like a solar cell. Indeed a spectral response (RS) is obtained comparable in intensity to that of phosphorus diffused cells. SIMS analysis show clearly that around Rp hydrogen concentration achieves 1021 cm-3 and electron like focus ion beam microscopy show the formation of nanobubbles. I-V and C-V curves confim the formation of a N type layer in which the donor concentration is about 5x1017 cm-3; the junctions are graduated as 1/C3 vs reverse voltage plots are linear. The investigation of the structures prepared at various energies suggest that the N type zone is located around Rp. Indeed the RS intensity increases, especially for wavelength between 400 and 600 nm, when ion energy decreases, or when the samples implanted at 250 or 120 KeV are sligthly etched. Square surface resistance leads to a doping level around 1017 cm-3 and confirms the presence of a the N type layer. The variation with temperature of this resistance leads to an activation energy of 30 meV. When the samples are annealed at temperatures higher than 850 K the counterdoping vanishes due to the exodiffusion of hydrogen and the formation of nanocavities around Rp. Notice that the observed behaviour of hydrogen is irrespective of oxygen concentration in the wafers as it occurs in Cz (oxygen rich) like in FZ (oxygen poor) wafers. If the wafers are ion implanted with helium at the same dose and energy no junction appears. It is concluded that the agglomeration of hydrogen in silicon after ion implantation at a dose exceeding 1016 cm-2 gives rise to the formation of shallow donors. Such donors seem to be connected with hydrogen nanobubbles and a highly doped N type layer is formed around the ion projected range.

2:30 PM H7.4
Si surface blistering induced by plasma hydrogenation.
Peng Chen[1], Paul Chu[1], Tobias Franz Hochbauer[2], Jung Kun Lee[2], Michael Nastasi[2], Dan Mihai Buca[3], Siegfried Mantl[3], Roger Loo[4], Matty Caymax[4], James W. Mayer[5], Ming Cai[6], Blair Schmidt[6] and Silvanus S. Lau[6]; [1]Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China; [2]Los Alamos National Laboratory, Los Alamos, New Mexico; [3]Institut fur Schicht- und Ionentechnik, Julich, Germany; [4]IMEC, Leuven, Belgium; [5]Arizona State University, Arizona, Arizona; [6]University of California at San Diego, San Diego, California.

Defects, strain and impurities intentionally introduced into Si wafers were found to trap H atoms upon hydrogenation using plasma source in a plasma ion immersion implantation (PIII) equipment. The trapped H atoms, in turn, cause surface blistering either during hydrogenation or after post-annealing at higher temperatures on samples without prior bonding to handle wafers. Two types of samples were investigated in this study: (i) Boron-implanted n-type Si (100) and (111) wafers, and (ii) SiGe epitaxial layers on p-type Si (100) substrates. The hydrogenated samples were examined using optical microscope with Normaski lenses, cross-section transmission electron microscopy, MeV ion scattering measurements including channeling and elastic recoil detection, and infrared absorption spectroscopy. It should be noted that bubble formation is essential for thermal and mechanical delamination of surface layers. The result suggests an innovative process of Si layer transfer by plasma hydrogenation to avoid the damage caused by H-implantation commonly used in the ion-cutting process. The physical mechanism of the bubble formation due to plasma hydrogenation will also be discussed.

SESSION H8: Hydrogen in Carbon Nanotubes and Diamond
Chair: Michael Stavola
Wednesday Afternoon, April 14, 2004
Room 2020 (Moscone West)

3:15 PM *H8.1
Molecular Simulations of Hydrogen Storage in Single Walled Carbon Nanotubes: Effects of Nanotube Size and Chirality.
Hansong Cheng[1], Alan C. Cooper[1], Guido P. Pez[1], Milen Kostov[2], Milton Cole[2] and Steve Stuart[3]; [1]Air Products & Chemicals, Inc., Allentown, Pennsylvania; [2]Department of Physics, Pennsylvania State University, University Park, Pennsylvania; [3]Dept of Chemistry, Clemson University, Clemson, South Carolina.

There are a number of fundamental questions concerning H2 storage in single walled carbon nanotubes. First, do carbon nanotubes differ significantly from other carbon materials, such as graphite and graphite intercalation compounds, and if they do, in what aspects? If carbon nanotubes are indeed different, what is their adsorption capacity under ambient conditions? Finally, does the adsorption depend on the nanotube architecture and size? Using first-principles based molecular simulation methods, we have performed extensive studies to address these questions. The computational results for several selected systems were first validated by comparison with the available experimental reports in the literature. Subsequently, we systematically examined the effects of nanotube chirality and size on the heat of adsorption for H2. We will present the detailed results of our simulation studies and summarize our findings in this presentation.

3:45 PM *H8.2
Formation of deuterium-related shallow donors in boron-doped diamond upon deuteration.
Jacques Paul Chevallier[1], Zephirin Teukam[1], Cecile Saguy[2], Rafi Kalish[2], Catherine Cytermann[2], Francois Jomard[1], Annie Tromson-Carli[1], Dominique Ballutaud[1], James E. Butler[3], Celine Baron[4] and Alain Deneuville[4]; [1]Laboratoire de Physique des Solides et de Cristallogenese, CNRS, Meudon, France; [2]Physics Department and Solid State Institute, Technion, Haifa, Israel; [3]Naval Research Laboratory, Washington, District of Columbia; [4]Laboratoire d'Etudes des Proprietes Electroniques des Solides, CNRS, Grenoble, France.

In diamond, the diffusion of deuterium and the passivation of boron acceptors have been established only recently. Because of the deep donor character of hydrogen in p-type diamond, free holes and neutral boron acceptors are compensated by hydrogen giving rise to the formation of protons which are fast diffusing species (migration energy of 0.1-0.2 eV) and to negatively charged boron forming pairs with the protons. In this work, we show that the deuteration of homoepitaxial boron-doped diamond can induce a p-type to n-type conductivity conversion under certain conditions. The electrical conductivity and the electron mobility can be as high as 1 ohm-1cm-1 and 430 cm2/Vs respectively at 300 K. The n-type conductivity is governed by the ionization of donors with a ionization energy of 0.34 eV. This is well below the lowest ionization energy of donors found up to now in diamond (0.6 eV for phosphorus donors). Under thermal annealing at 520 C, the shallow donors break-up until the samples return to their original p-type conductivity. The exact nature of these donors is not known yet. Careful SIMS analysis eliminate contaminants as being at the origin of the donors. The reversibility of the effect strongly suggests that deuterium is involved in the formation of the shallow donors. When a strong accumulation of deuterium is observed in the layer, there is no p-type to n-type conversion. Since this accumulation is the signature of the presence of

structural defects acting as deuterium deep traps, this means that the structural quality of the homoepitaxial layers appears to be a key parameter for the control of the conductivity conversion. The above results should contribute to the development of diamond-based electronic devices working at room temperature.

4:15 PM H8.3
Hydrogen diffusion in polycrystalline boron doped and undoped diamond. Dominique Ballutaud[1], Annick Boutry-Forveille[1], Jean-Michel Laroche[1] and Nathalie Simon[1]; [1]LPSC, CNRS, Meudon cedex, France; [2]LPSC, CNRS, Meudon, France; [3]LPSC, CNRS, Meudon, France; [4]IREM, UVSQ, Versailles, France.

Hydrogen is known to play an important role in the diamond film growth from a CH4/H2 precursor mixture. The diamond polycrystalline films are highly defective, and present a high density of grain boundaries or dislocations, and incorporated hydrogen in semiconductors is known to terminate dangling bonds and passivate both shallow and deep levels. Furthermore, the hydrogen present at the diamond surface induces a superficial highly p-type conductive layer, the origin of which is not completely understood. In a previous paper [1], it has been shown that the hydrogen concentration in an as-grown CVD polycrystalline diamond film with 1 μm grain size is about 10^{19} cm^{-3}. This paper deals with new data on the diffusion and thermal stability properties of hydogen (deuterium used as a tracer) in polycrystalline doped and undoped diamond films. Deuterium diffusion and effusion experiments are performed on undoped and boron doped diamond films ([B] = 10^{19} and 10^{20} cm^{-3}) grown by CVD or hot filament assisted CVD. The samples are exposed either to a radiofrequency plasma or a microwave plasma at different temperatures between 400°C and 900°C. The deuterium diffusion profiles are analysed by secondary ion mass spectrometry (SIMS). The effusion spectra of deuterium are measured with a mass spectrometer coupled to an UHV furnace. The deuterium diffusion profiles are explained mainly in term of trapping on inter- and intragranular defects (deep traps), although the presence of boron modifies the deuterium diffusion profiles. The passivation of the acceptors shallow levels, in the deuterium diffused superficial layers of the diamond films, is followed by electrochemeical measurements (I(V) and capacitance measurements) in 2M H2SO4 medium containig the Ce^{4+}/Ce^{3+} redox couple as an electrochemical probe. The results suggest a strong decrease of the free carrier density, which is in accordance with passivation of free carriers by hydrogen trapping on dopant. The thermal reactivation of the dopant is followed simultaneously by effusion experiments, SIMS analysis and electrochemical measurements. *[1] D. Ballutaud, F. Jomard, B. Theys, C. Mer, D. Tromson and P. Bergonzo, Diamond and related materials*, **10** (2001) 405-410.