In an attempt to fulfill the predictions of Moore's Law, the silicon device community is turning increasingly to SiGe alloys and to hydrogenated amorphous silicon (a-Si:H) as a chemical terminator of silicon dangling bonds. However, the inherent higher electron and hole mobilities in Germainium 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.

The Role of Hydrogen in the Creation of Metastable Defects in Hydrogenated Amorphous Silicon. P Craig Taylor¹, T Su², G Ganguly³ and D E Carlson, Symposium A, this meeting.

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.
Detection Analysis and by thermal desorption. These experiments indicate that the quantity of implanted hydrogen remains inside the InP up to a temperature of 300°C (just below the blistering temperature) and is lost by the dramatic release of hydrogen during the blister rupture process (T=350°C) 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. Zimney1, Michael S. Mazzola2, Harry A Atwater3, Martin M. Frank1 and Yves J. Chabal4; 1Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California; 2LPICM, C.N.R.S.-Ecole Polytechnique, Palaiseau, France; 3IBM, Yorktown Heights, New York; 4Chemistry 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 1x1015 cm^-2 under passive cooling conditions at a power density of 1000 W/m2. The samples were measured in transmission at 108, 458, and 68°C. 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 causes no significant change in the absorption spectrum, but annealing to 300 and 350°C causes the overall peak size to decrease while simultaneously revealing a shoulder near 1910 cm^-1. This shoulder is interpreted as 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 1975 cm^-1 respectively.1 However, TEM results indicate that internally fractured surfaces lie dominantly on the (001) planes. These surfaces coalesce into larger areas, leading by way of anisotropic 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 H2 and builds sufficient pressure to fracture a device to be driven in the plane of the implanted layer.1 Adams, S. et al. (1995) “Hydrogen interactions with cavities in helium-implanted germanium.” Physical Review B 51(15): 9745-9752.

11:45 AM H2.5

Non-metastable Recombination Induced Reactions Involving Hydrogen In ZnO. Yaroslav Koshka1, Michael S. Mazzola2, Bharat Krishna3 and Andrei Los4; 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. Furthermore, certain complexes can be identified as the 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 recombination-induced hole trapping 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. 86(6), 752-754 (2000); 2. Y. Koshka, M.S. Mazzola, Appl. Phys. Lett. 80, 4792-4764 (2002); 3. Y. Koshka, Appl. Phys. Lett. 82, 3290 (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 Hall effect and luminescence experiments we present evidence that a bound excited 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 behaviour 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, Washington 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 and crystallized ZnO samples annealed in dilute hydrogen (D2) gas. Using infrared (IR) spectroscopy, we have observed O-H and O-D stretch modes at 3292.3 cm^-1 and 2473.7 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 dissociation 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 calculations 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, IR spectroscopy and hydrogen effusion measurements. In state-of-the-art nominally undoped ZnO single crystals six local vibrational modes were observed at 2824, 2890, 2918, 2948, 2986, and 3065 cm^-1. While the six vibrational modes below 2850 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. 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 to 3x10^21 cm^-3 for polycrystalline ZnO.
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. Hydrogen atom, 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 structure will be explained as deduced from spectroscopic data. About 0.1 of the signal measured by XPS of our ZnO deposited film is obtained from OH-groups at the surface, the bulk and at grain boundaries. Annealing of films results in a conversion of (OH)2 to ZnO and water. Time dependent binding energy shifts in Photoemission data are used to determine the role of Hydrogen. Different binding sites and surface terminations will be discussed with respect to the energetics in the interface and the surface of the TCO.


ZnO contains a considerable amount of Hydrogen. Beside the intrinsic defect chemistry H 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 structure will be explained as deduced from spectroscopic data. About 0.1 of the signal measured by XPS of our ZnO deposited film is obtained from OH-groups at the surface, the bulk and at grain boundaries. Annealing of films results in a conversion of (OH)2 to ZnO and water. Time dependent binding energy shifts in Photoemission data are used to determine the role of Hydrogen. Different binding sites and surface terminations will be discussed with respect to the energetics in the interface and the surface of the TCO.

Highly Stable Hydrogenated Ga Doped ZnO Films. Satoshi Tagaka 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 present investigation, 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 pressures (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 H2/Ar gas mixture (H2/Ar-films). Secondary ion mass spectroscopy 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 hydrogen incorporated in the films was not sufficient to provide a reliable identification of 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 the H2/Ar-films was affected by 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 P H2O between Ar and H2/Ar-films.

Vibrational Signatures of Hydrogen in Semiconductors. Suktir Limpijummong, School of Physics, Institute of Science, Suranaree University of Technology, Nakdon 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. We 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 along with a very efficient way of calculating the harmonic approximation 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 of hydrogen (the bond center 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 atomic structure. We will also present an abinitio version of calculation of 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.


Effect of hydrogen doping to zinc oxide (ZnO) was investigated by using inductively coupled thermal plasma under pump-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, polycrystals and ZnO phosors with native or extrinsic luminescence centers. Some of the samples were prepared by irradiation of deuterium instead of hydrogen, so that concentration of hydrogen (deuterium) by ion mass spectroscopy could be easily measured. 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 giving yellow luminescence originated in D-A pair transition, the effect of hydrogen doping was complicated. Namely, the profile of the yellow band strongly depended on the concentration of hydrogen introduced by the plasma treatments. Details will be discussed at the conference site.

Electronic Conduction in a Nanoporous Crystal, 12CaO·7Al2O3 Doped with H- Ion. Katsuro Hayashi1, Masahiro Hirano1 and Hideo Hosono1, 2ERATO, Japan Science and Technology Agency, Kawasaki, Japan; 3Materials 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·7Al2O3 (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·cm-1). Upon a illumination of ultraviolet light (4 eV), the C12A7:H was converted into an electronic conductor with 0.3 S·cm-1 at 300 K. The conductive state remained persistently after the illumination because of the electronic recombination to the ground state level. During the illumination we created at empty cages by capturing photo-release electrons from H- ions, and the captured electrons hop among cages [3]. Restoration to the insulator occurred when the conductive sample was heated at more than 350°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 0.1-0.3 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).

First principles predictions of H sites in rutile. Simon W. deLeeuw1, Marina V. Koudracheva1 and Nicholas M. Harrison1. 1DCT, Delft University of Technology, Delft, Netherlands; 2Chemistry, 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-atoms 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 TiO2 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 a variety of experimental techniques. Of particular interest is the behaviour 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 experiments with different models, it has been proposed. However, none of the existing models is entirely
satisfactory. Here H-site in rutile structured titanin has been
considered in an ab initio study. High quality first principle
calculations were used to determine the preferred adsorption
sites for hydrogen on H-insertion in pure TiO2 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 Poster Session 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 Tartarin1,2, Laurent Escotte1,2, Mattia Borgarino3, Robert
Plana1,2 and Jacques Graffeuil1,2; 1CISTM Team, LAAS-CNRS,
Toulouse, France, 2Paul Sabatier University, Toulouse, France, 3University of Modena, Modena, Italy.

One of today’s challenges to enable the improved electrical
performance 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 (ambient
atmosphere, or associated with AsH3-VPE, AsCl3-VPE for example in
GaAs based devices). Hydrogen has already been investigated for many technologies Si or GaAs based (CMOS, FET,
HEMT, PHMET 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+, H2, H2O, or associated with impurities (Ge-H, B-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 and dynamic characteristics 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
GaPn) on the electrical behavior associated with hydrogen : low
frequency noise measurements will be performed in the range of 200
Hz to 100 kHz. The noise spectra evolution (current and voltage
noises 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 stockling
conditions (temperature and biasing of the devices) leading to
different functions of the static and high frequency noise measurements, associated with static and dynamic S parameters measurements will lead to the same conclusions about the hydrogen effects. Hydrogen content changes breaking, and diffusion of H4 towards the extrinsic surface of the device have been observed. Sealed devices have 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 Alquier1,
Esidor Ntoenok2, Chang Long Liu1,2, A Vengurlekar1 and S.
Ashok1; 1Laboratoire de Microelectronique de Puissante (LMP),
Tours, France, 2CERI-CNRS, Orleans, France, 3Department 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, C111, C2 silicon wafers doped at 1x1015 and 1x1018 cm-2 were used as substrates for this study. Helium
implantation was performed at room temperature at an energy of 100
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 Anneal (FA) was performed at 800°C for 1h to form the cavity band. During the FA
step, one set of the samples was contaminated by Copper.
Cross-sectional transmission electron microscopy (XTEM) and
Secondary Ion Mass Spectrometry (SIMS) measurements were
done 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 species 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 ZnxCd1-xHlg1-yTe is discussed
as a material alternative to world-wide known HgCdTe due to the
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-induced properties of the samples. H-ray diffractions and SEM investigations demonstrated the as-grown films were of
multicrystalline structure with thickness of 2 - 8 microns. Measurements of current-voltage characteristics carried out at the room temperature exhibited exponential form typical for barrier-like structures with large resistance series under both forward and reverse directions of applied electric field. The films demonstrated no sufficient
photosensitivity properties. The hydrogen treatment was performed 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 improvement of photosensitivity in visibile and near-IR spectral ranges. Data of numerical analysis and simulation of results are also available.

H4.4 Hydrogen Density-of-States Distribution in Compensated
Polycrystalline Silicon Thin Films. Rosari Saleh1, Norbert H
Nickel1 and Karsten Brendel, 1Department of Physics, Universitas
Indonesia, Depok, Indonesia, 2Department of Photovoltaics,
Hahn-Meitner Institut, Berlin, Germany.

Excimer laser crystallization is a well established method to produce
polycrystalline silicon (poly-Si) from amorphous silicon (a-Si) followed by
hydrogenation. Hydrogenation is widely used to modify the energy levels in polycrystalline silicon. In this paper we investigate hydrogen treatment of films produced by pulsed-YAG laser excimer excimer laser crystallization of hydrogenated amorphous silicon (n-Si:H). Since n-Si:H contain considerable amount of hydrogen laser crystallization has to be performed in a step-by-step procedure to avoid explosive outgassing of hydrogen and destruction of the film. We use low frequency noise measurements to study the hydrogen diffusion and hydrogen density distributions in polycrystalline silicon thin films. The hydrogen density of states is determined by the effusion spectra broadening and the influence of hydrogen on the density of states distribution is derived for samples prior to and after hydrogenation. In this paper we present hydrogen treatment and diffusion during step-by-step crystallization procedure in 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 a 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. While the diborane and phosphine is at equal levels, 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.
Silicon By Santo Martinuzzi and Olivier Palais Laboratory TECSEN - University of Marseilles, 13397 Marseille Cedex 20, France Tel. (33) 491298149; Fax. (33) 4912989852; e-mail: santo.martinuzzi@univ-u-bmr.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. This 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 induced current (LIC) 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 104 cm-2, respectively. Comparison 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 where 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 both samples, TiOx it is found that the recombination velocity of L increases by 80% in the SiN-H covered samples (i.e. from 0.14 to 0.26 mm). Lifetime 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.

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. A very strong bond between H and N is evidenced 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 iso-impurity level whose effective concentration vanishes at high H doses in a self-termination mechanism that has the optical, transport, and morphological properties of the (InGa)As host alloy. The band-gap increases, the electron effective mass decreases, the exciton binding energy increases, and the refractive index parameters change 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 GaP(N), 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. Infused absorption measurements support the formation of di-hydrogen complexes in both hydrogenated (InGa)(AsN) and GaP(N), as predicted by the theory. However, these measurements 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 impurities. Hydrogenation 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 quasirectband 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 common-anion nitrides are unable to answer. Here we show that N can qualitatively alter the electronic behavior of hydrogen: In GaAsN, an 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 some 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, GaAsN exhibits a giant photocurrent and red-shift of the optical absorption, a reduction of the lattice constant, and an increase of the effective electronic 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 GaAsN showing that the formation of N-H2* complexes explains all three effects. We also discuss the large, composition-dependent gap bowing (with at least a linear dependence b(x)≈5.3 - 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).
deposition and subsequent processing also allows H to be introduced into the bulk of the solar cell, where it passivates defects and impurities and lowers the solar cell efficiency. In a reactive ion etch, a commercial solar cell processing sequence, a thin SiN:H film 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 fired through 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 for two cases: (i) as-deposited with 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 Pelle Rech 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) has been employed to calculate the energy of formation for four types of hydrogenated silicon tetrahedra of the form Si-Si-H-n (n= 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-Si-H- n tetrahedra as a function of the hydrogen concentration was calculated. According to this distribution, the formation energy of hydrogenated amorphous silicon (s-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: s-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 by phase transitions 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 instabilities 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 Kamiura1, Namura Bao1, Kimihito Sato1, Kazuhiro Fukuda2, Yasuaki Iwagami1, Yoshifumi Yamashita1 and Takeshi Ishiyama2, 1Faculty of Engineering, Okayama University, Okayama, Japan; 2NEC 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-H2) 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 is slightly higher, the 250 K, while the Pt-H2 complex occurs as low as 80 K for the Pt-H2 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, the 250 K, while the Pt-H2 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-occupied charge state of the Pt-H2 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-H2 complex, the two hydrogen atoms are directly bonded to the platinum atom, and the defect reorientation occurs due to switching but only the rotation of the whole Pt-H2 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 are released outward, probably retarding their motion for the reorientation.

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


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—(110) (2072.5 cm-1) defects in 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—(110) is two orders of magnitude longer, 295 ps. The temperature dependence of the lifetime of H2* is governed by TA phonons, while HV—(110) is governed by LA phonons. The observed large disparity in measured lifetimes is unexpected based on simple theories and is 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 bond 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 7 9 cm-l modes. This work was supported in part by DOE through the DE-FG02-99ER45781 (C.W.M. and Y.U.), ONR (C.W.M. and V.U.), NSF through grants DMR-00-76927, DMR-02-42316 (C.W.M.), and the Thomas F. and Manley O. Jeffress Memorial Trust through grant J-545 (C.W.M.). 1. Luepke G., Toik N. H., and Feldman L. C. (2003) J. Appl. Phys. 93, 2316-2335. 2. Holbec J. D. et al. (1993) Phys. Rev. Lett. 71, 875-878


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 H/D isotope effect. It was later used in the measurement 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
found in Fig. 2 that the absorbance (magnitude) of the Si-Si TO phonon mode after hydrogen anneal (See Fig. 1). This exlusively suggests that there is energy coupling from the Si-Si vibrational mode to the Si-D bending mode which should be the Si-H bonding mode. Fig. 2 shows the FTIR spectra of a Si02/Si sample with oxide thickness of 32 nm before and after deuterium anneal. The peak at 2100 cm-1 appears 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 R. L. V. L. 2 C. G. Van de Walle and W. B. Jackson, J. Appl. Phys., 92, 2526 (1996). 3 C. C. Van de Waal and W. B. Jackson, Appl. Phys. Lett., 69, 2441 (1996).

2:15 PM H7.2 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 TECESEN, University of Marseille, 13397 Marseille Cedex 20 France Tel. (33) 491298434; Fax (33) 491288802; e-mail: santo.martinuzzi@univ-mrs.fr It was suggested that highly concentrated hydrogen behave as a shallow donor in crystaline silicon. It was also reported that hydrogen nanobubbles can be formed, which are transformed in nanowires by electrochemical technique. 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 2x1015 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 p-n junction is formed, and 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 shows the formation of nanobubbles. IV and C-V curves confirm the formation of a N type layer in which the donor concentration is about 5x1017 cm-3; the junctions are graduated as 1/C vs reverse voltage plots are linear. The investigation of the structural properties suggests that the N-type layer 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 slightly etched. Square surface resistance leads to a doping level around 1017 cm-3 and confirms the presence of a 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 nanovacancies 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 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 source of hydrogen trapped 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 Chen1, Paul Chu1, Tobias Franz Hochbauer1, Jung Kun Lee2, Michael Nastasi3, Dan Mihai Buca3, Siegfried Mantl4, Roger Leo5, Matty Cigunas6, James W. Mayer6, Ming Cai6, Blair Schmidt6 and Ming Chen6; 1University of Hong Kong, Hong Kong, China; 2Los Alamos National Laboratory, Los Alamos, New Mexico; 3Institut fur Schicht- und Ionentechnik, Julich, Germany; 4IMEC, Leuven, Belgium; 5Arizona State University, Arizona, Arizona; 6University of California at San Diego, San Diego, California.

Defects, strain and impurities intentionally introduced into Si wafers were found to trap H atoms within a plasma 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 hydrogenation. 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 microscopy with Nomarski 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 the 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
Borcon 2020 (Moscone West)

3:15 PM H8.1 Molecular Simulations of Hydrogen Storage in Single Walled Carbon Nanotubes: Size and Temperature Dependence, Hansong Cheng1, Alan C. Cooper2, Guido P. Pez3, Milen Kostov4, Milton Cole2 and Steve Stuart3; 1Air Products & Chemicals, Inc., Allentown, Pennsylvania; 2Department of Physics, Pennsylvania State University, University Park, Pennsylvania; 3Dept 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 Chevalier1, Zephirin Teukiam1, Cecile Saguy2, Rafi Kalish2, Catherine Cytermann2, Francois Jomard2, Annie Tromson-Cari1, Dominique Ballstadts3, James E. Butler3, Celine Brial3 and Alain Denœvilles4; 1Laboratoire de Cristallogenie, CNRS, Meudon, France; 2Laboratoire de 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 the homopitaxial 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-cm-1 and 430 cm2/Vs respectively at 300 K. The n-type conductivity is governed by the ionization of donors with an 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 homoeptaxial 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 Ballutaud¹, Annick Broutry-Forveille¹, Jean-Michel Laroche³ and Nathalie Simon¹;
¹LPSC, CNRS, Meudon cedex, France; ²LPSC, CNRS, Meudon, France; ³LPSC, CNRS, Meudon, France; ⁴IREM, 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 10¹⁹ cm⁻³. This paper deals with new data on the diffusion and thermal stability properties of hydrogen (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] = 10¹⁹ and 10²⁰ 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 electrochemical measurements (I(V) and capacitance measurements) in 2M H₂SO₄ medium containing the Ce⁴⁺/Ce³⁺ 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. Theye, C. Mer, D. Tromson and P. Bergonzo, Diamond and related materials, 10 (2001) 405-410.