Wednesday Afternoon, November 6, 2002

Electronic Materials and Devices
Room: C-107 - Session EL+SS+SC-WeA

Semiconductor Film Growth and Oxidation
Moderator: R.K. Ahrenkiel, National Renewable Energy Laboratory

2:00pm **EL+SS+SC-WeA1 Scanning Tunneling Microscopy and Spectroscopy of Gallium Oxide and Indium Oxide Deposition on GaAs(001)-(2x4)**, ***M.J. Hale***, *J.Z. Sexton,* University of California, San Diego, *S.I. Yi,* Applied Materials, *D.L. Winn, A.C. Kummel*, University of California, San Diego

The surface structures formed upon deposition of Ga$_2$O and In$_2$O onto the technologically important As-rich GaAs(001)-(2x4) surface have been studied using scanning tunneling microscopy (STM) and spectroscopy (STS), low energy electron diffraction (LEED), and density functional theory (DFT) calculations. At submonolayer coverage, the initial bonding sites are different for Ga$_2$O and In$_2$O adsorptions due to the different activation barriers for the two oxides to chemisorb at various sites onto the surface. In$_2$O initially bonds in the trough between the arsenic dimer rows, whereas Ga$_2$O first inserts into the top layer arsenic dimer rows. Conversely, at elevated surface temperatures, both Ga$_2$O and In$_2$O form a crystalline monolayer. Both oxides form crystalline (2x1) surface reconstructions that are electronically unpinned: there are no states within the band gap. Although both oxides form a (2x1) surface reconstruction, the surface structures differ. At monolayer coverage the Ga$_2$O/GaAs surface has a much larger step density while the In$_2$O/GaAs surface shows a broad distribution of row oxide spacing. The DFT calculations confirm the observed surface structures and show that both oxides form unpinned surfaces because the bonding to these oxides restore the charge on the first and second layer As and Ga atoms to near bulk values.

2:20pm **EL+SS+SC-WeA2 Structure-Sensitive Oxidation of the Indium Phosphide (001) Surface**, ***G. Chen***, University of California, Los Angeles, *S.B. Visbeck,* Siemens & Shell Solar Gmbh, Germany, *D.C. Law*, University of California, Los Angeles, *R.F. Hicks*, University of California, Los Angeles; AVS fellow

Abstract The properties of oxide/semiconductor interfaces significantly affect the performance of indium phosphide-based electronic and photonic devices. In this study, indium phosphide films were grown on InP (001) substrates by metalorganic chemical vapor deposition (MOCVD). Then the samples were transferred to an ultrahigh vacuum system, and annealed at 623 and 723 K to produce the (2x1) and delta(2x4) reconstructions with phosphorus coverages of 1.0 and 0.125 ML, respectively. These structures were exposed to unexcited molecular oxygen, and the reaction characterized by X-ray photoelectron spectroscopy (XPS), reflectance difference spectroscopy (RDS) and low energy electron diffraction (LEED). At 298 K and above, the In-rich InP (001) surface rapidly oxidizes upon exposure to O2. The oxygen dissociatively chemisorbs onto the delta (2x4), inserting into the In-P back bonds and the In-In dimer bonds. By contrast, the P-rich (2x1) reconstruction does not absorb O2 up to 500,000 L at 298 K. Above 453 K, the (2x1) becomes reactive with oxygen inserting into both the In-P back bonds and the phosphorus dimer bonds. Based on these results, we conclude that the oxidation of indium phosphide (001) is highly structure sensitive. This means that the oxide/semiconductor interface formed on InP devices can vary widely depending on the process history.

2:40pm **EL+SS+SC-WeA3 The Addition of Sb and Bi 'Surfactants' during GaN Growth by Metal Organic Vapor Phase Epitaxy**, ***T.F. Kuech***, *L. Zhang, H.F. Tang, J. Schieke, M. Mavrikakis*, University of Wisconsin - Madison **INVITED**

The addition of certain impurities has been shown to modify the growth behavior of several lattice-mismatched epitaxial semiconductor systems, most notably SiGe-Si. Of the many impurities studied, antimony and bismuth have been shown to act as 'surfactants' during SiGe epitaxy altering the critical thickness and surface morphology. Such impurities have not been studied in detail in other systems, such as GaN and related materials. We present data on the role and effect of isoelectronic centers, Sb and Bi, on the structure and properties of GaN epilayers during metal organic vapor phase epitaxy. The Sb addition slightly improved the optical and structural properties of GaN epilayer at a low level of Sb incorporation. The addition of Sb resulted in changes in the GaN surface morphology, which was further explored by the lateral overgrowth epitaxy technique through the changes in the growth rates and the facet formation. The presence of Sb in the gas phase greatly enhanced the lateral overgrowth rate and altered the formation of the dominant facets. While Sb altered the growth facet present during LEO, only a small amount of Sb was incorporated into the GaN, suggesting that Sb may be acting as a 'surfactant' during the GaN MOVPE growth. Sb addition produces surface conditions characteristic of a Ga-rich surface stoichiometry indicating both a possible change in the reactivity of NH$_3$ and/or enhanced surface diffusion of Ga adatom species. Other changes in the surface chemistry and transport were studied by the use of state-of-the-art periodic self-consistent DFT calculations. Bismuth has also been studied as a surfactant to alter the surface chemistry and defect structure during the GaN growth. Bi addition resulted in a decrease in surface roughness as measured by atomic force microscopy while no significant Bi was incorporated over a broad range of gas phase concentrations.

3:20pm **EL+SS+SC-WeA5 Surface Reaction Study of Tungsten Nitride Precursors Decomposition on Si(100)-(2 x 1)**, ***Y.-W. Yang***, Synchrotron Radiation Research Center, Taiwan, *J.-B. Wu, Y.-F. Lin, H.-T. Chiu*, National Chiao-Tung University, Taiwan

Reaching an atomic-scale understanding of the surface reaction pathways followed by precursors during MOCVD thin-film growth is a daunting task. We have been studying the transition metal nitride growth on both Cu and Si surfaces. Here, we report a thermal decomposition study of WN precursor on Si(100)-(2 x 1) using TDS and synchrotron-based XPS techniques. The studied precursors are (t-BuN)$_2$W(NHBu-t)$_2$ and (t-BuN)$_2$W(NEt$_2$)$_2$ and their structural characteristics consist of the presence of both W-N and W=N bonds and either the presence or the absence of β-H that influences the thermolysis of the precursors. XPS data show that the metallic tungsten already forms for a submonolayer dose of the precursors at room temperature, suggesting the complete abstraction of the amine ligands by the dangling bonds on Si(100) surface. The evolution of hydrocarbon and amine species during the pyrolysis are followed by the TDS and the results suggests the similarity to the amine adsorption on Si(100). High temperature annealing produces silicon carbides and silicon nitrides. In stark contrast, no metallic tungsten is ever formed during the pyrolysis of the same precursors on Cu(111) and the formation of tungsten nitride is secured through the gradual loss of excessive amine ligands. Based on these results, possible surface reaction mechanism and the structural effect of the precursor are to be discussed.

3:40pm **EL+SS+SC-WeA6 Thermal Decomposition and Desorption Study of Tetrakis(diethylamido)zirconium(TDEAZr) on Si(100) for MOCVD and ALD of ZrO$_2$**, ***K. Yong***, *J. Jeong, S. Lim*, Pohang University of Science and Technology, Korea

Tetrakis(diethylamido)zirconium (TDEAZr) is used as a zirconium-precursor to deposit zirconium oxide by metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD). Surface reaction study of precursors can aid in describing the kinetics of MOCVD and ALD. Surface reaction and desorption of TDEAZr (Zr(N(C$_2$H$_5$)$_2$)$_4$) on Si(100) were studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). During TPD, ethylethyleneimine, diethylamine, acetonitrile, ethylene and hydrogen desorbed as main decomposition products of diethylamido, which was chemisorbed on Si(100) through the scission of zirconium-diethylamido bond in TDEAZr. The formation of silicon-carbide and silicon-nitride was observed on the surface after TPD runs. These results indicated that a complete decomposition of diethylamido also proceeded. A reaction pathway model of TDEAZr/Si(100) was proposed. Also, the coadsorption of TDEAZr with water on Si(100) was studied.

4:00pm **EL+SS+SC-WeA7 Reactions of Organosulfur Compounds with Si(100) for Chemically Controlled Epitaxy of II-VI Semiconductors on Si(100)**, *Z. Zhu, A. Srivastava,* ***R.M. Osgood Jr.***, Columbia University

The growth of silicon-based quantum devices requires precise control of ultrathin Si/wide-bandgap-semiconductor/Si heterostructures. We have investigated the initial stages of chemistry-based low-temperature epitaxy using organosulfur precursors. The approach uses the chemical insight gained from organic functionalization of Si.[1] Thus we have studied the reaction of (CH$_3$S)$_2$, CH$_3$SH, (CH$_3$)$_2$S with Si(100) at room temperature, under UHV conditions for atomic layer growth of functional-group-terminated sulfur on Si(100). This reaction is the first step in the layer by layer self-limiting epitaxy of ZnS, for example, on Si(100). AES studies indicate that each of these organosulfur compounds have different reaction kinetics with the Si(100) surface and reach different levels of sulfur saturation coverage. The differences observed for (CH$_3$S)$_2$ and (CH$_3$)$_2$S reactions have been shown to be explained by the relative bond strengths and the number of sulfur atoms present in the adsorbate molecule. Our TPD studies from 25-825°C show no sulfur-related desorption. Instead AES studies confirm that sulfur atoms remain on surface until ~ 525°C and then diffuse into the Si(100) substrate upon further annealing. TPD studies also indicate evolution of H_2 at temperatures similar to those obtained for H_2 desorption from saturated atomic H on Si(100). In our studies methyl desorption also occur at T > 650° C, temperatures higher than that of H_2 desorption. The amount of m/e = 15,16 fragments is dependent on the organosulfur compound examined. Chemical strategies are now being explored to grow layers of Zn on methyl-terminated sulfur layer as shown in the epitaxy using sequential H_2S/dimethyl cadmium dosing on ZnSe.[2]

[1] Bent SF, J Phys Chem B, 106(11): 2830-2842, 2002.

[2] Luo Y, Han M, Slater DA, Osgood RM, J Vac Sci Tecnol A 18(2): 438-449, 2000.

4:20pm **EL+SS+SC-WeA8 Kinetics and Mechanism of Adsorption and Ultrathin Oxide Growth by Ozone on Si(100)2x1 and Si(111)7x7**, ***K. Nakamura***, *A. Kurokawa, H. Nonaka, S. Ichimura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Ozone is one of the promising oxidants to synthesize an ultrathin oxide film on silicon surfaces for the near-future MOSFET because of rapid oxidation rate at low substrate temperature, negligible thickness of structural transition layers in the oxide film, etc.[1] However, to control the thickness of an oxide film precisely and accurately,[2] kinetics and mechanism of initial oxide growth must be clarified. Thus, in this paper, we discuss chemistry of adsorption and ultrathin oxide growth by ozone on silicon surfaces. Si(100)2x1 and Si(111)7x7 were exposed to highly concentrated (>80%) ozone gas and monitored by x-ray photoelectron spectroscopy (XPS) and second harmonic generation (SHG). Kinetic analysis has suggested that initial dissociative adsorption of ozone on Si(100)2x1 and Si(111)7x7 proceed with the mechanism of leaving only one oxygen atom on the surface and of desorbing the other two, possibly, as a molecular oxygen. This adsorption, in contrast to that of oxygen, was featured with structure-insensitive kinetics, no activation barrier for the dissociation, and high sticking probability close to unity. After the adsorption was completed, first three oxide layers were synthesized by random adsorption of oxidant species on each layer in the consecutive manner. The formation of three layers led to the further growth of an oxide film with ozone with linear growth kinetics, but not with molecular oxygen. Each of these initial ozone-oxide layers has distinctively different activation energy for its growth: they were estimated 0 eV, 0.34 eV, 0.68 eV, and 0 eV for first, second, third, and above fourth layers on Si(100), respectively, enabling accurate control of the thickness of an oxide film.

[1] K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, J. Vac. Sci. Technol. A 17 (1999) 1275.

[2] K. Nakamura, A. Kurokawa, and S. Ichimura, Jpn. J. Appl. Phys. 39 (2000) L357.

4:40pm **EL+SS+SC-WeA9 Stress-induced Dissociative Chemisorption of Oxygen on Si(001)**, ***M. Yata***, *Y. Uesugi-Saitow*, National Institute for Materials Science, Japan

We have investigated the role of surface stress in dissociative adsorption process of O_2 on Si(001)-2x1by supersonic molecular beam technique. The tensile stress was externally applied on the surface along[110] direction. The Si(001)-2x1surface reconstructs by dimerization of atoms in adjacent rows. In areas of the surface separated by an odd number of monoatomic steps the orientation of the dimer bonds is rotated by 90° giving 2x1 and 1x2 orientational domains. Their domain populations are changed to relax the stress at the surface and the kinetics of the change depend on the surface temperature.[1] Below room temperature, the domain populations were almost equal during the molecular beam experiments. Two co-existing dissociation channels are seen, a trapping-dissociation channel at low translational energy of incident O_2 and a direct activated channel at high translational energy.[2] In case of the trapping-dissociation, O_2 molecule is trapped to a precursor state and undergoes a kinetic competition between desorption and dissociation. We have estimated a difference in activation barrier heights between desorption and dissociation at 30 meV. The initial dissociative sticking probability for low translational energy of incidence increases as the tensile stress increases. This indicates that trapping-mediated dissociation is enhanced by the stress. We have found that the difference in the activation barrier heights between desorption and dissociation decreases as the stress increases. We will discuss the change of dissociation dynamics with the tensile stress in detail.

[1] F. K. Men, W.E. Packard and M. B. Webb, Phys. Rev. Lett. 61(1988) 2469.

[2] B. A. Ferguson, C. T. Reeves and C. B. Mullins, J. Chem. Phys.110(1999)11574.

5:00pm **EL+SS+SC-WeA10 Direct Detection of D_2O and D_2 on D/Si(111) Surfaces under O Atom Exposures**, ***F. Rahman***, *F. Khanom, A. Aoki, S. Inanaga, A. Namiki*, Kyushu Institute of Technology, Japan

Initial oxidation stage of D/Si(111) surfaces by atomic oxygen (O) have been studied from the absorption point of view. O/D/Si(111) co-adsorbed surfaces were prepared by various O exposure on 1.25ML D/Si(111). TPD measurement shows nearly 50% reduction of D adatoms from the surface for 2 min O exposure indicating the D adatoms abstraction by incident O atoms. Measurement of desorbing species have been done with a QMS during O exposures on the 1ML D/Si(111) surface for various surface temperatures (T_S). D_2O as well as D_2 molecules were observed. Rate curves of both species show an initial rate jump and then a gradual increase having a peak, which is followed by a nearly exponential decay with exposure time. Both D_2O and D_2 rates vs. T_S curves show similar line shape to the similar plot of D_2 rates vs. T_S curve obtained for the reaction system of H + D/Si(111) --> D_2. In a previous work, the later reaction was understood as due to the so-called β_2 TPD desorption arising from a dideuteride phase. Therefore, we consider that the O induced D_2 formation proceeds along the same mechanism as for the β_2-channel TPD. Regarding D_2O formation, it is significant and interesting since the reaction takes place as a result of picking up two D adatoms by single O atom upon collision. We will propose a possible mechanism to explain the O-induced D_2O formation on the D/Si(111) surfaces.

Authors Index

Bold page numbers indicate the presenter