Wednesday Afternoon, November 9, 2016

Surface Science Room 104D - Session SS+AS+EM-WeA

Semiconductor Surfaces and Interfaces

Moderator: Andrew Gellman, Carnegie Mellon University

2:20pm SS+AS+EM-WeA1 Adsorption of Triethylenediamine on Si(100)-2×1 Surface via N-Si Dative Bonding and C-N Dissociation, Jing Zhao, M. Madachik, University of Delaware; K. O'Donnell, Curtin University, Australia; O. Warschkow, University of Sydney, Australia; L. Thomsen, Australian Synchrotron, Australia; G. Moore, S. Schofield, University College London; A.V. Teplyakov, University of Delaware

The functionalization of silicon surfaces with thin layers of organic materials is an important area of studies with current and potential in microelectronics, catalysis, applications and bio-sensing. Triethylenediamine (also known as 1,4-diazabicyclo[2.2.2]octane, or DABCO) presents an interesting case study for silicon functionalization because of its symmetric structure with two x nitrogen atoms in tertiary amine configuration. Each of these atoms could potentially form a dative bond with a clean Si(100)-2x1 surface while the other may remain accessible for further modification. We applied infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) supported by density functional theory calculations (DFT) to investigate the reaction mechanism of triethylendiamine with a clean Si(100)-2×1 surface, focusing specifically on dative bond formation and C-N dissociation.

2:40pm SS+AS+EM-WeA2 Chemoselective Adsorption of Functionalized Cyclooctynes on Silicon, M. Reutzel, N. Munster, M.A. Lipponer, Philipps-Universität Marburg, Germany; C. Langer, Justus Liebig University Giessen, Germany; U. Hofer, U. Koert, Philipps-Universität Marburg, Germany; Michael Durr, Justus Liebig University Giessen, Germany

The adsorption of organic molecules on silicon surfaces has been subject of intense research due to the potential applications of organic functionalization of silicon surfaces in semiconductor technology. The high reactivity of the silicon dangling bonds, however, presents a major hindrance for the first basic reaction step of such a functionalization, i.e., chemoselective attachment of bifunctional organic molecules on the pristine silicon surface. Due to the high reactivity of the dangling bonds, each functional group of a bifunctional molecule adsorbs with an initial sticking coefficient close to unity and thus the final adsorption product will typically consist of a mixture of molecules adsorbed via different functional groups.

We overcome this problem employing cyclooctyne as the major building block of our strategy. Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, cyclooctyne derivatives with different functional side groups are shown to react on Si(001) selectively via the strained cyclooctyne triple bond while leaving the side groups intact. The origin of this chemoselectivity is traced back to the different adsorption dynamics of the functional groups involved. We show that cyclooctyne's strained triple bond is associated with a direct adsorption channel on the Si(001) surface, in contrast to most other organic molecules which adsorb via weakly bound intermediates. In these intermediate states, the molecules have a finite lifetime and are often mobile and free to rotate on the surface. This allows the bifunctional molecule to sample the surface with the strained triple bond during its finite lifetime in the trapped state and in consequence, bifunctional molecules with a strained triple bond as one functional group will end up with this group attached to Si(001) even if the initial interaction proceeds via the second functional group.

Chemoselectivity can thus be achieved even on the highly reactive Si(001) surface when exploiting the adsorption dynamics of the respective reaction channels.

3:00pm SS+AS+EM-WeA3 Compositions, Structures, and Electronic Properties of Grain Boundaries of Cu(InGa)Se₂, *Xudong Xiao*, Chinese University of Hong Kong INVITED

Polycrystalline semiconductors are important energy materials and the grain boundaries play crucial role in their electrical transport property. While in general grain boundary is detrimental, for Cu(InGa)Se₂ (CIGS), it was found that the grain boundary is benign to the electrical transport and a record solar cell energy conversion efficiency of 22.3%, the best among all thin film solar cells, has been achieved with a polycrystalline film. This peculiar benign behavior has attracted great attention in the materials

science community, unfortunately, even with tremendous effort, the mechanism of the benignity of CIGS grain boundary remains as an outstanding problem, mostly due to the lack of convincing experimental evidences.

We performed our study by design and prepare well controlled CIGS samples with two different Cu content. By careful treatment of the samples to remove artifacts, we used a combination of techniques, namely AFM, STM, and TEM, to probe at nanoscales the composition, structure, and electrical properties of the individual grain boundary in direct comparison to those of the individual grain interior. We discovered that the grain boundary in fact consists of a boundary layer of finite thickness in addition to the grain boundary surface/interface for the non Σ3 grain boundaries. This boundary layer has a definitive composition, structure, and electronic band, independent of the overall Cu content in the CIGS films. The observation of similar grain interior and similar grain boundary except the boundary layer thickness for the two samples with very different overall Cu content is indeed a surprising finding that has never been reported before. The band alignment between grain boundary and grain interior was discovered to be of type II with downward offset for both conduction and valence bands at grain boundary, well correlating to the local copper deficiency and structure. Our findings expressively support the type inversion and large hole barrier in this grain boundary layer, and establish a comprehensive mechanism for the suppression of carrier recombination therein.

4:20pm SS+AS+EM-WeA7 Thermal Self-limiting CVD Silicon and ALD Silicon Nitride Containing Control Layers on In_{0.53}Ga_{0.47}As(001)-(2x4), Si_{0.5}Ge_{0.5}(110), and Si_{0.7}Ge_{0.3}(001), Steven Wolf, M. Edmonds, T. Kent, K. Sardashti, University of California at San Diego; M. Chang, J. Kachian, Applied Materials; R. Droopad, Texas State University; E. Chagarov, A.C. Kummel, University of California at San Diego

Compound semiconductors with high mobilities such as InGaAs and SiGe are being employed in metal oxide semiconductor field effect transistors (MOSFETs) to increase transistor performance. However, these surfaces contain dangling bonds that can affect the surface Fermi level; thus, depositing a control layer via ALD or self-limiting CVD on multiple materials and crystallographic faces is required . Silicon uniquely bonds strongly to all crystallographic faces of InGa1-xAs, InxGa1-xSb, InxGa1-xN, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which can then be passivated by atomic hydrogen. Subsequently, the surface may be functionalized with an oxidant such as HOOH in order to create a terminating Si-OH layer, or a nitriding agent such as N₂H₄ in order to create an Si-Nx diffusion barrier and surface protection layer. This study focuses on depositing saturated Si-H_x and Si-OH seed layers via a self-limiting CVD process on InGaAs(001)-(2x4), and depositing a Si-Nx seed layer on Si_{0.5}Ge_{0.5}(110) and Si_{0.7}Ge_{0.3}(001) via an ALD process. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of these control layers on the various surfaces. A thin Si-H_x capping layer (2.5 monolayers) was deposited in a self-limiting CVD fashion on InGaAs(001)-(2x4) by exposing to Si₂Cl₆ at 350°C. This layer allows for multilayer silicon or Si-O_x growth by ALD through cyclically dosing Si_2Cl_6 with either atomic H or anhydrous HOOH. STM and STS measurements show the Si₂Cl₆ exposed InGaAs(001)-(2x4) surface is atomically locally ordered and has an unpinned surface Fermi level. Exposure to anhydrous HOOH at 350°C terminates the surface with Si-O bonds and does not lead to oxidation of substrate peaks. The HOOH treated surface then nucleates TMA at 250°C and ultimately further high-k gate oxide growth. MOSCAP device fabrication was performed on n-type InGaAs(001) substrates with and without a Si-H_x passivation control layer deposited by self-limiting CVD in order to determine the effects on C_{max}, frequency dispersion, and midgap trap states. Deposition of a SiO_xN_y diffusion barrier and surface protection layer was achieved on the Si_{0.5}Ge_{0.5}(110) and Si_{0.7}Ge_{0.3}(001) surfaces via an ALD process at 275°C through cyclically dosing Si₂Cl₆ and anhydrous N₂H₄. MOSCAP device fabrication was performed on Si_{0.7}Ge_{0.3}(001) with and without a SiO_xN_y passivation control layer to compare device performance. Ultimately, the Si-H_x passivation layer gave less frequency dispersion at flat band and a lower $D_{it},$ and the SiO_xN_y passivation layer yielded lower gate leakage and Dit when compared to the respective wet clean only devices.

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4:40pm SS+AS+EM-WeA8 Formation of Atomically Ordered and Chemically Selective Si-O-Ti Monolayer on Si_0.5Ge_0.5(110) for a MIS Structure via $H_2O_2(g)$ Functionalization, SangWook Park, J.Y. Choi, University of California, San Diego; E. Chagarov, University of California, San Diego; B. Sahu, S. Siddiqui, GLOBALFOUNDRIES; N. Yoshida, J. Kachian, Applied Materials; A.C. Kummel, University of California, San Diego

To overcome challenges when scaling down silicon-based complementary metal-oxide semiconductor (CMOS) devices, SiGe has received much attention due to its high carrier mobility and applications in strain engineering. Extremely thin oxides with appropriate band offsets can be utilized to form unpinned contacts on SiGe for a metal-insulatorsemiconductor (MIS) structure. The TiO₂ interfacial layer on Ge is known to form a MIS structure which reduces the tunneling resistance due to the nearly zero conduction band offset (CBO) between TiO2 and Ge. In this study, formation of TiO_x monolayer on SiGe(110) via $H_2O_2(g)$ functionalization was investigated using in-situ scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS). H₂O₂(g) was employed instead of the conventional H₂O(g) oxidant since H₂O₂(g) can form a uniform monolayer of -OH ligands on the surface without subsurface oxidation which should be ideal for forming the most stable possible interface which is a layer of Si-O-Ti bonds. STM verified that clean Si_{0.5}Ge_{0.5}(110) surfaces were terminated with both Si and Ge adatoms. STS measurements indicated that the Fermi level of clean Si_{0.5}Ge_{0.5}(110) surfaces was pinned near midgap between the valence and conduction band edges due to the half-filled dangling bonds of the adatoms. In order to passivate the dangling bonds, atomic H was dosed onto clean Si_{0.5}Ge_{0.5}(110) at 300°C which unpinned the Fermi level as demonstrated by STS. XPS analysis showed a saturation dose of H₂O₂(g) at 25°C left the Si_{0.5}Ge_{0.5}(110) surfaces terminated with a monolayer of both Ge-OH and Si-OH sites. STS indicated that the Fermi level on H₂O₂(g) dosed Si_{0.5}Ge_{0.5}(110) was shifted to near the valence band edge due to the formation of surface dipoles induced by hydroxyl bonds. Tetrakis(dimethylamido)titanium (TDMAT) or titanium tetrachloride (TiCl₄) was subsequently dosed onto hydroxyl-terminated Si_{0.5}Ge_{0.5}(110) at 25°C forming Ti bonds on surface. Both TDMAT and TiCl₄ dosed Si_{0.5}Ge_{0.5}(110) surfaces were annealed at 300°C and XPS verified that the Ti-O bonds were totally transferred from Ge atoms to Si atoms forming exclusively Ti-O-Si bonds on Si_{0.5}Ge_{0.5}(110) surfaces consistent with the strong bonding between Si and oxygen pulling Si atoms toward the surface to bond with oxygen while pushing Ge atoms into the subsurface during the annealing. STM demonstrated an ordered TiO_x monolayer was formed with a row spacing which doubles the spacing of adatoms on clean $Si_{0.5}Ge_{0.5}(110)$. In addition, STS indicated a TiO_x monolayer on SiGe(110) was unpinned and therefore can serve as an ultra-thin insulating layer for a MIS structure.

5:00pm SS+AS+EM-WeA9 The Effect of Ultrasonic Treatment (UST) on the Defect Structure of the Si–SiO₂ System, Daniel Kropman, T. Laas, Tallinn University, Estonia

The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO₂ system by means of electron spin resonance(ESR),selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=1.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers.Defect density at the interface grows with an increase of US wave intencity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the $Si{-}SiO_2$ interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

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[2]D.Kropman,S.Dolgov.Physica satatus Solidi (c) v.9,issue 10-11,pp.2173-2176,2012.

5:20pm SS+AS+EM-WeA10 Adsorption of C₆₀ Buckminster Fullerenes on a Carbon-free Hydrazine-modified Silicon Surface, *Fei Gao*^{*}, *A.V. Teplyakov*, University of Delaware

Buckminster fullerene C₆₀ was used as a model to understand the attachment chemistry of large molecules on amine-terminated semiconductor surfaces. The resulting interface may serve as a foundation for devices in such fields as solar energy conversion, biosensing, catalysis, and molecular electronics. In this work, a monolayer of buckminster fullerenes C₆₀ was covalently attached to silicon surfaces using an efficient wet chemistry method. The starting chlorine-terminated Si(111) surface was initially modified with hydrazine to produce NH-NH functionality. Then the C₆₀ fullerenes were reacted directly with this surface. The chemical state and surface topography of the C60-modified surface were characterized by surface analytical spectroscopic and microscopic methods, including X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM). The experimental results were also supported by computational investigation, density functional theory (DFT) calculations, that were performed to predict core-level energies of surface species formed and to propose the possible mechanism of surface reactions.

5:40pm SS+AS+EM-WeA11 Passivation of SiGe Surfaces with Aqueous Ammonium Sulfide, Stacy Heslop, A.J. Muscat, University of Arizona

Ge and SiGe are promising materials for future p-type metal-oxide semiconductor field effect transistors (MOSFETs) due to their higher hole mobilities and narrower bandgap compared to Si. In contrast to silicon, Ge and SiGe readily oxidize in ambient air forming nonstoichiometric Ge oxides that are detrimental to the electrical performance of the device. One approach is to remove these oxides and passivate the surface. SiGe with molar ratios of 25 and 75% Ge were treated with aqueous ammonium sulfide, (NH₄)₂S, to deposit sulfur. The composition of the surface was measured using x-ray photoelectron spectroscopy (XPS) as a function of concentration and pH. The (NH₄)₂S concentration was varied from 3 mM to 3 M, and the pH was varied from 10 to 8 using HCl and HF. Film thicknesses were measured with spectroscopic ellipsometry.

A fresh SiGe starting surface was produced by immersing in SC-1 (1:1:500 v/v) to form oxides and stripping the oxides using HF:HCl:H₂O (1:3:300 v/v). In the case of SiGe 25%, sulfides were not detected based on the S 2p XPS state for surfaces treated with (NH₄)₂S (Figure 1a). The oxygen coverage increased with increasing (NH₄)₂S concentration, forming primarily SiO₂ and a small coverage of GeO. The surface was enriched in Si and oxidized, and there was not enough Ge atoms exposed for S to bond to. HCl and HF were added to remove the Si and Ge oxides that formed. The addition of HCl and HF resulted in the deposition of sulfides on SiGe 25% (Figure 1b). The Si/Ge peak area ratio after oxide removal was 1.7. After immersion in 30 mM $(NH_4)_2S$ at a pH of 10 the surface composition was unchanged (Si/Ge=1.7). For the same (NH₄)₂S concentration at a pH of 8 the surface was only slightly enriched with Si (Si/Ge=2.4). Overall, (NH₄)₂S is not an effective passivation reagent for Si-rich SiGe surfaces due to the lack of S deposited and the undesirable oxides which form during processing. By dropping the pH to 8, less than a monolayer of S is deposited but oxides still remain. In contrast, SiGe 75% did not oxidize as a function of the (NH₄)₂S concentration. Sulfur was detected based on the S 2p XPS state and the S coverage was independent of (NH₄)₂S concentration. The sulfur thickness increased from about 2.3 Å for (NH₄)₂S (30 mM or 1:100 v/v) at a pH of 10 to 3.4 Å for the same (NH₄)₂S dilution at a pH of 8 (Figure 1c and d). These film thicknesses were approximated from XPS peak areas based on a single layer model for S on Ge. The deposition of the S layer did not affect the surface stoichiometry between oxide removal steps (Si/Ge=0.19) and 30 mM passivation (Si/Ge=0.20).

6:00pm SS+AS+EM-WeA12 Novel Electrical Circuit Model for the Design of InGaAs/GaAs (001) Strained-Layer-Super-Lattice, *Tedi Kujofsa*, J.E. Ayers, University of Connecticut

Understanding lattice relaxation and dislocation dynamics has important implications in the design of highly functional and reliable semiconductor device heterostructures. Strain-layer-superlattices (SLSs) have been commonly used as dislocation filters whereby threading dislocations (TDs)

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can be removed by the insertion of a series of mismatched interfaces. The reduction of the threading dislocation in SLSs can be explained by the bending over of TDs associated with misfit segments of one sense by misfit dislocations having the opposite sense. Furthermore, the use of multilayered metamorphic buffer layers (MBLs) with intentionally mismatched interfaces may be used to take advantage of the strain compensation mechanism.

Previously, we developed a generalized energy minimization model, which determines the equilibrium configuration of an arbitrary compositionallygraded or multilayered heterostructure. The present work focuses on the development of a novel electrical circuit model for understanding equilibrium lattice relaxation in InGaAs/GaAs (001) strained-layersuperlattice heterostructures. This work focuses on the design of the SLS buffer layer of $In_xGa_{1-x}As$ deposited on a GaAs (001) substrate. The SL contains a set of 10 uniform layers with alternating mismatch. In other words, the SSL contains alternating uniform layers of In_xGa_{1-x}As with indium compositions x and x + Δx respectively. For each structure, we present minimum energy calculations and show that for a given SLS total layer thickness h_{SLS} , it is possible to find the combination x and Δx such that it provides tight control of the in-plane strain of the strained-layersuperlattice. In addition, for each structure type we present minimum energy calculations by studying the (i) depth profile of strain and (ii) the misfit dislocation density profile. Most importantly, the use of the electrical circuit model allows the analysis of semiconductor heterostructures using a standard SPICE circuit simulator and provides an intuitive understanding of the relaxation process in these multilayered heterostructures.

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