

Thursday Afternoon, November 1, 2012

Surface Science

Room: 21 - Session SS+NS-ThA

Surface Science of Nanostructures

Moderator: J.M. Millunchick, University of Michigan

2:00pm **SS+NS-ThA1 Direct Atomic Scale Imaging and Spectroscopy of III-V Semiconductor Nanowire Surfaces**, A. Mikkelsen, Lund University, Sweden **INVITED**

Free-standing III-V nanowires have the potential to become central components in future electronics and photonics with applications in IT, life-science and energy[1]. The atomic scale structure and morphology of semiconductor nanowire surfaces are central in determining both growth and function of the wires. Surface diffusion and nucleation will directly influence the final appearance of the wires, and transport and optical properties of semiconductor nanowires is often governed by their surfaces.

We develop and use scanning probe and synchrotron based microscopy/spectroscopy to completely determine structure, chemistry and physical properties of III-V nanowire surfaces with extreme precision. We use our novel methods to directly image both interior and exterior surfaces of the nanowires down to the single atom level, revealing geometric structure as well as both electrical and mechanical properties[2-4]. With our rather diverse toolbox we can obtain a real understanding of the connections between nanowire structure, growth and function.

We present recent Scanning Tunneling Microscopy/spectroscopy (STM/S) results, on nanowires consisting of various III-V materials and of polytypic heterostructures with wurtzite (WZ) and zincblende (ZB) crystal segments - only possible in nanowires. We have obtained images of the atomic scale structure for all common WZ and ZB facets as well as information about the electronic structure using STS. We are now developing these methods to perform STM/S on individual nanowires under device operation. Further, we show that STM, can be used for direct top view imaging of the micrometer high free-standing nanowires. We then determine mechanical resonances up to hundreds of MHz with sub Ångström precision[4].

Finally, using synchrotron based Photo Emission / Low Energy Electron Microscopy/Spectroscopy (PEEM/LEEM/XPS) we have characterized III-V nanowire surface chemistry and electronic properties and investigated the influence of various ultra-thin dielectrics to reduce surface band-bending effects[5-8]. A complete picture of oxide thicknesses, effects on bandbending and information on axial and radial doping is obtained.

1. C.M. Lieber and Z.L. Wang, *MRS Bull.* **32**, 99 (2007), and other papers in this issue.
2. A. Mikkelsen et al, *Nature Mater.* **3**, 519 (2004) ; L. Ouattara et al, *Nano Lett.* **7**, 2859 (2007)
3. E. Hilner, et al, *Nano Lett.* **8**, 3978 (2008)
4. A. Fian, et al, *Nano Lett.* **10**, 3893 (2010)
5. R. Timm et al., *Appl. Phys. Lett.* **99**, 222907 (2011).
6. B. Mandl et al., *Nano Lett.* **10**, 4443 (2012)
7. R. Timm et al., *Microelectron. Eng.* **88**, 1091 (2011).
8. M. Hjort et al, *Appl. Phys. Lett.* **99**, 233113 (2011)

2:40pm **SS+NS-ThA3 Spontaneous Assembly of Ordered Atomic Wires with a Long Interwire Distance on a Stepped Nanotemplate**, B.G. Shin, M.K. Kim, D.-H. Oh, C.-Y. Park, J.R. Ahn, Sungkyunkwan University, Republic of Korea

Atomic wires do not interact directly with each other and are therefore ordered by an indirect substrate mediated interaction, whereas molecular structures can be assembled spontaneously by a direct interaction with each other. Such interwire interactions were very short and subsequently an interwire distance of ordered atomic wires were a few Å. Because of the interwire interaction, atomic wires have been described as a quasi 1D system rather than an ideal 1D system. Therefore, an atomic wire with a long interwire distance needs to study an ideal 1D system but, as mentioned before, atomic wires were not ordered with a long interwire distance. Assembly of a long interwire distance atomic wire is thus very challenging and demanded to widen experimental scope of studies on one-dimensional physics. In this study, indium atomic wires with a long interwire distance of 5.7 nm were ordered spontaneously at room temperature on a stepwise nanotemplate, a Si(557) surface. In general, interwire interactions are required to produce ordered nanowires so that other ordered atomic wires have a short interwire distance of a few Å, as described above. The long interwire distance of the ordered indium atomic wires is therefore very

unique. Indium atoms were mobile at room temperature and were adsorbed on a only specific step among four steps, one (111) and three (112) steps of the reconstructed Si(557) surface, maintaining the stepwise nanotemplate structure, as observed by scanning tunneling microscopy (STM), despite the fact that the triple steps have similar local atomic structures. The energetic stability of the indium atomic wires was calculated by first-principles calculations. The reconstructed Si(557) structure model was based on the dimer-adatom-stacking fault (DAS) model and adatom-parallel dimer (AD) model of (111) and (112) facets, respectively.[1, 2] Total energy differences between indium atomic wires on the three (112) steps was very small and the most stable atomic structure was located at the second (112) step, which was consistent with STM images. STM simulations also reproduced the x2 periodicity of the In-induced atomic wires along the wire direction.

[1] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, *J. Vac. Sci. Technol.* A **3**, 1502 (1985)

[2] D. Oh, M. Kim, J. Nam, I. Song, C. Park, S. Woo, H. Hwang, C. Hwang, J. Ahn, *Phys. Rev. B*, **77**, 155430 (2008)

3:00pm **SS+NS-ThA4 Influence of Surface Steps on the Initial Oxidation of TiN (100)**, M. Hong, S.R. Phillpot, S.B. Sinnott, University of Florida

Titanium nitride (TiN) film has extreme hardness, high chemical reactivity and high electrical conductivity and thus is widely used for wear and corrosion resistant coatings as well as diffusion barriers and gate electrodes in microelectronic devices. They are thus routinely subjected to extreme conditions such as high pressure and temperature, corrosive environments, and consequently undergo oxidation. Here, density functional theory calculations are used to determine the mechanisms associated with step-related oxidation process and the formation of TiO_x induced by both the dissociation of O₂ and Ti surface diffusion on TiN (100). Preliminary calculations reveal stable adsorption sites near surface steps for O₂ molecules and single O adatoms, both of which have adsorption energies larger than on terraces. This indicates that the dissipated energy during O₂ dissociation near the surface step is larger than that on (100) terraces so that consequent oxidation reactions can occur more easily. The calculations reveal potential O₂ dissociation paths with activation energies in the range of 1-2 eV. This work is supported by the National Science Foundation (DMR-1005779).

3:40pm **SS+NS-ThA6 Growth of Ag/Ge(111) Phases Studied with LEEM and LEED**, S. Chiang, C. Mullet, UC Davis

Low energy electron microscopy (LEEM) and low energy electron diffraction (LEED) were used to study the growth of structural phases of Ag deposited on Ge(111) above and below the Ag desorption temperature. Ag deposited on Ge(111) formed three main surface phases above 100°C: (4x4), (√3x√3)R30°, and (3x1). At a given coverage, (4x4) island size increased with deposition temperature and decreased with deposition rate. The (4x4) structure nucleated at steps edges and grew only at steps for samples with very high step density. While the √3 structure did not show a preference for nucleating at steps, its growth was bounded by substrate step bunches. The (3x1) was the only Ag phase on the surface for deposition at 370°C and coverage Θ < 0.1 ML, forming domains large enough to be resolved in LEEM images. The (3x1) and (4x4) phases coexisted for T < 350°C and 0.1 < Θ < 0.38 ML, while the (3x1) and √3 phases coexisted for T > 400°C and Θ > 0.4 ML. LEEM images of Ag desorption from Ge(111) at T > 575°C showed that Ag (4x4) and √3 phases reversibly transform to a disordered (1x1) phase, with desorption proceeding from the edges of disordered (1x1) domains and the (1x1) phase being slightly less dense than the (4x4) phase. For sufficiently high deposition rates, Ag was observed to accumulate on Ge(111) above the 575°C desorption temperature. For deposition between 580 and 640°C, a silver layer formed with a (3x1) LEED pattern; upon completion of that layer, a √3 layer formed. For deposition at 660°C, only the (3x1) layer formed. Desorption proceeded by the reverse sequence of phases.

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4:00pm **SS+NS-ThA7 A Synchrotron XPS Study of the Radio-Frequency SF₆ Plasma Fluorination of Single-Walled Carbon Nanotubes**, A.J. Barlow, NEXUS XPS Facility, Newcastle University UK, A.J. Blanch, A.D. Slattery, J.S. Quinton, Flinders University, Australia

With the ever increasing utilisation of carbon nanostructures across many fields, researchers are continuously looking for new and more efficient methods for the reliable and controllable functionalisation of these

materials, in a way that is easily scalable. This is particularly true for the one dimensional carbon nanotube (CNT). While plasma science is not a new field, its application towards the covalent attachment of chemically reactive species to the sidewalls of the initially somewhat inert CNT structure has only more recently been investigated. Furthermore, in-depth studies of the plasma functionalisation of CNTs using fluorine-rich species such as sulphur hexafluoride (SF₆) are limited for a process that is capable of not only providing reactive sites for further chemical attachment but also the modification of the electronic structure of the nanotube [1, 2].

In this presentation research efforts into the fluorination of single-walled CNTs (SWCNTs) in a controlled manner using SF₆ plasma will be discussed. Control over the amount of fluorine attached to the CNT surfaces is demonstrated through variation in experimental conditions such as plasma power. Furthermore, the type of fluorine bonding present on the surface (covalent or semi-ionic) is shown to be controllable through the addition of oxygen containing species into the fluorination mechanism. This can be achieved through either the doping of the plasma itself with oxygen or water vapour, or by an oxidative surface pretreatment of the CNTs through wet-chemical or plasma methods. With this level of control, greatly enhanced C-F covalency can be achieved over a pure SF₆ plasma treatment alone. Results will be presented from lab-based XPS analysis of SWCNT surfaces performed at Flinders University, South Australia, as well as synchrotron-based XPS analysis performed at the Australian Synchrotron.

1. Park, K.A., Y.S. Choi, and Y.H. Lee, *Atomic and electronic structures of fluorinated single-walled carbon nanotubes*. Phys. Rev. B, 2003. **68**: p. 045429.

2. Plank, N.O.V., et al., *Electronic properties of n-type carbon nanotubes prepared by CF₄ plasma fluorination and amino functionalisation*. J. Phys. Chem. Lett. B, 2005. **109**: p. 22096-22101.

4:20pm **SS+NS-ThA8 Solving the Shape of Micellar Pt Nanoparticles Supported on TiO₂(110) and γ -Al₂O₃: A STM, TEM and EXAFS Study**, F. Behafarid, B. Roldan Cuenya, University of Central Florida

Nanoparticles (NPs) with well-defined sizes and shapes were synthesized via inverse micelle encapsulation methods. For 2-4 nm Pt and Au NPs supported on TiO₂(110), the shape was resolved by scanning tunneling microscopy (STM). Geometrical information on smaller Pt NPs supported on nanocrystalline γ -Al₂O₃ was extracted by a combination of transmission electron microscopy (TEM) and extended x-ray absorption fine-structure spectroscopy (EXAFS) measurements. It will be shown that the size, interparticle distance, and the geometry (2D vs 3D) of the NPs can be tuned via our micellar synthesis.

Pt NPs in the size range of 2-4 nm supported on TiO₂(110) were studied by STM after heating in UHV at high temperature (>1000°C). This thermal treatment facilitates the melting of the NPs and the formation of NP-support epitaxial interfaces. High resolution STM images allowed us to determine the shape of the NPs as well as facet orientations. Three different shape types were observed, and each category of shapes was found to appear within a particular NP size regime. In addition, the epitaxial relationship between the NPs and the TiO₂(110) surface was investigated in order to explain the specific orientation of the NPs observed in our study. It was also found that due to interface-induced strain, the NP shapes obtained do not follow the Wulff theorem, namely {100}/{111} facet area ratios deviating from the value obtained for support-free clusters.

Pt NPs in the size range of 0.8-1.5 nm supported on γ -Al₂O₃ were studied by EXAFS, and the nearest neighbor coordination numbers up to the 4th shell were obtained following multiple scattering analysis. These coordination numbers, together with the NP diameter obtained by TEM were examined against a theoretically generated database of possible NPs shapes to determine the most representative shape of Pt NPs in each of the samples. Correlations between the reactivity and the shape of the Pt NPs were established.

4:40pm **SS+NS-ThA9 Geometrical, Electronic, and Vibrational Properties of Bare and H-covered Pt_n(n=22, 33, 44, 55, and 85) Nanoparticles**, G. Shaifai, S. Hong, M. Alcantara, T.S. Rahman, University of Central Florida

We have performed systematic density functional theory (DFT) calculations of the geometrical, electronic, and vibrational properties of small Pt_n nanoparticles (NPs) (n=22, 33, 44, 55, and 85) and their changes with NP size and adsorbate (H₂) coverage. We find our calculated H adsorption energy to be in range of -0.42 eV and -0.62 eV, and with increasing hydrogen coverage the H adsorption energy decreases due to adsorbate-adsorbate interactions. We find increase of Pt-Pt bond length upon hydrogen adsorption and, strikingly, the red shift of the center of the unoccupied d-bands of the bare Pt clusters turns to a blue shift upon hydrogen adsorption in good agreement with experiment [1]. We also find that there is a net charge transfer from all Pt atoms within the NPs to all hydrogen atoms of 0.55 (Pt₂₂H₂₂) and 1.37 electrons (Pt₄₄H₄₄). Thus, the

remarkable hydrogen effect on the electronic structure of Pt NPs can be attributed to charge transfer from the Pt NPs to hydrogen. Regarding the optimal H coverage on Pt NPs, our calculated free-energy phase diagram shows non-zero H coverage even at beyond 600K under ambient H₂ pressure. This work is supported in part by US-DOE under Grant No. DE-FG02-07ER46354.

[1] F. Behafarid, L.K. Ono, S. Mostafa, J. R. Croy, G. Shaifai, S. Hong, T. S. Rahman, Simon R. Bare, and B. Roldan Cuenya, submitted.

5:00pm **SS+NS-ThA10 The Effect of S to Se Substitution in SAMs: Odd-Even Polymorphism of Biphenyl-Substituted Alkaneselenolate on Au(111)**, M. Dendzik, Jagiellonian University, Poland, A. Terfort, Goethe University, Germany, P. Cyganik, Jagiellonian University, Poland

To fabricate aromatic self-assembled monolayers (SAMs) of practical importance for molecular electronics and other applications, high level of control over the SAMs properties should be achieved. In particular, besides monitoring the electronic properties, the control of structure and stability, is an issue of equal importance. As demonstrated previously one way to improve structure and stability of these systems can be achieved by the substitution of the headgroup atom (S versus Se, which binds SAMs constituent to the substrate) [1-3]. In the present study [4], to elucidate how the S to Se substitution influences SAMs structure and stability, we investigate influence of the BPnSe/Au(111) (BPnSe, CH₃-(C₆H₄)₂-(CH₂)_n-Se-, n =2-6) formation temperature and compare obtained results with the corresponding data obtained for their thiol analogues i.e. for BPnS/Au(111) SAMs. Obtained STM data are discussed and analysed in view of the spectroscopic [2] and spectrometric [3] results reported by us recently for these systems, as well as compared to the previously reported STM data [1]. Observed odd-even effect in polymorphism for BPnSe/Au(111) indicates that bonding configuration at the molecule-substrate interface contributes significantly to the energetics of the SAM. We conclude that S to Se substitution increases strength of the molecule-substrate bonding at the expense of reducing strength of the Au_{surface}-Au_{bulk} and Se-C bonding.

References

(1) P. Cyganik, K. Szelagowska-Kunstman, et al. *J. Phys. Chem. C* **2008**, *112*, 15466.

(2) K. Szelagowska-Kunstman, P. Cyganik, et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.

(3) S. Wyczawska, P. Cyganik, A. Terfort, P. Lievens, *ChemPhysChem* **2011**, *12*, 2554.

(4) M. Dendzik, A. Terfort, and P. Cyganik *in preparation*

5:20pm **SS+NS-ThA11 Molecular Self-Assembly by Ionic Bonding in a Series of Carboxylate Species on the Cu(100) Surface**, D. Skomski, S.L. Tai, Indiana University - Bloomington

To expand the catalogue of available interactions for the efficient self-assembly of highly-ordered nanoscale structures, we have investigated the formation of high-stability supramolecular networks constructed with anionic carboxylate species and sodium cations. Our experiments demonstrate that these two-component approaches can steer organic molecules towards efficient self-assembly, even with molecules that do not show a strong tendency towards long-range, two-dimensional ordering when deposited alone. Biphenyl-3,3',5,5'-tetracarboxylic acid (BTA) on Cu(100) serves as a model system to illustrate this effect. Ionic structures have been resolved with molecular and atomic resolution using scanning tunneling microscopy (STM). Chemical shifts in the Na 1s, C 1s, and O 1s core level binding energies, measured by X-ray photoelectron spectroscopy, confirm the active chemical interactions inferred from the STM results.

Ionic self-assembly has been achieved on the Cu(100) surface with terephthalic acid, trimesic acid, as well as BTA. We have shown that the carboxylate and sodium chloride undergo a replacement reaction producing a new salt with long range periodic structure. Chemical shifts in the sodium 1s photoelectron peak have been observed upon addition of the organic species to the surface, confirming a direct interaction. Resulting extended network structures demonstrate very high stability, maintaining their supramolecular structure up to at least 165 °C. The formation of new structures illustrates the interplay between adsorbate-substrate and ionic interactions and opens new possibilities for ionic self-assemblies at surfaces with highly-ordered structure and specific chemical function.

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