

Monday Afternoon, October 18, 2010

Surface Science

Room: Santa Ana - Session SS2-MoA

Stress and Bonding Energetics in Nucleation and Growth

Moderator: G.L. Kellogg, Sandia National Laboratories

2:00pm **SS2-MoA1 Epitaxy of Disilane on Si(100)-H using Scanning Tunneling Microscope-induced Hydrogen Depassivation Patterns**, *J.B. Ballard, J.R. Von Ehr, J.N. Randall, J. Alexander, R. Saini*, Zyvex Labs, *M. Huang, H.-S. Choi, K.J. Cho, J.-F. Veyan, Y.J. Chabal*, University of Texas at Dallas, *J.W. Lyding*, University of Illinois at Urbana-Champaign

INVITED

Atomically precise manufacturing on silicon requires a precise understanding both of patterning techniques as well as the chemistry of molecular deposition. Using a UHV Scanning Tunneling Microscope (STM), we show progress towards a constant temperature process for creating epitaxial structures on Si(100) by alternating STM induced hydrogen depassivation and disilane dosing of the atomically flat surfaces. Emphasizing the detailed mechanisms of patterned deposition, large area patterns are studied as well as patterns consisting of small numbers of dangling bonds revealing a minimum size constraint for patterning. Work is being done towards elevated temperature deposition of disilane with the goal of enhancing epitaxial versus amorphous growth. In addition to growth on atomically flat regions three-dimensional structures are studied. Large area IR spectroscopy as well as theoretical modeling of small area deposition support the STM results. A successful understanding of the physics of patterned epitaxy will lead the way toward high precision manufacturing of previously unobtainable structures and devices.

2:40pm **SS2-MoA3 Stress Balance in Nanopatterned N/Cu(001) Surfaces**, *T.S. Rahman, S. Hong*, University of Central Florida, *E.Z. Ciftlikli, B.J. Hinch*, Rutgers University

Helium atom scattering (HAS) and density functional theory (DFT) within pseudopotential methods have been used to investigate stress balance in nano-patterned N/Cu(001) surfaces. HAS shows that the stress-relief-driven lateral expansion of the averaged lattice parameter within finite-sized N containing patches reduces, with increasing N coverage (and decreasing stripe widths), from 3.5% to 1.8% and then, beyond a critical exposure, the patches' lateral expansion increases again slightly to 2.4%. This implies that, in this higher coverage range, the compressive stress is partially relieved with another mechanism; namely Cu vacancy trenches are nucleated. The trenches serve to enable further surface stress reduction and expansion in the N lattice parameters. In full agreement with above and previous experimental observations, DFT calculations show that an optimized N-induced $c(2 \times 2)$ structure has a net surface stress level ~ 4 N/m and such stress is effectively relieved when stripes of clean Cu(001) form along the $\langle 100 \rangle$ direction or when trench-like steps of Cu atoms form along the $\langle 110 \rangle$ direction. On the other hand, the calculations demonstrate that (contrary to the suggestions of Driver *et al.*[1]) rumpling displacements within the outermost Cu layer do not act to relieve the compressive surface stress levels while clock-like displacements could relieve stress levels, although such displacements are energetically unstable.

[1] S. M. Driver, J-T Hoefl, M. Polcik, M. Kittel, R. Terborg, R. L. Toomes, J-H. Kang, and D. P. Woodruff, *J. Phys. Cond. Mat.* 13, L601 (2001).

Work supported in part by NSF Grant CHE-0741423

3:00pm **SS2-MoA4 The Effect of Lattice Strain on Adatom Diffusion Barriers on Terraces and Step Edges**, *T.S. Rahman, H. Yildirim*, University of Central Florida

While it is well known that lattice strain has an effect on adatom diffusion barriers, its material specificity has not yet been explored. In a comparative study based on density functional theory, we find that self diffusion barriers for Pd(100) terraces and step edges are not affected by tensile strain (up to 5%) as much as their counterparts on Ag(100) and Cu(100). This difference is particularly significant for the step edge barriers (Ehrlich-Schwoebel) which for the cases of the Ag and Cu surfaces may be reduced to zero (or become negative) under strain but remain positive for the Pd surface. In other words, growth modes on Pd surfaces are less susceptible to changes in strain, as compared to Ag and Cu surfaces. We trace these differences to local geometric response and characteristics in the electronic structure. In particular we argue that strain is less effective in changing diffusion barriers on transition metal surfaces than on the coinage metal surfaces.

3:40pm **SS2-MoA6 Long-range Self-ordered Ge Nanostressors on Silicon Nanomembranes**, *M. Huang, F. Chen*, University of Wisconsin-Madison, *Y. Zhang*, University of Utah, *D.M. Paskiewicz, F.S. Flack, D.E. Savage*, University of Wisconsin-Madison, *F. Liu*, University of Utah, *M.G. Lagally*, University of Wisconsin-Madison

Silicon nanomembranes (SiNMs) are defect-free, single-crystal Si sheets with thickness ranging from 2 to 500 nm. This thinness makes them flexible, transferable, bondable and, most importantly, mechanically ultracompliant. This compliance makes nanomembranes fundamentally different from bulk materials [1,2]. Growth of three-dimensional Ge islands (Ge "huts", or quantum dots) on freestanding Si membranes exploits this unique mechanical behavior to induce self-organization of the dots, resulting in a periodic strain in Si nanomembranes or nanoribbons [1,2].

To understand better the effects of strain and substrate compliance on lattice-mismatched heteroepitaxy, we grow Ge islands on stretched (i.e., tensilely strained), freestanding, (001)-oriented SiNMs. We drape a SiNM over a substrate patterned with high ridges. The bending of the SiNM over the edges of the ridges creates regions of local strain that enhance and direct Ge island nucleation. The ridge height and separation are varied to manipulate the draped-membrane strain. Ge 3D islands are grown on the draped SiNM via chemical vapor deposition or molecular beam epitaxy. We demonstrate two-dimensional self-ordering of a single layer of Ge dots, with uniform dot size and spacing. The islands, however, differ from the classic [105]-faceted structures. We find that, while our new Ge dots still have square or rectangular bases, they have steeper facets than those of conventional Ge "huts". We perform finite-element analysis to map the local strain in the draped membrane and to investigate the influence of membrane thickness and substrate ridge height on the dot ordering.

This work is supported by DOE, NSF, and AFOSR.

References:

- [1] M. Huang et. al., *ACS Nano* 3, 721 (2009)
- [2] H-J. Kim-Lee et. al., *Phys. Rev. Lett.*, 102, 226103 (2009)

4:00pm **SS2-MoA7 Atomic Layer Epitaxy of Ge on Si(100)-(2x1)**, *J.-F. Veyan, M.P. Nadesalingam, M. Huang, H. Dong*, University of Texas at Dallas, *J.N. Randall*, Zyvex Labs, *W.P. Kirk, J. Cho, R.M. Wallace, Y.J. Chabal*, University of Texas at Dallas

Atomic Layer Epitaxy (ALE) is a critical step for constructing 3-D structures at the atomic scale, necessary for Atomically Precise Manufacturing (APM) of new devices such as quantum dots. We present here a comprehensive study of Ge ALE on Si(100) \times (2x1) surface using digermane (Ge₂H₆) as a precursor. Si(100) samples are clean at passivated by SiO₂ by standard wet chemical procedures. The oxide is then removed in ultra high vacuum (1.5×10^{-10} Torr) by resistive annealing (1173 K). The clean and Ge₂H₆ exposed Si(100)-(2x1) surfaces are characterized using Infrared absorption spectroscopy (IRAS) and X-ray Photoelectron Spectroscopy (XPS). IRAS measurements are performed in transmission at the Brewster angle, and XPS measurements at a takeoff angle of 45 degrees. The Ge₂H₆ is introduced through either capillaries for the IR measurements or a directed doser for the XPS studies. In both cases, the fluxes on the samples are calculated to be $\sim 10^{-6}$ Torr.sec.

At room temperatures, a saturation coverage was achieved on a clean Si(100) surface after ~ 10 L, corresponding to an estimated sticking coefficient of ~ 0.5 . IR absorption bands in the ~ 1950 - 2000 cm^{-1} range indicate that mono- (GeH), di- (GeH₂) and tri- (GeH₃)-hydrides species are chemisorbed on the surface, consistent with the shifts of the Ge 2p_{3/2} core level observed by XPS. In addition, a feature observed at 2098 cm^{-1} , associated with silicon monohydride (Si-H), indicates that Ge₂H₆ dissociates via beta-hydride elimination, involving the intermediate states Si-H and Si-GeH₂-GeH₃. Measurements of Ge-H and Si-H stretch intensities at saturation coverage as a function of substrate temperature from 173 K up to 700 K suggest that the mechanism involved in the chemisorption of Ge₂H₆ on Si(100) proceeds via dissociation of Ge₂H₅ into GeH₃, GeH₂, and GeH. At a temperature of 600 K, all the vibrational modes associated with Ge hydrides species vanish, which is consistent with the thermal desorption temperature of H on pure Ge(100) surface. However, the intensity of the Si-H vibrational mode increases with the temperature, reaching a maximum intensity around 600 K, and then decreases and vanishes at 713 K, which is 100 K lower than the normal desorption temperature of H on pure Si(100). A quantitative understanding of both the

chemisorption pathway and desorption mechanisms is achieved using Density Functional Theory (DFT) calculations.

This work is supported by the Defense Advanced Research Project Agency (DARPA), Space, Naval Warfare Center, San Diego (# N66001-08-C-2040), and the Emerging Technology Fund of the State of Texas to the A.P.M. Consortium.

4:20pm **SS2-MoA8 The Influence of Metal – Substrate Bonding Energetics on Metal Atom Adsorption, Cluster Nucleation and Film Growth, C.T. Campbell**, University of Washington **INVITED**

Oxide-supported late transition metal nanoparticles form the basis for many important industrial catalysts. The activity, selectivity and sintering rates of these catalysts can depend strongly on the particle size, the oxide support, and the extent of reduction of the oxide. The microkinetics of sintering are essentially the same as for nucleation and growth. All of these kinetic properties are closely related to the variation of metal atom energy (chemical potential) with nanoparticle size. We will review our calorimetric measurements of the energies of metal atoms in nanoparticles supported on different oxide surfaces, and relate those to nucleation/growth kinetics. We will discuss these results in the light of DFT calculations by our collaborators, H. Jonsson, G. Henkelman and L. Xu. The stability of Ag nanoparticles increases with particle size on both MgO(100) and reduced CeO₂(111), until the number of atoms per particle exceeds ~5000. At any given size, Ag nanoparticles have much higher stability on reduced CeO₂(111) than on MgO(100). This difference is due to the much larger adhesion energy of Ag nanoparticles to reduced CeO₂(111) compared to MgO(100). Increasing the extent of reduction of the CeO₂ surface increases Ag particle stability. The energetics and growth of Li and Ca on MgO(100) are dominated by defect sites, and differences in migration barriers there. The migration rates of Pd clusters on MgO(100) vary in unusual ways with size below 5 atoms, and this impacts nucleation.

The above results for oxide surfaces will be contrasted with similar studies of metal film growth on polymer surfaces, where diffusion of metal atoms below the surface and highly exothermic reactions with subsurface heteroatoms can dominate the early stages of growth.

Work supported by NSD and DOE-OBES.

5:00pm **SS2-MoA10 Growth of Ag on Ge(110) and Ge(111) Studied by LEEM, C. Mullet***, S. Chiang, University of California, Davis

We studied Ag island growth on reconstructed Ge(110) and Ge(111) surfaces with low energy electron microscopy (LEEM). At 480 C, one-dimensional (1D) island growth was observed on Ge(110). Island nucleation proceeds from defects in the Ge substrate, with island thickness corresponding to the size of the substrate defect where the island nucleation occurred. As Ag is deposited, islands lengthen but do not thicken. At 9 ML, Ag coverage islands were up to 10 μm long, and thicknesses varied from 100 nm to 250 nm. One-dimensional islands were also produced by Ag deposition at room temperature followed by sample heating. Round Ag islands resolvable in LEEM were observed and coalesced into many long 1D islands as temperature was increased. Islands formed by deposition at room temperature followed by heating to a particular temperature were shorter and thicker than islands grown by deposition on a substrate held at that same temperature. Ag growth on Ge(111) is Stranski-Krastanov. Multilayer Ag island formation begins after the Ag (√3x√3)R30° phase completes at one monolayer. Ag islands exhibit hexagonal faceting. For both the Ge(111) and Ge(110) surfaces, Ag islands induce changes in the Ge substrate that leave a “footprint” observable in LEEM after all Ag has been desorbed from the surface.

*Funding from NSF CHE-0719504; NSF PHY-0649297 (REU)

5:20pm **SS2-MoA11 Growth of Au Islands and Thin Films on NiAl(110): STM Experiments and DFT - Based Analysis, C. Yuen, T. Duguet**, Iowa State University & Ames Laboratory U.S. D.O.E., Y. Han, Institute of Physical Research and Technology, J. Evans, Iowa State University, P.A. Thiel, Iowa State University & Ames Laboratory U.S. D.O.E.

Both Au(110) and Ag(110) have a 0.29x0.41 nm² rectangular surface unit cell matching almost perfectly that for NiAl(110). This provides the opportunity to grow epitaxial thin films free of lateral mismatch strain. One might expect in both cases layer-by-layer growth of two-dimensional fcc(110) islands given the low surface energy of Au and Ag. However, observed behavior is distinctly different for the two metals. Our STM experiments of Au deposition on NiAl(110) between 200-350 K reveal initial formation of islands with a height of 0.23-0.25 nm. Island densities and size distributions are determined. At 300 K, islands are irregular and regions with 3x1 periodicity are sometimes evident. For the coverage of

about 60%, there is significant population by islands of second “layer” or level with heights of ~0.24 nm. Extensive DFT analysis were performed to determine low-energy structures of supported Au films for various coverages. Isolated Au atoms on NiAl(110) prefer sites between two Ni separated by 0.29 nm. However, rather than a simple (110) overlayer with Au at these sites, lower energy structures exist also populating 3-fold sites (e.g., NiAl₂) and displaying combinations of square and hexagonal motifs of adatoms. We believe that observed islands have such structures and present a model for their formation. Behavior is contrasted with Ag/NiAl(110) where bilayer Ag(110) islands form due to quantum size effects (QSE) [1]. However, Ag/NiAl(110) is known to exhibit a bilayer-by-bilayer growth mode due to QSE [1], and the bulk Au(110) surface exhibits 2x1 and 3x1 reconstructions.

[1] Y. Han et al. PRL 100, 116105 (2008); PRB 81, 115462 (2010).

* Morton S. Traum Award Finalist

Authors Index

Bold page numbers indicate the presenter

— A —

Alexander, J.: SS2-MoA1, 1

— B —

Ballard, J.B.: SS2-MoA1, **1**

— C —

Campbell, C.T.: SS2-MoA8, **2**

Chabal, Y.J.: SS2-MoA1, 1; SS2-MoA7, 1

Chen, F.: SS2-MoA6, 1

Chiang, S.: SS2-MoA10, 2

Cho, J.: SS2-MoA7, 1

Cho, K.J.: SS2-MoA1, 1

Choi, H.-S.: SS2-MoA1, 1

Ciftlikli, E.Z.: SS2-MoA3, 1

— D —

Dong, H.: SS2-MoA7, 1

Duguet, T.: SS2-MoA11, 2

— E —

Evans, J.: SS2-MoA11, 2

— F —

Flack, F.S.: SS2-MoA6, 1

— H —

Han, Y.: SS2-MoA11, 2

Hinch, B.J.: SS2-MoA3, 1

Hong, S.: SS2-MoA3, **1**

Huang, M.: SS2-MoA1, 1; SS2-MoA6, **1**; SS2-MoA7, 1

— K —

Kirk, W.P.: SS2-MoA7, 1

— L —

Lagally, M.G.: SS2-MoA6, 1

Liu, F.: SS2-MoA6, 1

Lyding, J.W.: SS2-MoA1, 1

— M —

Mullet, C.: SS2-MoA10, 2

— N —

Nadesalingam, M.P.: SS2-MoA7, 1

— P —

Paskiewicz, D.M.: SS2-MoA6, 1

— R —

Rahman, T.S.: SS2-MoA3, 1; SS2-MoA4, 1

Randall, J.N.: SS2-MoA1, 1; SS2-MoA7, 1

— S —

Saini, R.: SS2-MoA1, 1

Savage, D.E.: SS2-MoA6, 1

— T —

Thiel, P.A.: SS2-MoA11, 2

— V —

Veyan, J.-F.: SS2-MoA1, 1; SS2-MoA7, **1**

Von Ehr, J.R.: SS2-MoA1, 1

— W —

Wallace, R.M.: SS2-MoA7, 1

— Y —

Yildirim, H.: SS2-MoA4, **1**

Yuen, C.: SS2-MoA11, 2

— Z —

Zhang, Y.: SS2-MoA6, 1