

Surface Science

Room 328 - Session SS3-MoM

Surface Diffusion and Wetting

Moderator: J.B. Hannon, IBM Research Division

8:20am **SS3-MoM1 Determining Diffusion Mechanisms Using STM, B.S. Swartzentruber**, Sandia National Laboratories **INVITED**

Determining a diffusion path is not a simple task; for it is the nature of kinetic processes that atomic configurations are arranged in low energy states most of the time. The move from one low energy state to another occurs on timescales usually not accessible to experimental observation. Although the transition path is inaccessible to direct measurement, in some cases it is possible to infer how motion occurs through indirect means. Using atom-tracking STM, in which the tip is "locked" onto the diffusing species using lateral feedback, the diffusion statistics are measured explicitly. >From the diffusion statistics of a dilute surface alloy of palladium or lead impurity atoms embedded in the outermost layer of Cu(001), we determine that the mass transport occurs predominantly via exchange with surface vacancies. Furthermore, the nature of the vacancy-impurity interaction has a dramatic effect on the overall diffusivity. For the case of Pb embedded in the Cu(111) surface, measurements of diffusion on two length scales are necessary to determine the active mechanisms. Short-range motion is predominantly vacancy mediated, while long-range diffusion occurs through exchange with surface adatoms and subsequent transport on top of the surface. Comparison of measurements with first-principles calculations yields valuable insight into diffusion processes, because the energetics of arbitrary diffusion paths can be calculated. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. .

9:00am **SS3-MoM3 Surface Characterization and Inter-diffusion Study of Copper on Ruthenium Thin Film Deposited on Silicon Substrate, O. Chyan, T. Arunagiri, R. Chan, R.M. Wallace, M.J. Kim**, University of North Texas; T.G. Hurd, Texas Instruments

The dual-damascene patterning processing, coupled with the bottom-up Cu electrofill of damascene features and chemical-mechanical planarization, will continue to be the key for the future success of advanced IC chips. Recent advances in physical vapor deposition development allow highly engineered Ta/TaN diffusion barrier to be extended through 90 nm node. However, the tri-layer Cu-seed/Ta/TaN will likely encounter scaling difficulties in the Cu damascene trench/via features of advanced 65 and 45 nm nodes. We recently reported, *J. Electrochem. Soc.*, 150, C347(2003), that Ruthenium (Ru) metal can function as a directly plate-able, seedless barrier materials. In this presentation, we report new findings centered on the interfacial and inter-diffusion studies of Cu/Ru system. Specifically, comparative study of wetting properties between electroplated-Cu and PVD-Cu on Ru barrier film (~ 10 nm) was carried out by XPS, SEM and AFM. Both electroplated and PVD Cu were found to wet well on Ru, based on SEM, AFM imaging and the scribe/peeled test, before and after thermal annealing over 450C. A strong adhesion between Cu/Ru interconnect microstructures is critical in order to withstand the demanding chemical-mechanical planarization process. Interfacial profiling was performed on Cu/Ru/Si samples using secondary ions mass spectroscopy (SIMS) depth profiling. To avoid knock-in ion-mixing interference, SIMS profiling was directed through the silicon back substrate. The backside SIMS profiling through Cu/Ru/Si samples show distinct interfaces without Cu inter-diffusion after annealed at 450C. TEM was further used to provide detailed cross-sectional imaging of Cu/Ru/Si interfaces. The wetting and inter-diffusion data of Cu/Ru systems will be discussed in the context of Cu diffusion barrier application.

9:20am **SS3-MoM4 Dynamics of Surface Alloys: Decay of 2D Islands on Pb/Cu(111), M.L. Anderson, N.C. Bartelt, G.L. Kellogg, B.S. Swartzentruber**, Sandia National Laboratories

To achieve control of nanostructure formation via self-assembly or growth processes, it is critical to gain an understanding of the complex physics governing mass transport. Observing thermal decay of 2D islands has proven useful to quantify atomic mechanisms of surface diffusion in single component systems. In this work we use this method to study more complicated issues of diffusion in multi-component systems. Using both STM and LEEM, we studied thermal decay of Pb-overlayer and Pb-Cu alloy islands on Pb/Cu(111). By combining techniques we extend the length scale

from nanometers to microns and measure decay rates over 4 orders of magnitude. When Pb atoms are deposited on Cu(111), they place exchange with surface Cu atoms, forming a 2D surface-alloy phase. At Pb coverages above 0.22 ML, the surface alloy is saturated and further deposition causes Pb to de-alloy and form overlayer (pure Pb) islands. Despite large differences in structure, measured decay rates of both overlayer and alloy islands as a function of temperature follow an Arrhenius form with the same activation barrier (~0.8 eV). Equivalent barriers indicate that the same rate-limiting process is effective for both types of islands. The measured energy is comparable to DFT calculations of Cu adatom formation plus diffusion energies@footnote 1@ suggesting that transport of Cu is the rate-limiting process. Although the barriers are the same, the absolute rate at a given temperature is ~20 times slower for the alloy than for the overlayer islands. The rate difference is partially accounted for by the fact that, for equal size islands, there are 5 times more Cu atoms to transport in the coarsening of alloy islands. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE. @FootnoteText@@footnote 1@ P. J. Feibelman, private communication.

9:40am **SS3-MoM5 Edge Diffusion on Spiral Steps on Pb(111) Microfacets*, D.B. Dougherty, W.G. Cullen, J.E. Reutt-Robey, E.D. Williams**, University of Maryland at College Park

A classic source of steps on solid surfaces is a screw dislocation intersecting the surface.@footnote 1@ From the intersection a spiral step emerges that can provide active sites for mass transport. To investigate the local kinetics associated with spiral steps, we have employed highly pure micron-size Pb crystallites grown on Ru(0001) with spiral steps on flat Pb(111) facets. Spiral step fluctuations have been observed with STM from 300-390 K and analyzed using the temporal correlation function and the persistence probability.@footnote 2@ The scaling of both functions points to a rate-limiting relaxation mechanism of step edge diffusion, exactly as observed for steps on single-crystal Pb(111).@footnote 3@ The kinetic parameter governing edge diffusion, the hopping mobility, has been extracted from the temporal correlation function and an activation energy has been extracted from the temperature dependence of the mobility. To investigate step fluctuations away from equilibrium, we have made fluctuation measurements on slowly rotating spiral steps on Pb crystallites in the process of thermal equilibration. The continuous unwinding due to the presence of the dislocation is distinct from the previously observed layer peeling process.@footnote 4@ The magnitude of the temporal correlation function for the fluctuations of a rotating spiral was observed to increase with the spiral curvature. The dynamic scaling was unaffected, showing that edge diffusion is still the rate-limiting transport mechanism. * Supported by UMD-NSF-MRSEC DMR-00-80008. @FootnoteText@@footnote 1@ W.K. Burton, N. Cabrera, F.C. Frank, *Proc. R. Soc. London, Ser. A* 243 (1951) 299.@footnote 2@ D.B. Dougherty, O. Bondarchuk, M. Degawa, E.D. Williams, *Surf. Sci.* 527 (2003) L213. @footnote 3@ S. Speller, et al., *Surf. Sci.* 331-333 (1995) 1056; L. Kuipers et al., *Phys. Rev. B* 52 (1995) 11387.@footnote 4@ K. Thurmer, et al., *Phys. Rev. Lett.* 87 (2001) 186102.

10:00am **SS3-MoM6 Sb-mediated Ge and Si Growth on Ge(001), J. Wang, M. Li, E.I. Altman**, Yale University

Antimony-mediated Ge and Si growth on Ge(001) were studied using scanning tunneling microscopy and other surface characterization techniques. For the homoepitaxial growth on intermixed SbGe(001) with submonolayer Sb incorporated into the surface and below the Sb-Ge exchange temperature (470 K), Sb decreased the Ge island size with isolated ad-dimers seen on intermixed surfaces but not on pure Ge. The islands were found on top of Ge not Sb indicating that diffusion was not significantly inhibited on the Sb-passivated surface. The islands were always seen near Sb-Ge substrate domain boundaries. STM movies recorded at elevated temperatures showed that Ge dimers rapidly moved along Ge substrate dimer rows but could not pass or move onto Sb dimers embedded in the surface. These results can be explained by a repulsive barrier at Sb-Ge domain boundaries that inhibits Ge dimer diffusion from Ge to Sb domains but not from Sb to Ge domains. For Si heteroepitaxial growth at 520 K where Sb-Si and Sb-Ge exchange happens, a high density of small clusters were observed when Si was pre-deposited at 520 K and then 0.3 ML Sb was deposited at room temperature. The observed enhanced nucleation was attributed to zero-order nucleation due to both surface defects and adatom-surfactant exchange. The surface becomes smoother than Si deposition on bare Ge(001), with a much lower density of deep trenches on the terraces. Further annealing up to 590 K caused the

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small clusters to disappear producing a surface with square-shaped islands with typical sizes of 6×6 nm². The isotropic island shape suggests that the anisotropic surface diffusion was disrupted due to the existence of domain boundary barriers between Sb and Si or Ge. Growth with different Sb coverages will also be discussed.

10:20am **SS3-MoM7 The Frustrated Alloying of Ge on Ultra-Flat Si(001)**, **J.B. Hannon**, M. Copel, M.C. Reuter, R.M. Tromp, IBM

Using low-energy electron microscopy and atomic-force microscopy, we have investigated the alloying of Ge at the Si(001) surface during growth at elevated temperature (750 to 900 C). We show that alloying occurs primarily via step flow during growth. However, on large terraces, where step flow does not occur, complex and coordinated step structures ("stripes") spontaneously form and migrate over the surface. The stripes consist of a string of alternating adatom and vacancy islands, and move at speeds approaching 1 micron per sec. As these structures traverse the large terraces, they leave alloyed regions in their wake.

10:40am **SS3-MoM8 New Diffusion Mechanisms on Amorphous Surfaces**, **A.S. Dalton**, D. Llera-Hurlburt, E.G. Seebauer, University of Illinois at Urbana Champaign; K.R. Bray, G.N. Parsons, North Carolina State University

The structural and energetic heterogeneity of amorphous surfaces should lead to effective values of the diffusivity that differ significantly from those on crystalline surfaces. However, little work has been done to investigate this possibility. The present work employs a combination of molecular dynamics simulations and experiments involving fractal analysis of surface topography to examine diffusion mechanisms on amorphous silicon (a-Si). Simulations indicate that surface diffusion on a-Si involves substantial exchange with the underlying bulk, but is dominated primarily by short-lived atoms generated from strained three-membered ring structures. The total effective activation energy for mass transport is 2.3 eV, and the formation energy for the most mobile species is about 0.8 eV. Experiments probed crystalline grains grown on a-Si surfaces by simple annealing at 635 to 665°C. Atomic force microscopy images were examined using dimensional fractal analysis to extract the static scaling coefficient and lateral correlation length. The transport rate varied with the length scale over which it was measured—a new result that represents the first experimental measurement of this theoretically predicted phenomenon. At short length scales near 50 nm on amorphous fields, surface diffusion was found to obey an Arrhenius law with an activation energy of 0.9 eV. Measurements over larger length scales including multiple crystal grains exhibited a larger activation energy of 2.4 eV. The significance of the correspondence between the computational and experimental values is discussed.

11:00am **SS3-MoM9 Mobility of Nanostructures on the Surface of a Desorbing Solid: Friction at the Nanoscale**, **V.N. Antonov**, J.S. Palmer, A.S. Bhatti, J.H. Weaver, University of Illinois at Urbana-Champaign

Physical vapor deposition of Au (or other atoms) on rare gas solids leads to spontaneous formation of clusters. The thermal desorption of the buffer causes the clusters to move and aggregate into larger structures, a process known as buffer-layer-assisted growth (BLAG) and desorption assisted coalescence. Our results demonstrate that the initial nucleation density is independent of the buffer thickness. We have studied the extent of aggregation and the size distribution of Au nanostructures as a function of the buffer composition (Xe, Kr, or Ar) and thickness. In the limit of large Au nanostructures (>20 nm), the diffusivity scales as the inverse of the contact area, in agreement with molecular dynamics simulations of fast slip-diffusion of nanocrystals on incommensurate surfaces. A model for BLAG is proposed, based on the concept that nanostructure growth kinetics is controlled by competition between the rate of diffusion and the rate of buffer depletion. From this model, the effective activation energy for Au cluster diffusion is found to be within a few times the single atom binding energy on the surface. For small Au nanostructures (

11:20am **SS3-MoM10 Time-space Height Correlations of Thermally Fluctuating 2-d Systems; Application to Vicinal Surfaces and Analysis of STM Images**, **L. Barbier**, B. Salanon, E. Le Goff, CEA Saclay, France

For thermally fluctuating 2-d systems, like solid surfaces, time and space correlation of the local surface height diverge logarithmically in the rough phase, whereas saturation is obtained below the roughening transition (at $T_{\text{sub R}}$). A 2-d Langevin formalism with matter conservation within the surface plane is presented. An overall expression for correlation functions is obtained that are related to atom hopping rates and surface stiffnesses¹. In contrast with previous 1-d approaches of step dynamics on vicinal surfaces,²⁻⁴ solution of the 2-d Langevin

equation for anisotropic systems gives time correlation functions $G(t)$ depending on energetic and hopping rates in the two main directions and the influence of surface stiffnesses on surface dynamics can be emphasized. At finite times, $G(t)$ cross over to power laws $\sim t^{-(1/n)}$ ($n = 1, 2$ or 4), within limited time ranges as it was observed for isolated fluctuating steps. Limits of time ranges are related to stiffnesses and diffusion anisotropies. For long times, logarithmic divergence ($T > T_{\text{sub R}}$) or saturation ($T < T_{\text{sub R}}$) of $G(t)$ are recovered. Applications to the analysis of STM images of vicinal surfaces are given.¹
¹ @FootnoteText@¹ E. Le Goff, L. Barbier and B. Salanon, Surface Science 531(3) (2003) 337. ² M. Giesen, Progress in Surface Science 68 (2001) p 1, and references therein. ³ A. Pimpinelli, J. Villain, D.E. Wolf, J.J. Métois, J.C. Heyraud, I. Elkinani, G. Uimin Surf. Sci. 295 (1993) 143. ⁴ T. Ihle, C. Misbah, O. Pierre-Louis, Phys Rev. B 58 (1998) 2289.

11:40am **SS3-MoM11 STM Tip-induced Translation through Excitations of the H₂O and D₂O Bending Modes on Pd(111)**, **E. Fomin**, University of California at Berkeley; T. Mitsui, Lawrence Berkeley National Laboratory; M.K. Rose, University of California at Berkeley; D.F. Ogletree, M. Salmeron, Lawrence Berkeley National Laboratory

We have studied the adsorption and manipulation of H₂O and D₂O molecules on Pd(111) using low temperature (~40 K) scanning tunneling microscopy (STM). We investigated the temperature dependence of molecular diffusion using two different approaches: tracking of individual molecules with the STM tip sitting on top of the molecules; and a "movie" technique - a series of consecutive scans showing hopping for an ensemble of molecules. In the course of this work it became clear that under certain conditions the STM tip had a strong influence on molecular motion. We found that the tip-induced hopping rate starts to grow exponentially as the bias reaches 200 meV for H₂O or 160 meV for D₂O, which corresponds to the molecular bending-mode excitation energy. This allows us to propose a coupling between vibrational excitation and molecular translation for water on Pd(111).

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