

Thursday Afternoon, November 3, 2005

Surface Science

Room 202 - Session SS1-ThA

Transport and Structural Stabilization of Surfaces

Moderator: L. Bartels, University of California at Riverside

2:00pm **SS1-ThA1 Living on the Edge: Life and Death of Vacancies in Cu(100)**, *K. Schoots, M.J. Rost, J.W.M. Frenken*, Leiden University, The Netherlands

We have used STM to investigate where surface vacancies originate and annihilate on Cu(100). Because of the extremely high mobility of the surface vacancies, we have been forced to use tracer particles to follow the vacancy motion, in the form of In atoms, incorporated in the top layer. The "slide-puzzle"-diffusion of the vacancies makes the In atoms move through the surface, as has been reported in.¹⁻³ In the present study, we have employed tailor-made geometries, in which the In atoms were surrounded exclusively by upward or by downward steps. Our STM movies show a striking difference between these two cases, with differences in jump frequencies and average jump lengths of more than one order of magnitude. These results show that vacancies are primarily created at the upper side of a step and can be formulated in analogy with the energetics of ad-atoms, in terms of an Ehrlich-Schwoebel barrier⁴ for surface vacancies. ¹ R. van Gastel et al., Nature 408 (2000) 665, Phys. Rev. Lett. 86 (2001) 1562, Surf. Sci 521 (2002) 10, Surf. Sci. 521 (2002) 26. ² M.L. Grant et al., Phys. Rev. Lett. 86 (2001) 4588. ³ R. van Gastel et al., The Chemical Physics of Solid Surfaces, vol. 11, Surface Dynamics, ed. D.P. Woodruff, (Elsevier, Amsterdam, 2003), p. 351-370. ⁴ G. Ehrlich et al., J. Chem. Phys. 44 (1966) 1039.

2:20pm **SS1-ThA2 Diffusion of Two Dimensional Cu Adatom Islands on Cu(111) using a "Self Learning" Kinetic Monte Carlo Technique**, *T.S. Rahman*, Kansas State University; *O. Trushin*, Russian Academy of Sciences; *A. Kara, A. Karim*, Kansas State University; *P. Vikulov*, Russian Academy of Sciences

Diffusion of two dimensional Cu adatom islands, containing 1 to 100 atoms, on Cu (111) has been studied using a newly developed "self learning" Kinetic Monte Carlo (SLKMC) technique in which the standard KMC method is combined with procedures for automatic generation of a table of microscopic events and calculation of their activation energy barriers. Nontrivial paths thus revealed and fully characterized are permanently recorded in a database for future usage, through a pattern recognition scheme. The system thus automatically builds all possible single and multiple atom processes that it needs for sustained simulation and evolves according to processes of its choosing. The diffusion coefficients calculated for 300K, 500K, and 700K, show that the effective diffusion barriers increase almost monotonically with increasing island size. From the tabulated frequencies of events we find that concerted motion and multiple particle processes play a key role in the diffusion of small islands, however, periphery diffusion and single particle processes dominate for the larger sized islands. Contrary to the case of small Cu islands on Cu (100), we do not find any oscillatory behavior for the effective diffusion barrier or for the diffusion coefficients as a function of island size.

2:40pm **SS1-ThA3 Exclusively Linear Diffusion of 9,10-Dithioanthracene on an Isotropic Cu(111) Surface**, *K.-Y. Kwon, K.L. Wong, G. Pawin, L. Bartels*, University of California at Riverside

One-dimensional diffusion of adsorbates is a common feature of anisotropic surfaces such as the (110) and (211) cuts of an fcc crystal. The technologically-relevant lowest energy (111) surfaces of coinage metals have sixfold symmetry in the top layer and, hence, generally allow diffusion of adsorbates along more than one direction. Here, we report on the diffusion of individual 9,10-dithioanthracene (DTA) molecules on Cu(111). DTA adsorbs with the aromatic system lying flat on the substrate. In variable-temperature STM studies, we find that it diffuses exclusively in the direction in which its aromatic moiety happened to adsorb. We neither find rotation of the molecule in the surface plane nor diffusion perpendicular to the aromatic axis of the molecule. We investigated the dynamics of the one-dimensional diffusion of DTA and find an energy barrier of 130meV and an attempt frequency of 4 GHz. Density Functional Theory modeling of the diffusion potential shows, that DTA achieves unidirectional motion by sequential placement of its two substrate linker in a fashion that strikingly resembles bipedal locomotion.

3:00pm **SS1-ThA4 Bustling Bi/Cu(111): Phase Transitions and Atomic Structure**, *R. van Gastel*, University of Twente, The Netherlands; *D. Kaminski, E. Vlieg*, Radboud University Nijmegen, The Netherlands; *B. Poelsema*, University of Twente, The Netherlands

We have combined surface X-ray diffraction (SXRD) and low-energy electron microscopy (LEEM) to investigate atomic structure and pattern formation in the Bi/Cu(111) system. Deposition of submonolayer amounts of Bi on Cu(111) leads to the formation of a two-phase system consisting of a surface alloy phase and an overlayer phase that forms patterns similar to those previously observed in the Pb/Cu(111) system.^{1,2} The patterns however exhibit several phase transitions that are unseen in Pb/Cu(111). Through SXRD measurements investigating the structure of the different surface phases,³ the origin of these transitions can be pinpointed to changes in the atomic structure of those phases. A rich variety of surface phases, covering the whole spectrum, from solid to liquid to lattice-gas-like and from ordered to disordered is observed. In LEEM movies, structural contrast between e.g. solid and liquid Bi overlayers lets us image the pattern dynamics and phase transitions directly. The pattern dynamics and the dramatic changes that occur during the transitions are analyzed to extract information and quantify the thermodynamic quantities that control the rich phase behavior in this system. ¹ R. Plass, N.C. Bartelt and G.L. Kellogg, J. Phys. Cond. Mat. 14 (2002), 4227. ² R. van Gastel, R. Plass, N.C. Bartelt and G.L. Kellogg, Phys. Rev. Lett. 91 (2003), 055503. ³ D. Kaminski, P. Poedt, E. Aret, N. Radenovic and E. Vlieg, Surf. Sci. 575 (2005), 233.

3:20pm **SS1-ThA5 Quantum Stabilization of Atomically Flat Films of Pb at 300 K**, *R. Miranda*, Universidad Autónoma de Madrid, Spain **INVITED**

The 1D confinement of electrons within quantum wells produces a set of new states, the quantum well states (QWS), which may influence substantially the electronic energy and, thus, the total energy of the system. Pb grown on Cu(111) shows these effects in the form of "magic heights" for the 3D nanoislands that appear upon deposition at 300K.¹ The "magic heights" are equivalent to the "magic numbers" reported for clusters, He droplets or nuclei. Deposition of Pb at 60 K, however, produces flat, metastable films that cover uniformly the Cu substrate. Their thicknesses can be determined by the characteristic energy of the QWS measured with Tunnelling Spectroscopy. The films grow layer by layer at low temperatures because of kinetic constraints, but upon heating, they decompose into the heights more stable. The dynamics of the thermal evolution of films of different thicknesses is explored by movies recorded with a Variable Temperature STM and compared to electronic energy calculations. We find that each Pb thickness becomes unstable at a different temperature (with films with QWS at the Fermi level (such as 9 ML-thick) being particularly unstable), while layers with thickness corresponding to "magic heights" are more stable. Some thicknesses are particularly stable, giving rise to atomically flat films of Pb over micron scales even at room temperature. ¹ R. Otero, A.L. Vazquez de Parga and R. Miranda, Phys. Rev. B 55, 10791 (2002).

4:00pm **SS1-ThA7 Atom Transport in One-Dimensional Surface Diffusion**, *G. Antczak, G. Ehrlich*, University of Illinois at Urbana-Champaign

We present an investigation of self-diffusion on the W(211) plane, done using atomic resolution field ion microscopy, which gives insight into the mechanism of migration of atoms in a one-dimensional system. We distinguish two temperature regions in diffusion over this surface. A low temperature region, where diffusion proceeds by the standard, well-known mechanism - jumps to nearest-neighbor sites, and a slightly higher temperature region, where double transitions start to play a significant role. The transition between these two regions is gradual. The existence of double jumps starts to be non-negligible at a temperature $T = 310$ K and the ratio of double to single transitions reaches 0.66 at a temperature $T = 325$ K. The importance of transitions occurring during the transient time is also examined. To get information about ratios of long jumps, the distributions of displacements consisting of 1200 observations for each temperature, is analyzed for regular measurement as well as for transient time measurements. In the lower temperature range, 300 measurements for each temperature are used to establish an Arrhenius plot for the diffusivity. For the first time it is shown that long transitions raise the prefactor for the diffusivity above the usual values. However, this increase is smaller than expected from a model of independent jumps. Activation energies and prefactors for double as well as single transitions are derived. A mechanism of long transitions on W(211) is proposed and compared to

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the mechanism for two-dimensional diffusion on W(110). Research supported by the Department of Energy under Grant No. DEFG02-91ER45439 to the Materials Research Lab.

4:20pm **SS1-ThA8 Diffusion and Ordering of CO Coadsorbed with H on Pd(111) Studied by Variable-Temperature STM**, *T. Mitsui*, Lawrence Berkeley National Laboratory; *M.K. Rose, E. Fomin*, University of California, Berkeley; *D.F. Ogletree, M. Salmeron*, Lawrence Berkeley National Laboratory

CO adsorbs on Pd(111) in fcc hollow sites at low coverage. As coverage increases, ordered $\sqrt{3}\times\sqrt{3}$ domains form with 1/3 of fcc sites occupied by CO. At higher coverage $c(4\times 2)$ domains form with a density of 1/2, with CO adsorbed in either bridge sites, or in fcc and hcp hollow sites. Additional CO structures are formed at still higher coverage. H also adsorbs on Pd(111) in fcc sites, forming ordered $\sqrt{3}\times\sqrt{3}$ domains with first 1/3 then 2/3 of fcc hollow sites occupied by H. At still higher coverage, H occupies all fcc sites forming 1×1 domains. When H was adsorbed on Pd(111) pre-covered with 0.12 to 0.33 ML of CO, the CO was compressed into $c(4\times 2)$ domains, however higher-density CO domains were not observed even in a constant background pressure of 10^{-7} Torr. Co-adsorption of H has little effect on the diffusion of isolated CO molecules until the H coverage approaches 1/3 ML. At this point the CO diffusivity drops more than two orders of magnitude. CO diffusivity rises significantly as the H coverage passes 1/3 ML, then drops again as coverage approaches 2/3 ML. Very stable CO clusters were observed as H coverage approached 1 ML. Isolated CO molecules could be followed by STM up to ~ 110 K, while isolated CO diffusion on clean Pd(111) can be observed by STM as low as 45 K, and becomes too fast to follow by ~ 55 K. In small clusters CO molecules occupy both fcc and hcp sites, and diffusivity is a dramatic function of cluster size. 2 and 4 molecule clusters diffuse significantly faster than 1, 3 or 5 molecule clusters, and cluster diffusivity generally increases with size up to at least 7 CO molecules. The implications of these observations for inter-adsorbate interactions will be discussed. M. K. Rose et al, Surface Science 2002, T. Mitsui et al, Surface Science 2003, T. Mitsui et al, Phys. Rev. Lett. 2005.

4:40pm **SS1-ThA9 Sintering of Au Clusters Supported on TiO₂(110): An In-Situ Scanning Tunneling Microscopic Study**, *F. Yang*, Texas A&M University; *A. Kolmakov*, University of California at Santa Barbara; *A.K. Santra*, Halliburton Company; *D.W. Goodman*, Texas A&M University
Sintering, i.e. an increase in the average size of nanoclusters, is a frequently encountered problem in nanotechnology and a principal cause of deactivation in nanocatalysts. For example, Au supported on high-surface-area titania is a highly efficient catalyst for selective oxidation and hydrogenation reactions; however, commercial development is seriously hampered because Au nanoclusters sinter rapidly. The mechanisms of sintering are not well understood and depend, to a large extent, on understanding elementary surface diffusion processes. Scanning tunneling microscopy (STM) is capable of atomic-level measurements over a variety of conditions. In-situ STM allows the morphological changes of specific nanoclusters to be monitored over a variety of reaction conditions from ultrahigh vacuum to realistic reactant pressures. Using in-situ STM, the growth kinetics of Au on TiO₂(110) have been measured directly, allowing sintering mechanisms to be proposed for supported Au model catalysts under realistic reaction conditions. The STM results also show that substrate hydroxylation blocks the preferential growth of Au clusters and alters their growth kinetics on a TiO₂(110) surface. Furthermore, the sintering kinetics of Au clusters during the CO oxidation reaction have been studied for Au clusters supported on TiO₂(110) and on hydroxylated TiO₂(110).

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