## 11-Surfaces, Interfaces and Thin Films



Recently, we have studied the surface order-disorder transition of $Cu_3Au(001)$ using grazing incidence x-ray diffraction [1]. Detailed surface x-ray truncation rod scans reveal novel surface ordering phenomena. In this presentation, we will discuss the analysis of the rod intensity based on a modified dynamical theory. The wavefields are derived in a form which can be treated as decoupled refraction modes characterized by Fresnel's coefficients. The corresponding dispersion surface is analytically constructed from the Bragg law and Snell law in k-space so that the geometric picture of surface-normal scan is readily described. Using this formulation, the calculated (100)-(101) rod profile of $Cu_3Au$ in the order phase agree with the experimental ones. Problems in the calculation for the disordered phase will be discussed.

1. K.S. Liang, H.H. Hung, S.L. Chang, Z. Fu, S.C. Moss, and K. Oshima, in *Surface X-ray and Neutron Scattering*, ed. H. Zabel & I.K. Robinson (Springer-Verlag, 1992) p.65.

**MS-11.01.05** Phase Transformations on Stepped Surfaces:

Chiral Melting of Si(113) * and Facetting of Miscut Pt(001) †

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Two x-ray scattering experiments carried out on stepped surfaces – Si(113) and miscut Pt(001) – will be described.

(i) Theorists generally believe that they understand continuous phase transformations in two-dimensions. The exception is the disordering of a 3-fold commensurate solid into an incommensurate fluid. The $(3 \times 1)$-to-disordered transition of the Si(113) surface provides an experimental realization of such a transformation. Our results provide a detailed characterization of the critical behavior, including the observation of anisotropic scaling, which any complete theory of two-dimensional phase transformations must be able to explain.

(ii) What happens to a stepped surface at elevated temperatures? One striking phenomenon that may occur is facetting, so that the distribution of steps is no longer uniform across the surface; instead the surface separates into highly-stepped regions and step-free regions. Facetting is analogous to the phase separation of a binary liquid mixture. Our recent experiments have revealed that stepped Pt(001) surfaces show two reversible facetting transformations. Above $T_c = 1820$ K, the steps are uniformly distributed. Between $T_c$ and 1650 K, the surface is composed of smooth, hexagonally-reconstructed regions, together with rough, stepped, unreconstructed regions. The step separation varies as $((T_c-T)/T_c)^{-1/2}$ consistent with simple theoretical ideas. By 1650 K, the step separation reaches 8Å, whereupon there is a second transformation. At the second facetting transition, the step separation jumps to 60Å while at the same time the stepped surface reconstructs.

*with D. Abernathy, R. Birgeneau and K. Blum (MIT)

†with M. Yoon (MIT), G. Watson and D. Gibbs (BNL), and D. Zehner (ORNL)

**MS-11.01.06** APPLICATIONS OF X-RAY SCATTERING TECHNIQUES FOR THE STUDY OF ELECTROCHEMICAL INTERFACES. By Hoydoo You*, Materials Science Division, Zoltan Nagy, and D. J. Zurawski, Materials Science Division and Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

A brief description of the theory and practice of synchrotron x-ray scattering technique will be presented with emphasis on the unique characteristics of this technique that make possible the *in situ* structural examination of solid interfaces buried under a layer of solution; and some recent applications of the technique will be reviewed for the investigation of electrochemical interfaces. The examples will include (1) structural studies of under-potential-deposited monolayers, (2) studies of surface reconstruction of gold single crystals, (3) study of electrochemical passive film formation at the copper/solution interface, and (4) a study of structural changes of Pt(111) single crystal surface associated with incipient oxidation and reduction. In the latter work, it was shown that lifting of Pt atoms occurred, and this result substantiated the long-standing hypothesis for the *place-exchange* mechanism of oxidation of metal/solution interfaces. It was found that if the amount of charge transferred during the oxidation did not exceed 1.5 $e^-$/Pt atom, the initial flat surface could be completely recovered after reduction of the oxide. While, if more charge was transferred during oxidation (up to 3.5 $e^-$/Pt at 1.7 V measured from hydrogen evolution), the top layer of the surface was irreversibly roughened.

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**MS-11.01.07** ADSORPTION OF HEXAETHYLENE GLYCOL MONODODECYL ETHER AT THE AIR–WATER INTERFACE STUDIED BY NEUTRON REFLECTION. By J.R.Lu*, R.K.Thomas and J.Penfold, Physical Chemistry Lab, Oxford University, U.K.

Neutron reflection has been used to study the structure of the soluble monolayer of hexaethylene glycol monododecyl ether ($C_{12}EO_6$) adsorbed at the air–water interface. The concentration was fixed at the c.m.c. ($7.5 \times 10^{-5}$ M). To obtain a unique structure solution, the mesurements of reflectivity profiles involved using a group of partially deuterated surfactants: $dC_{12}dEO_6$, $dC_{12}hEO_6$, $hC_{12}dEO_6$, $hC_{12}hEO_6$, $hC_{12}dEO_3hEO_3$ and $hC_{12}dEO_3EO_3$ and a combination of ten reflectivity profiles were measured.

The structure parameters were obtained by analysing the reflectivity profiles using the recently developed kinematic approximation. The area per molecule at the c.m.c. was found to be $55 \pm 2$ Å$^2$, and the number of water molecules associated with each surfactant to be $11 \pm 1$. Assuming the distribution of the alkyl chain, the head group and the water disturbed region to be uniform in shape, the thicknesses were $19 \pm 2$ Å, $19.5 \pm 2$ Å and $13 \pm 1$ Å respectively. The cross distances between the centres of the three distributions were determined directly and that between the alkyl chain and the head was found to be $9 \pm 0.5$ Å, that between the chain and the solvent to be $10 \pm 0.5$ Å, and that between the head and the solvent to be $2 \pm 1$ Å. The degree of the extent of alkyl chain associated with water was thus calculated to be 0.32 and that of the chain with the EO groups was 0.54.

The distribution of the first three EO groups was found to be nearly overlapped with that of second three EO groups. The widths were found to be $18 \pm 2$ Å, compared with $19.5 \pm 2$ Å for the total six EO groups.

  