11–Surfaces, Interfaces and Thin Films

11.01 – Surface/Interface Structures

MS–11.01.01 3D SURFACE STRUCTURE DETERMINATION BY X-RAY DIFFRACTION. By R.G. van Silfhout, EMBL, c/o DESY, Hamburg, Germany.

For many years X-ray diffraction has been a standard technique to determine the atomic structure of bulk crystals. Its application to the study of surfaces is more recent and became possible with the availability of synchrotron radiation sources. The object of most experimental surface X-ray diffraction work performed so far was to figure out the in-plane (2D) structure of surfaces using a grazing incidence geometry.
A new development is to include measurements along crystal truncation rods (CTR's) in the analysis. This integration of 2D crystallography with CTR analysis enables a full 3D structural determination.

We review the basic principles of CTR analysis, 3D structural determinations and show examples of recent accomplishments in the field with the emphasis on (111) semi-conductor surfaces, which have been studied intensively.

MS–11.01.02 STRUCTURE DETERMINATION OF THE 3x3 SUPERSTRUCTURE OF THE (111)-B-SURFACE OF InSb BY THREE DIMENSIONAL X-RAY DATA. By J. Wever, H.L. Meyerheim, V. Jahns, W. Moritz and H. Schulz, Institut für Kristallographie, Universität München, Theresienstr. 41, 8000 München, Germany

Several attemps have been made to solve this structure by two-dimensional in-plane data, including our group. Up to now all attemps were successless. We combined now the in-plane data with the intensities along of the superstructure reflections perpendicular to the surface. We used these data for the first time to calculate a so called periodic-nonperiodic Patterson function. The structure could be solved by interpretation of a section through this Patterson-density at w=0. This density showed main features which did not appear in the Patterson density calculated with the in-plane data only which represents a projection of the three dimensioned Patterson-density on the (uv) plane. This demonstrates clearly, that the whole three dimensional information is needed for solving more complicated surface structures. The structure refinements gave an excellent weighted R-value of 5% and a GOF of 1.3. The InSb($\bar{1}\bar{1}\bar{1}$) surface was prepared in UHV by Ar$^+$ ion bombardement and annealing at 673 K for ca. 1/2 h and subsequent slow cooling to room temperature at about 2K/min. X-ray measurements were performed at the wiggler beam line at the HASYLAB (Hamburg, Germany) and in the laboratory using a rotating anode source. An incidence angle of 0.7° was chosen. The maximum X-ray exit angle was 60° which allowed to measure reflections up to l = 7.2. The angular resolution was limited by Soller slits to 0.4° in-plane and 0.8° out of plane. The sample size was 12x8 mm². The data set consisted of 24 superstructure lattice rods measured in steps of l = 0.4. A total of 218 symmetrically independent reflections were used. The inplane data set consisted of 73 reflections. All vacancy and trimer models which had been proposed for the ($\bar{1}\bar{1}\bar{1}$) surfaces of compound semiconductors can be ruled out. Additionally all models based on relaxations and models preserving the 3m1 symmetry of the unreconstructed surface could be ruled out as well. This is in agreement with recent STM measurements which showed the existence of two types of rings of atoms above the top layer, one type of elliptic shape occurs with three orientations and a second type of trigonal shape occurs with two orientations [1]. The final structure model exhibits similarities to the model derived recently for the ($\sqrt{19}$x$\sqrt{19}$) reconstruction of the GaAs($\bar{1}\bar{1}\bar{1}$) surface from STM measurements [2].
These two types of atom rings are arranged above the top layer such that each ring saturates 6 dangling bonds. The rings are centered around an Sb atom.
The surface undergoes a reversible phase transition at about 600K. No hysteresis could be detected indicating an order-disorder transition. However, the possible existence of an ordered high temperature phase cannot be ruled out because only the disappearance of the reflections in [h0]* direction could be measured.

References
[1] Seehofer and R.L. Johnson, private communication.
[2] D. K. Biegelsen, R. D. Bringans, J. E.Northrup and L. E. Schwarz, Phys. Rev. Letters 65 (1990) 452.

MS–11.01.03 IN-PLANE STRUCTURE OF Si(111):As–1×1 SURFACE STUDIED BY GRAZING-ANGLE X-RAY STANDING WAVE MEASUREMENTS, By Osami Sakata* and Hiroo Hashizume, Res. Lab. of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama 227, Japan

Arsenic deposition on clean Si(111) surface removes the 7×7 reconstruction to give a simple 1×1 LEED pattern. There is a great deal of data supporting As atoms substituting for the top half of the silicon (111) double plane to terminate the surface with a nonreactive lone-pair orbital. X-ray standing-wave (XSW) work (Patel, Golovchenko et al., Phys. Rev. B 1987, 36, 7715) shows As atoms lying at 0.17 Å above the unrelaxed bulk terminated (111) top-layer Si atoms with a nearly perfect crystalline order in the vertical direction, but ion scattering data suggests some disorder in the Si(111):As–1×1 surface structure (Copel, Tromp & Koeller, Phys. Rev. B 1988, 37, 10756). We will show here that the As atoms actually occupy the high-symmetry sites on Si(111) surface with little disorder in the in-plane direction. An As K emission signal was observed from Si(111):As–1×1 samples in a utrahigh vacuum chamber using XSW's in the grazing-angle geometry (Jach & Bedzyk, Phys. Rev. B 1990, 42, 5399). XSW's created from the Si($2\bar{2}0$) Bragg planes with 16.5 keV synchrotron X-rays had an intensity modulation parallel to the surface. Emission profiles were observed from monolayer As atoms at glancing incidence angles ϕ close to the critical angle for total external reflection, ϕ_c. Unlike in the ordinary geometries, emission profiles at $\phi < \phi_c$ in our geometry with an h vector nearly parallel to the surface show characteristic dependence on the degree of order of fluorescing surface atoms in the in-plane direction. A very good agreement was found in the observed and calculated profiles assuming As atoms lying on the ($2\bar{2}0$) planes with a high order.

MS–11.01.04 A DYNAMICAL EFFECT OF CRYSTAL TRUNCATION ROD AND ITS APPLICATION TO X-RAY STUDY OF Cu$_3$Au (001) SURFACE. By H.-H. Hung*[1], S.L. Chang[1,2] and K.S. Liang[3], [1]Synchrotron Radiation Research Center and [2]Department of Physics, National Tsing-Hua University, Taiwan and [3]Exxon Corporate Research, NJ, USA.

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 (3×1)-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.

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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.

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. (7.5×10^{-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 ± 2 Å^2, and the number of water molecules associated with each surfactant to be 11 ± 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 ± 2 Å, 19.5 ± 2 Å and 13 ± 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 ± 0.5 Å, that between the chain and the solvent to be 10 ± 0.5 Å, and that between the head and the solvent to be 2 ± 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 ± 2 Å, compared with 19.5 ± 2 Å for the total six EO groups.