with $\delta = \frac{1}{8}$ induced by opposite fields, $+E$ and $-E$, and characterized by opposite electric polarizations, or, equivalently, by a phase difference of $\pi/8$.

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(a)Permanent address: Laboratoire de Physique des Solides, F-91405 Orsay, France.

(b)Permanent address: Atomic Energy of Canada, Ltd., Chalk River, Ontario K0J 1J0, Canada,

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Solution to the Surface Registration Problem Using X-Ray Standing Waves

J. A. Golovchenko, J. R. Patel, and D. R. Kaplan

Bell Laboratories, Murray Hill, New Jersey 07974

and

P. L. Cowan

National Bureau of Standards, Washington, D. C. 20234

and

M. J. Bedzyk

State University of New York at Albany, Albany, New York 12222

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Standing waves of x rays have been used to determine the positions of bromine atoms in submonolayer coverages on a (111) silicon surface. In addition to the bromine position normal to the crystal surface its components relative to a plane inclined to the surface are also measured. This information suffices to establish the registration of the surface atoms relative to the crystal below.

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Some years ago Andersen, Golovchenko, and Mair[1] predicted that fluorescent scattering from x-ray standing waves could provide a method for accurately determining impurity atom positions on crystal surfaces. This prediction evolved naturally from pioneering observations by Batter-

man[2,3] of fluorescent x-ray scattering in the vicinity of the Bragg total reflection region. Subsequent studies[1,4] concentrating on the region of total reflectivity demonstrated that bulk impurity-atom locations could be determined with accuracies of a hundredth of a lattice constant provided extinction effects could be suppressed. Cowan, Golovchenko, and Robbins[5] recently took the first step in realizing the prediction of Ref. 1 by using x-ray standing waves to demonstrate that sub-monolayer amounts of bromine atoms could be adsorbed into surface lattice sites strongly correlated to the crystal substrate (i.e., coherent atomic positions). The bromine atomic position normal to the (110) crystal surface was measured and the covalent nature of the bond inferred.

In the following we report on two significant developments in the evolution of the application of x-ray standing waves to surface studies. First we demonstrate that these methods can solve the "registration problem" of surface physics. This is the problem of determining the absolute position of the periodic impurity sites on a crystal surface particularly with regard to translation of the surface impurity lattice vectors in the surface plane. Secondly we extend the original measurements of Cowan, Golovchenko, and Robbins[5] to the silicon (111) surface which seems to be of more interest because it is a surface with which one must more commonly deal in applications.

It is possible to localize very small numbers of impurity atoms on a crystal surface by studying their fluorescent scattering under conditions of toal Bragg reflection from the crystal below. Within this angular range the strong interference between incident and reflected beams results in a standing x-ray wave field that extends outside the surface of the diffracting crystal and has the periodicity of the Miller planes responsible for the reflection. As the crystal is tilted through the region of total reflection the standing waves move continuously a half a planar spacing along the operative reciprocal-lattice vector. If the impurity fluorescent scattering from the standing-wave field is monitored, a minimum is expected when the standing wave nodal plane passes through the impurity position. If the antinode passes through this position a corresponding maximum is to be expected. Since the dynamical theory of x-ray diffraction predicts the position of the standing-wave field relative to the crystal lattice as one tilts through the total reflection region, the position of the impurity relative to the lattice may be simply deduced.

Until now lattice location studies by this method have utilized standing waves with nodal planes that lie parallel to the crystal surface. Consequently, only position information perpendicular to the surface has been obtained. If, however, the reciprocal-lattice vector of the reflection does not lie perpendicular to the surface, the impurity can be located with respect to a plane that intercepts the surface at an angle. Such a measurement together with the distance measured normal to the surface constitutes a solution to the registration problem since by triangulation the impurity position along the surface in the direction of the reciprocal-lattice projection is completely determined. It should be pointed out that this type of determination of the bromine position utilizes phase information which is not normally available from elastic scattering measurements (x-ray diffraction, low-energy electron diffraction) because the diffracted intensities do not contain absolute phase information.

We report here on the positions of bromine atoms adsorbed on a (111) silicon surface. We have studied the fluorescent signals from standing waves excited from both (111) and (220) reflections for the same crystal. The first reflection provides the surface-normal distance which is designated as distance A in the schematic diagram of the (110) projection in Fig. 1. The (220) reflection data provides the distance labeled B in
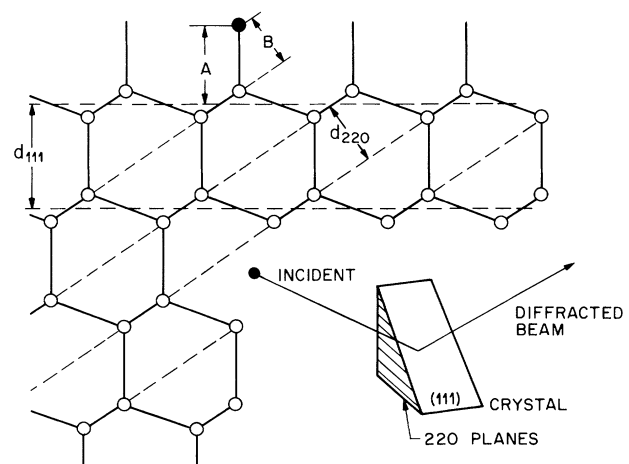

FIG. 1. Schematic illustration of a silicon (111) surface viewed edge-on along a (110) projection. Distances A and B indicate bromine-atom positions above surface. Silicon and bromine atoms are represented by open and closed circles, respectively. The position of the relevant (111) and (220) Fourier components of the charge density are indicated by dashed lines.

that figure. The complexities caused by an asymmetrical reflection in this case are avoided by having the plane formed by incident and diffracted beams lie perpendicular to Fig. 1, with small angular divergence along the diffraction cone (see Fig. 1 inset).

The sample was prepared with a Syton-polish mirror finish. Oxide was stripped off in a HF etch after which the surface was rinsed in anhydrous ethyl alcohol. The surface was then rubbed on a pad saturated with an ~0.01% solution of bromine in ethanol under UV illumination for five minutes. This treatment is similar to one recently reported by Aspnes and Studna.[6] Little or no loss of coherent or incoherent bromine atoms from a (111) surface prepared in this way has been noted over a period of three days. This is in contrast to recent observations on (220) surfaces where substantial loss over approximately 12 hours was observed.[7]

The experimental arrangement is similar to that shown in Ref. 1 except that each of the reflections reported here required its own collimating crystal. Also we have found that bromine on the (111) surface is so stable that the sample need not be immersed in alcohol during the measurement. All measurements were thus performed in open air.

Figure 2 shows an angular scan of both the intensity of the reflecting beam and the bromine fluorescence in the vicinity of the (111) reflection. Here the standing waves move normal to the surface and hence the bromine position along this direction can be deduced. The data were ac-

quired over a period of three days with use of a rotating-anode molybdenum x-ray tube whose output beam was collimated with an asymmetrically cut (111) silicon crystal. A beam flux of 10^6 to 10^7 photons per sec was delivered to the sample in an angular divergence of $\sim\frac{1}{6}$ the natural (111) reflection width. The bromine fluorescence signal shows a clear minimum inside the region of total reflection which corresponds to the nodal plane of the exciting standing wave passing through the bromine atom positions. The theoretical fit to the data also shown in the figure takes into account both the positions of the bromine atoms and the fraction that actually occupy a coherent lattice site.

The deduced position is 2.56 ± 0.03 Å above the extrapolated last maximum in the (111) Fourier component of the silicon charge density at the surface (which, the reader should know, does not correspond to a physical silicon atomic plane; see Fig. 1). This position is indicated as distance A in Fig. 1. Within the experimental error this is just where covalently bonded bromine atoms would reside if they terminated the silicon lattice on the (111) plane that would yield only one terminating bond per surface Si atom. Therefore we see directly that the last silicon layers are the closely spaced physical (111) atom planes as drawn in Fig. 1. Furthermore, to within 0.03 Å no surface relaxation can be allowed without changing the Si-Br covalent bondlength (2.17 Å) by a corresponding amount. A perusal of tetrahedrally bonded silicon halide bond lengths from electron scattering on vapors[8] excludes this possibility. The coherent part of the bromine signal in Fig. 2 amounts to 67% of the total coverage. The latter was $\sim 10^{14}/cm^2$.

The above discussion of the bromine atom location is based upon a single distance measurement and bonding arguments from physical chemistry The x-ray standing-wave data by itself could support a model where bromine atoms lay a distance A above the surface and form a two-dimensional liquid along the surface uncorrelated to the crystal below. Alternatively, bromine atoms could occupy sites correlated to the crystal below but not directly above the top most silicon atoms as required by the discussion of the previous paragraph. This matter can be resolved by performing standing-wave experiments with diffraction planes that do not lie parallel to the surface. In this geometry a liquid layer would show no coherent fluorescence signal. Not only does observation of a coherent signal here show the presence
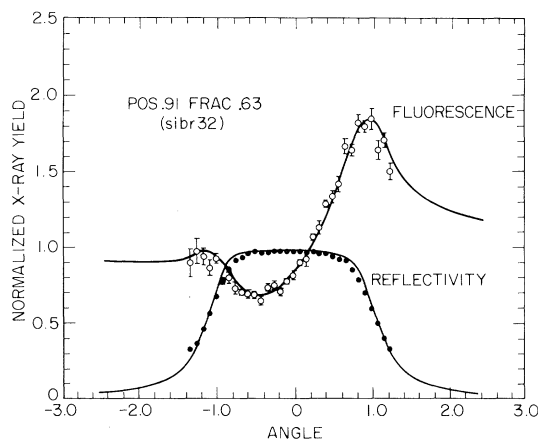

FIG. 2. Bromine fluorescence and reflectivity angular yields for (111) Bragg diffraction on a silicon (111) surface. Angular scale is in reduced units where rocking curve width is 2.
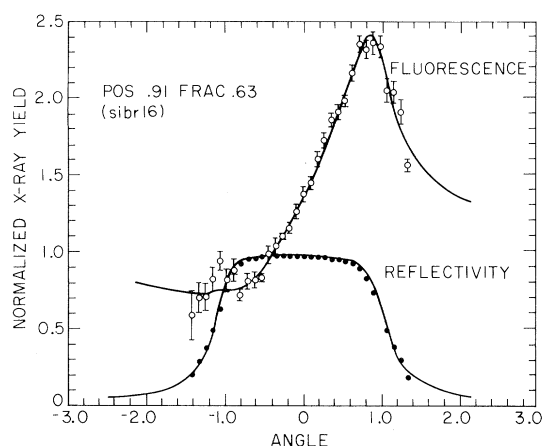
FIG. 3. Bromine fluorescence and reflectivity angular yields for (220) Bragg diffraction on a silicon (111) surface. Angular scale is in reduced units where rocking curve width is 2.

of atoms in sites correlated to the crystal, but the absolute transverse position can be extracted from the details of the fluorescence angular yield data.

Figure 3 shows the results of a standing-wave experiment with use of one of the (220) planes for the diffraction which intersects the (111) surface at an angle of 35.26 degrees. A clear coherent signal is observed. Its magnitude is 63% of the total signal which is similar to the (111) case. The theoretical fit in the figure corresponds to a bromine position 1.75 ± 0.02 Å normal to the (220) plane of silicon atoms pointing away from the surface. This is the value for distance B in Fig. 1. Taking this together with the analogous results from the two other (220) planes that intersect the surface at the same angle, we uniquely deduce that the bromine atoms sit directly above the topmost silicon surface atoms to an accuracy of ~ 0.04 Å. Coverage of bromine and coherent fraction of atoms are as in the (111) reflection study.

There are several important points to be addressed concerning the interpretation of these atom location results. Except for the coherent bromine atom locations we are completely ignorant of the state of the surface. Thus 90% of the

surface Si atoms are terminated either by bonding to oxygen or other surface impurities or are reconstructed in some undetermined way. The simple result we deduce with regard to both bromine position and surface relaxation seems remarkable in view of the conceivable complications our uncharacterized surface could induce. To our knowledge no one has yet been equal to the challenge of performing an x-ray standing-wave measurement in a controlled ultrahigh-vacuum environment. The relationship of our results on "practical" surfaces to the more controlled surfaces that would thereby be obtained awaits such an achievement. We are particularly interested in the possibility of terminating all (111) surface atoms in covalent Si-Br bonds. Such a surface would be well suited as a base for studies of further physically adsorbed layers by standing-wave measurements. For example, melting and crystallization of two-dimensional inert-atom layers physically adsorbed on such a substrate could be characterized in great detail by the methods demonstrated in this note.

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