Grazing-angle x-ray standing waves

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We have observed fluorescent radiation from surface adatoms of I on Ge(111) using x-ray standing waves created in the grazing-angle geometry. We demonstrate that standing waves which are determined by the real part of the x-ray wave vectors provide accurate atomic positions of adatoms or impurities parallel to the surface. The effect of changing evanescence due to the imaginary part of the wave vectors is directly visible in the standing-wave signal detected from the substrate. When combined with x-ray standing-wave results normal to the surface obtained from diffraction in the Bragg geometry, the measurements reveal that I reacted chemically with the (111) surface of Ge binds to the atop site of the Ge atom.

The technique of x-ray standing waves (XSW) has proven to be a useful technique of surface and bulk studies because of its ability to locate impurity atoms precisely with respect to the bulk lattice.[1-6] Furthermore, it is one of the few techniques for locating atoms in this respect on surfaces exposed to high-pressure gases or liquids.[4,5] One area in which XSW has made a significant contribution is the location of Br binding sites on Si surfaces.[6]

The reaction of halogens with semiconductors is important for several areas of semiconductor processing. Recent studies with the scanning tunneling microscope (STM) have shown that the reaction of Cl with the Si(111)-(7×7) surface allows for multiple binding of Cl on Si which is coverage dependent.[7] While they were not resolved by the STM, the inferred positions of the Cl atoms with respect to the underlying Si lattice should be directly observable in XSW measurements, as should similar reactions with other halogens if they occur on semiconductors. We report here the results of a study of I reacted with the (111) surface of Ge by chemical means, using a new type of XSW measurement made at grazing angles to a surface. It provides positional information *parallel* to the surface.

X-ray standing waves result from the interference of the incident and diffracted beam in a crystal of sufficient perfection that the diffraction is described by dynamical theory.[8] The x-ray fluorescence[1] or photoemission[9] observed when the phase of the standing wave is varied at the Bragg condition permits the locating of impurity or adatoms along the direction of the reciprocal lattice vector associated with the diffracted beam. The majority of XSW measurements have been performed in the Bragg geometry. The Laue geometry[10] and the total external reflection geometry[5] have also been used.

Recent treatments of diffraction at grazing angles, where the reciprocal-lattice vector is parallel to the surface of the crystal, describe a geometry where the x-ray field consists of incident, specularly reflected, and reflected-diffracted beams outside the surface and Laue beams inside the surface.[11-13] These beams are coherent and therefore contribute to standing waves, both inside

and outside the surface, whose behavior is more complicated than the Bragg case. In particular, the variation of the field amplitudes of the various components and the possibility that the wave vector of those components becomes imaginary makes for field intensities which differ markedly above and below the surface. Experiments in the grazing-angle geometry are considerably hampered by limits on the divergence of the x-ray beam in two dimensions (instead of one) and the low flux density on a crystal surface at a grazing angle. Previous attempts to observe standing-wave effects in the fluorescence of atoms in even the substrate crystal with grazing-angle diffraction (GAD) have been difficult.[14,15] The signal is further reduced when attempting to detect the positions of atoms present in submonolayer coverages on the surface.

We have successfully observed grazing-angle x-ray standing waves (GAXSW) in the fluorescent radiation from iodine atoms on the surface of germanium. The statistical accuracy of the data is sufficient to obtain positional information about the atoms parallel to the crystal surface. The fluorescent radiation observed from GAXSW from the substrate atoms demonstrates the strongly varying evanescence of the x-ray beams below the surface in the vicinity of the Bragg condition.

The experiment was performed on an x-ray beamline at the Cornell High Energy Synchrotron Source (CHESS). The measurements were made using a monochromatic beam of energy 5.98 keV. The experimental configuration, including the manner of monochromating and collimating the x-ray beam has been described elsewhere.[16]

The sample consisted of a Ge crystal with a (111) surface which was polished optically flat and free of stress. The surface was chemically reacted with iodine using wet chemistry, and was kept thereafter in an inert atmosphere. The sample was mounted in a two-axis goniometer; scanning was done by holding the angle of incidence φ constant and varying the diffraction angle θ about the Bragg angle $\theta_B = 31.22°$. The specularly reflected and reflected-diffracted fluxes from the crystal surface were monitored using ion chambers. The specular and diffracted beam photon fluxes were typically of the order 10^7/s. A

complete fluorescence spectrum was taken for the energy region 1–12 keV for each angular position using a Si(Li) detector. The net integrated x-ray fluorescence was determined from the Ge L lines (1.18–1.22 keV) and I L lines (3.93–4.80 keV).

Additional XSW measurements of I atoms deposited on a Ge(111) surface in ultrahigh vacuum (UHV) (Ref. 17) were made using photoemission in UHV and fluorescence in open air with the standard Bragg diffraction geometry. The purpose of these measurements was to obtain the height of the I atoms above the (111) Ge diffraction plane.

The geometry of the GAD experiment is shown in Fig. 1. For an adsorbate atom which is located on the crystal surface, the intensity of the field is given by

$$I = | E_0 e^{-i(\mathbf{k}_0 \cdot \mathbf{r} - \omega t)} + E_S e^{-i(\mathbf{k}_S \cdot \mathbf{r} - \omega t)}$$
$$+ E_H e^{-i(\mathbf{k}_H \cdot \mathbf{r} - \omega t)} |^2, \quad (1)$$

where E_0, E_S, and E_H are the electric fields of the incident, specularly reflected, and reflected-diffracted beams, respectively. The wave vectors are the external wave vectors for these beams, $|\mathbf{k}_0| = |\mathbf{k}_S| = |\mathbf{k}_H| = \omega/c$. The experiments were conducted in a geometry where the beams are σ polarized, so the electric-field vectors may be treated as parallel in the limit of the grazing angle.

The output (fluorescence, photoelectrons, etc.), proportional to the local field intensity at the atoms, is normally parametrized by the coherent fraction and the coherent position. The coherent fraction f is defined as the amplitude of the Fourier position component for the reciprocal-lattice vector $\mathbf{H}$ of the normalized atom distribution.[18] The coherent position p is defined as the phase of the Fourier component of $\mathbf{H}$ of the normalized atom distribution. The origin of p is the origin selected in calculating the dielectric susceptibility of the crystal unit cell. For the ($\bar{2}20$) reflection selected here, the origin is located on a (110) crystal plane as shown in Fig. 2. The three symmetry sites located at $p = 0$ are (111) atop sites, threefold hollow sites (H_3), and depressed (111) sites (T_4).

It can be shown that the fluorescent yield from atoms located a distance z above the surface is given by an expression of the form

$$Y = C\{1 + R_1^2 + R_2^2 e^{-2k_0 \varphi_H'' z} + 2R_1 \cos(V_1 + 2k_0 \varphi z)$$
$$+ 2R_2 e^{-k_0 \varphi_H'' z} f \cos[V_2 + k_0(\varphi_H' + \varphi)z + 2\pi p]$$
$$+ 2R_1 R_2 e^{-k_0 \varphi_H'' z} f \cos[V_2 - V_1 + k_0(\varphi_H' - \varphi)z + 2\pi p]\}$$

$$(2)$$

where $E_S/E_0 = R_1 e^{iV_1}$, $E_H/E_0 = R_2 e^{iV_2}$, and the coherent position is defined by $p = -\mathbf{H} \cdot \mathbf{r}/2\pi$. The takeoff angle of the reflected-diffracted beam is generally complex: $\varphi_H = \varphi_H' + i\varphi_H''$. The expressions R_1, V_1, R_2, and V_2 are all functions of φ, θ, and k_0. The $+\hat{z}$ direction is defined as going into the crystal.

For an atom which is inside the surface, the field intensity is given by

$$I = | D_{0\alpha} e^{-i(\mathbf{K}_{0\alpha} \cdot \mathbf{r} - \omega t)} + D_{0\beta} e^{-i(\mathbf{K}_{0\beta} \cdot \mathbf{r} - \omega t)}$$
$$+ D_{H\alpha} e^{-i(\mathbf{K}_{H\alpha} \cdot \mathbf{r} - \omega t)} + D_{H\beta} e^{-i(\mathbf{K}_{H\beta} \cdot \mathbf{r} - \omega t)} |^2, \quad (3)$$
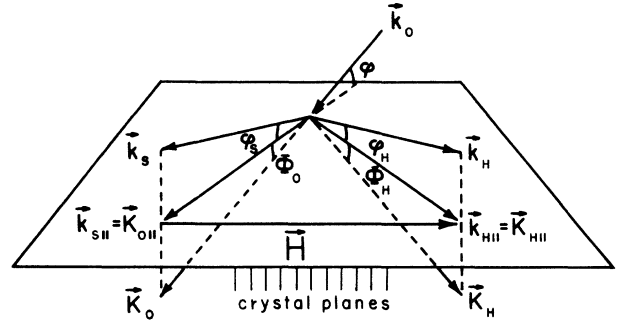

FIG. 1. Diagram showing the beams which can result from an x-ray beam of wave vector $\mathbf{k}_0$ on a crystal and diffracted by a reciprocal-lattice vector $\mathbf{H}$ parallel to the crystal surface.

where D_{0i} and D_{Hi} are the fields of the undiffracted and diffracted beams, respectively, for $i = \alpha, \beta$ the two branches of the diffraction solution in the crystal. The wave vectors $\mathbf{K}_{0i}$ and $\mathbf{K}_{Hi}$ are the internal wave vectors for the undiffracted and diffracted beams. The fluorescent yield from atoms at a depth z inside the crystal takes the form:

$$Y = Ce^{-\alpha z}\{(|D_{0\alpha}|^2 + |D_{H\alpha}|^2)d_1 + (|D_{0\beta}|^2 + |D_{H\beta}|^2)d_2$$
$$+ 2T_1 R_3 \cos V_3(z) + 2T_2 R_3 \sin V_3(z)$$
$$+ 2R_0 f \cos[V_0(z) - 2\pi p]\}, \quad (4)$$

where d_1, d_2, R_0, R_3, T_1, T_2, V_0, and V_3 are all functions of φ, θ, k_0, and z, and α is an escape coefficient for the fluorescent radiation.

Figure 3(a) shows the specularly reflected flux and the reflected-diffracted flux measured as a function of the deviation from the geometric Bragg angle $\Delta\theta = \theta - \theta_B$. The nominal angle of incidence $\varphi = 7.2$ mrad was close to the critical angle at this energy $\varphi_c = 7.32$ mrad. The specular-
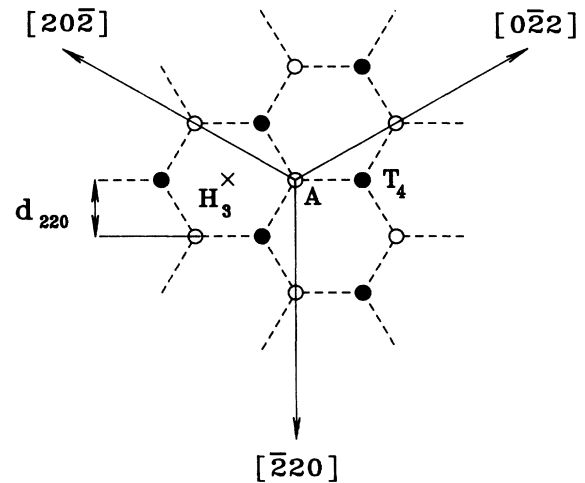

FIG. 2. Top view of the (111) surface of Ge showing the location of atop (A), H_3, and T_4 sites with respect to the wavelength and origin of an x-ray standing wave originating from a ($\bar{2}20$) reflection. The open circles are raised atoms in the (111) plane, and the solid circles are depressed atoms.
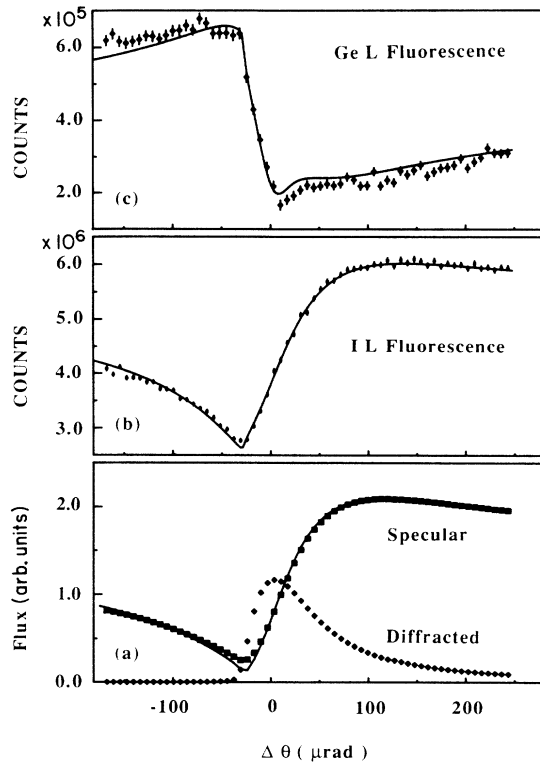
FIG. 3. (a) Ge specular beam flux (■) (220) and reflected-diffracted beam flux (♦) vs diffraction angle $\Delta\theta=\theta-\theta_B$ for a nominal angle of incidence $\varphi=7.2$ mrad. The solid line is the fit of the specular beam flux from theory for $\delta\varphi=0.3$ mrad and $\delta\theta=17$ μrad, and $\varphi=7.43$ mrad. (b) I L fluorescence (●) as a function of the same $\Delta\theta$. The solid line is the fit from GAXSW theory for $f=0.31\pm0.05$ and $p=-0.01\pm0.04$. (c) Ge L fluorescence (♦) from the entire escape depth of the crystal as a function of $\Delta\theta$. The solid line is the fit obtained by GAXSW theory for $f=1.0$, $p=0.04\pm0.04$.

ly reflected flux is observed to undergo a dip in the vicinity of the Bragg condition. The reflected-diffracted flux appears to be highly asymmetric, because it becomes evanescent outside the crystal for $\Delta\theta<-5$ μrad.[12,16]

It is customary in Bragg XSW to correct linear errors in the diffraction angle by fitting the rocking curve of the diffracted peak. In this case, the specular reflection about the Bragg condition was chosen rather than the diffracted peak because the real component of the takeoff angle φ_H' of the reflected-diffracted beam decreases as $\Delta\theta$ decreases, and the exact shape of the cutoff is dependent on the overall flatness of the crystal.

The solid line in Fig. 3(a) shows the result obtained by fitting the specular flux to the theory. The fit takes into account the angular divergence of the beam $\delta\theta=17$ μrad due to the monochromator and the angular divergence $\delta\varphi=0.3$ mrad due to the finite source size of the synchrotron beam and the limits of flatness of the sample crystal. The corrected angle of incidence obtained by the fit $\varphi=7.43$ mrad and the corrections to the scale for θ were then applied to the fits of the fluorescence data.

Figure 3(b) shows the I-L fluorescence detected over the same angular range. In order to obtain the vertical

height of the I atoms, we made a Bragg XSW measurement on a separate sample in which the I atoms were deposited on the Ge(111) surface in UHV (Ref. 17) and promptly removed. Using the Ge(111) reflection, we obtained a coherent position of $p=0.874\pm0.01$ for both the atomically clean and the open air surfaces. The coherent fraction was $f=0.97\pm0.02$ for the UHV surface and was as high as $f=0.87$ for the open air surface. Since $d_{111}=3.2664$ Å, this corresponds to a position of 2.85 ±0.03 Å above the (111) diffraction plane or 2.49 ± 0.03 Å above the uppermost (111) bulklike layer of atoms. This distance is also consistent with previous surface-extended x-ray-absorption fine structure (SEXAFS) measurements of I on Ge in UHV.[19]

This value of z was used to fit the fluorescence data in Fig. 3(b). For the ($\bar{2}20$) GAD reflection from Ge we obtain an I coherent fraction of $f=0.31\pm0.05$ and coherent position of $p=-0.01\pm0.04$, where $d_{220}=2.000$ Å. Data taken for $\varphi=6.9$ and 5.0 mrad gave similar results, all consistent with $p=0$. The relatively low coherent fraction is attributed to the length of time required to obtain data with good statistics in this initial study, and attempts to fit the I atoms to multiple coherent sites were not successful. A coherent position of $p=0$ is consistent with atop, $H3$, and T_4 sites. If we take the nearest-neighbor distance 2.50 ± 0.04 Å between I and Ge(111) obtained in UHV by SEXAFS,[19] this gives vertical positions with respect to the diffraction plane of 2.9, 2.1, and 1.3 Å for the atop, T_4, and $H3$ sites, respectively. We conclude that for I deposited on Ge by wet chemistry, we see I atoms binding only to the Ge(111) atop site.

Figure 3(c) shows the Ge L fluorescence detected over the same angular range of $\Delta\theta$. The angular dependence of the Ge fluorescence data differs markedly from that of the I fluorescence. This is due to the strong changes in the extinction effect in this region as well as from standing-wave effects.[16] The data were fitted by integrating the expression (4) over all $z\geq0$, to obtain the total fluorescence yield from the crystal. By setting the coherent fraction to $f=1.0$, we obtain the fit (solid line) which gives a coherent position of $p=0.04\pm0.04$. The fit reproduces all the variation of the Ge fluorescence.

It should be noted that this type of measurement is different from other XSW measurements in one respect. The position of atoms is determined with high precision parallel to the surface, since the location of $r_\parallel=0$ is defined by calculating the dielectric susceptibility χ_H used in the diffraction calculation. The variation of fields in the z direction is determined, however, from the location of the boundary condition at the surface. The present theory assumes matching interior and exterior boundary conditions at a discontinuous step in charge density at $z=0$. This is sufficient to describe the data because the variation in the field intensities normal to the surface is not nearly as rapid as it is parallel to the surface. It would be desirable to establish the effective location of the interface plane using actual calculated charge densities for the semiconductor substrates. The dynamical theory should also take into account the direct contribution from scattering of the adsorbed layer. This has been neglected in XSW calculations up to now, but may be visible due to

the surface sensitivity of GAXSW.

While the slow variation in field intensities normal to the surface precludes obtaining the same precision as from the interference parallel to the surface, this variation differs sufficiently inside and outside the crystal that it should be possible to determine on which side of the interface the impurity atom is located.

The results obtained in this experiment are not limited to surfaces. An advantage of GAXSW over Bragg standing-wave measurements is that the total external reflection of beams from the surface is accomplished at any interface which consists of crystalline material of lower dielectric susceptibility on top of material of higher susceptibility. This includes many heterojunctions of semiconducting materials made by molecular-beam epitaxy. Potential uses for GAXSW would be to identify the location of impurities at these heterojunctions.

In summary, we demonstrate by means of a new technique of grazing angle x-ray standing waves that I atoms reacted with the Ge(111) surface by chemical means occupy the atop sites. The observations are consistent with a single coherent position of I atoms with respect to the Ge surface.

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