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X-Ray Diffraction Study of the Ge(001) Reconstructed Surface

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Standard x-ray diffraction in which a reflection goemetry is used is shown to have a simple interpretation and adequate sensitivity for determining the structure of monolayers. It has been utilized to verify that subsurface strain occurs in Ge(001)-(2×1) reconstruction.

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The structural determination of reconstructed single-crystal surfaces has been an area of considerable interest for many years. Since the initial studies of Farnsworth and co-workers,[1] many authors have reported surface reconstruction on a variety of clean surfaces.[2] To data, almost all surface structure determinations have been carried out by using or comparing calculated structures to low-energy electron-diffraction (LEED) or photoemission data.[3-9] However, even with all this work there is still a scarcity of solved reconstructed structures. One possible explanation is the well-known problem that LEED intensities are difficult to analyze because of multiple scattering.

Marra, Eisenberger, and Cho[10] have developed an alternative method called x-ray total-external-reflection Bragg diffraction (TRBD). In TRBD, a monochromatic x-ray beam is incident upon a surface at very glancing angles, typically less than 1°. The incident beam can be both reflected out of the surface at small angles and diffracted parallel to the surface over large angles. Using TRBD,[10] one is measuring Bragg reflections $(h,k,0)$ where h and k are Miller indices parallel to the surface. The measured Bragg intensities are directly amendable to straightforward interpretation, since they can be explained kinematically because of the absence of multiple scattering. In this study we increased our signal by increasing the tilting of the sample in the reflecting plane above the critical angle.[10] While this increases the substrate contribution, one also has more beam hitting the surface. The momentum necessary to get the scattered beam out of the surface was provided by the two-dimensional (2D) character of the reconstructed surface. For 2D order the Bragg scattering contours are rods perpendicular to surface and not spots. The intensity variation for momentum transfers perpendicular to the surface will depend upon the molecular form factor of the reconstructed unit cell. In the future, we intend to utilize this to determine the displacements of the atoms perpendicular to the surface. In this case the reflecting angle did not exceed 1° and so for all practical purposes we were only measuring $(h,k,0)$ intensities.

Ge(001)-(2×1) LEED studies have shown no agreement between theory and experiment.[8] Our results clearly indicate that Ge(001) reconstruction involves displacements that are not limited to the first layer. This is in agreement with the theoretical predictions of Appelbaum and Hamann[7] and Chadi.[9] With the small number of reflections measured to date, our results for the displacements of the atoms in the first two layers are in rough agreement with theoretical predictions.

The x-ray scattering procedure, diffractometer, and electronics are essentially the same as that described in our study of Al-GaAs interface.[10] One difference was that the experimental resolution for these studies was 0.014 $Å^{-1}$, obtained by using both slits and pyrolitic graphite crystals on

the input and output of the x-ray spectrometer. Another difference was that an ultrahigh-vacuum (UHV) x-ray cell was used as a housing for the Ge sample. The x-ray cell is a UHV stainless-steel assembly. X rays enter and leave the cell through a 0.010-in.-thick Be window which has an access of 260 deg. The x-ray cell can be separated under vacuum from a larger UHV sample preparation chamber (SPC). The SPC has characteristic surface analysis and preparation equipment such as a LEED, Auger-electron optics system, and an argon-ion sputtering gun. A detailed description of the vacuum system is given elsewhere.[11]

Germanium (001) surfaces were cleaned by argon-ion sputtering for 3–8 h and followed by several anneals at 700 °C for 20 min each. The resulting structure was a reconstructed 2×1 Ge surface, i.e., a doubling of the unit cell along the [110] direction. It should be noted that no $\frac{1}{4}$-order LEED reflections were observed. A prepared Ge(001)-(2×1) sample was moved to the x-ray cell; detached from the SPC and mounted on the x-ray diffractometer. Periodic checks of the reconstructed surface showed that good LEED patterns were observed for periods in excess of two weeks; a H_2 overlayer had probably stabilized the surface.

We will adopt the representation that h is along the conventional [110] direction and k is along the $[\bar{1}10]$ both corresponding to units of $2\pi/a$, a being equal to $a_0/\sqrt{2}$ ($a_0 = 5.65$ Å). The room-temperature results for the $(\frac{3}{2},0)$ Bragg reflection are shown in Fig. 1. For each reflection both radial scans as a function of the momentum transfer Q and angular scans as a function of sample orientation were performed so that the total integrated x-ray intensity could be determined. Note that each curve shows two spectra. In addition to the data obtained on a 60-kW rotating-anode x-ray tube at Bell Telephone Laboratories, indentical experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL). We found a 100-fold increase in integrated intensity at SSRL due to the brightness of the synchrotron source. The relatively larger signal rate means that the variety of problems one can study is virtually unlimited if synchrotron radiation is used. Although the results given in this Letter are based upon the $(\frac{1}{2},0)$, $(\frac{3}{2},0)$, $(\frac{5}{2},0)$, $(\frac{1}{2},\bar{1})$, and $(\frac{3}{2},\bar{1})$ Bragg reflections measured at Bell Laboratories, our preliminary results of the SSRL data indicate that varying degrees of surface disorder can alter top-layer displacements. All experimental data ob-

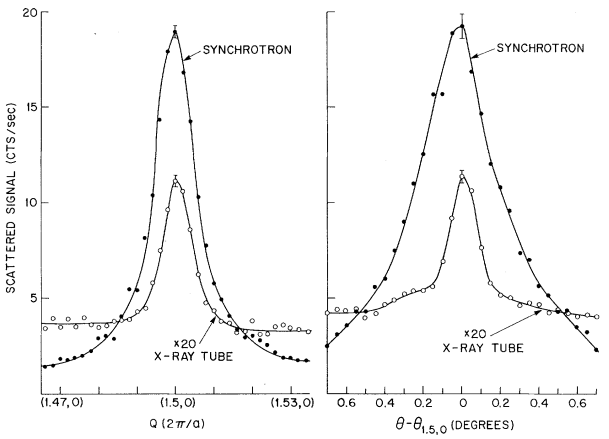

FIG. 1. A plot of the $(\frac{3}{2},0)$ Bragg reflection as a function of the momentum transfer $Q(2\pi/a)$ and the crystal's mosaic spread (deg).

tained by doing a radial scan had a width determined by the resolution of the spectrometer. Thus the ordered regions are in excess of 200 Å. Secondly, all reflections with use of the rotating-anode source exhibited similar mosaic spreads [full width at half maximum (FWHM) $\cong 0.2°$]. These two results are strong indications that the sample surface was very uniformly prepared. All reflections were checked at the beginning and completion of the experiment to be sure that the intensities stayed constant. Two identical fractional order reflections $(h,k,0)$ and $(-h,-k,0)$ gave the same intensities. We also searched unsuccessfully for $\frac{1}{4}$-order reflections along the [100] and $[\frac{1}{2}\,\bar{\frac{1}{2}}\,0]$ directions and the presence of a $(\frac{1}{2},\bar{\frac{1}{2}},0)$ Bragg reflection.

The total measured integrated intensity $I(h,k)$ for a given (h,k) reflection in an unpolarized incident beam[12] of intensity I_0 can be written from simple kinematic theory as

$$I(h,k) = I_0 \frac{1+\cos^2 2\theta_B}{\cos\theta_B} f^2(Q) I_c(h,k), \qquad (1)$$

where $Q = 2\pi/d_{hk}$ is the magnitude of the momentum transfer and d_{hk} is the spacing between consecutive (h,k) Bragg reflecting planes. θ_B is the Bragg angle and $f(Q)$ is the Ge atomic form factor. $I_c(h,k)$ is the term to be determined and contains all the structural information about the surface reconstruction and is given by

$$I_c(h,k) = C\left|\sum \exp[(2\pi i/a)(hX_{n,p} + kY_{n,p})]\right|^2 \times \exp[(-4\pi/a^2)(\langle\mu_x^2\rangle h^2 + \langle\mu_y^2\rangle k^2)], \qquad (2)$$

where C is a normalization constant and the sum

is over the n sites of the unit cell in the pth layer. The mean squared displacement of the unit cell due to thermal motion around the equilibrium positions X_{np} and Y_{np} are represented by $\langle\mu_x^2\rangle$ and $\langle\mu_y^2\rangle$ and are assumed to be layer independent. For a synchrotron source the term $1+\cos^2 2\theta_B$ in Eq. (1) becomes unity. In Eq. (1), the term $\cos\theta_B$ has replaced the characteristic $\sin 2\theta_B$ term. This is a property of 2D scattering.

The experimental results obtained for our integrated intensities lead to the following: $I_c(\frac{1}{2},0) = 2.28C$, $I_c(\frac{3}{2},0) = 2.80C$, $I_c(\frac{5}{2},0) \leq 0.035C$, $I_c(\frac{1}{2},1) = 1.11C$, and $I_c(\frac{3}{2},1) = 0.526C$. We have performed a nonlinear least-squares analysis in order to fit the integrated intensities to the following theoretical models. First is the Farnsworth and Schlier (F-S) simple dimer model allowing only symmetrical top-layer displacements: $X_{11} = -X_{21}$, $Y_{11} = Y_{21} = 0$, and $\langle\mu_x^2\rangle \neq \langle\mu_y^2\rangle$ (see Fig. 2). Secondly, we use the two-layer model proposed by Appelbaum and Hamann (A-H) which uses symmetrical displacements in the top layer, i.e., $X_{11} = -X_{21}$, $Y_{11} = Y_{21} = 0$, $X_{12} = -X_{22}$, $Y_{12} = Y_{22} = 0$, $\langle\mu_x^2\rangle = \langle\mu_y^2\rangle$; and Chadi's model for Si with use of asymmetric displacements in the first layer, i.e., $X_{11} \neq X_{21}$, other conditions being the same.

The results of our least-squares analysis are given in Table I. The columns "Expt" give the results determined by our x-ray intensities. For each model the mean result is given based upon $I_c(\frac{5}{2},0) \leq 0.034$. The empirically determined results are followed by the theoretical results. The quality of the fitted data is determined by a standard R factor defined as

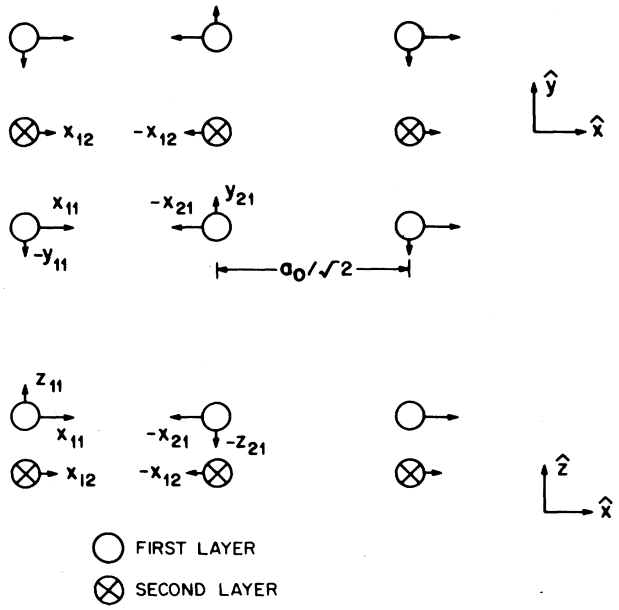

FIG. 2. An illustration of the displacements of the first two layers both parallel and perpendicular to the surface.

$$R = [\sum_i (I_i^{obs} - I_i^{calc})^2 / \sum_i (I_i^{obs})^2]. \quad (3)$$

Here ob and calc denote the observed and calculated quantities, respectively, and the sum runs over the number of reflections. Since the ratio of variable parameters to observed intensities is al-

TABLE I. Atomic displacements of the first two layers for the F-S, A-H, and Chadi models calculated from x-ray intensities, followed by their corresponding theoretical values. All parameters are given in angstroms.

	Models					
	I. F-S		II. A-H		III. Chadi	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
X_{11}	0.83 ± 0.01	0.78	0.92 ± 0.04	0.723	0.92 ± 0.04	0.46
X_{21}	−0.83 ± 0.01	−0.78	−0.92 ± 0.04	−0.723	−0.92 ± 0.04	−1.08
Y_{11}	0	0	0	0	0	0
Y_{21}	0	0	0	0	0	0
Z_{11}[a]	0.33 ± 0.06	···	0.64 ± 0.05	0.09	0.64 ± 0.05	0.04
Z_{21}[a]	−0.33 ± 0.06	···	−0.64 ± 0.05	−0.09	−0.64 ± 0.05	−0.43
X_{12}	···	···	0.116 ± 0.01	0.124	0.116 ± 0.01	0.115
X_{22}	···	···	−0.116 ± 0.01	−0.124	−0.116 ± 0.01	−0.115
$\langle\mu_x^2\rangle^{1/2}$	0.37 ± 0.02	···	0.24 ± 0.02	···	0.245 ± 0.02	···
$\langle\mu_y^2\rangle^{1/2}$	0.68	···	0.24 ± 0.02	···	0.24 ± 0.02	···
R	1.9×10^{-2}	···	6×10^{-5}	···	6×10^{-5}	···

[a] Calculated for an assumed bond length of 2.44 Å.

most unity, the R factor should be viewed as a measure of the quality of the fitted data to the above models in a relative sense. Model I gives a very poor fit. However, the two models labeled II and III give not only good fits but also nearly identical results. This occurs in spite of the fact that we only use four parameters in the A-H model and demand that $X_{21} = -X_{11}$, and use five parameters in the Chadi model with no constant on X_{21}. Comparing our results to the theoretical models in Table I, we see that the magnitudes of our displacements are closer to Chadi's[9] silicon results when scaled for Ge by their relative lattice parameters. We find that the magnitude of the first-layer displacements are 0.92 Å along the [10] direction. These paired atoms must move in opposite directions along the [001] direction by an amount of 0.64 Å if one has a bond length of 2.44 Å (see Fig. 2). This motion is consistent with Chadi's results; however, our displacements are symmetric around the center position of the reconstructed lattice, unlike Chadi. The need for displacements in the second layer clearly support the contention of Appelbaum and Hamann[7] that reconstruction induces subsurface stain. Before continuing, it should be mentioned that we did attempt to fit a one layer model with arbitrary X-Y displacements which preserved a simple unit cell doubling. The results gave a good fit to our integrated intensities; however, the Debye mean square displacements were as large as the static displacements.

We are in the process of measuring more reflections which should significantly increase the accuracy of our parameters. We already know that varying degrees of disorder on the surface can alter the top-layer displacements by as much as 5%. What we can confidently say from these studies is that for the above-mentioned models the distortion must involve more than the first layer. We also have found that the displacements are roughly in agreement with existing theories.

Of equal or greater importance to the specific results of these studies is the existence as demonstrated in this work of a technique that has the sensitivity and simplicity of interpretation to successfully perform reconstructed and adsorbate crystallography. It is, of course equally apparent that TRBD or the variant used here, reflection Bragg diffraction (RBD), can be used to investigate 2D physics including the study of phase transitions of which melting may be one of the most interesting.[13]

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