Synchrotron X-Ray Diffraction Study of the Disordering of the Ge(111) Surface at High Temperatures

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The Ge(111) surface has been reported to undergo a disordering phase transition at approximately 1050 K. Our synchrotron x-ray diffraction study demonstrates that there is, instead, a progressive disordering of the topmost layers, which retain long-range order up to at least 1150 K. Neither diffuse scattering associated with roughening or surface melting nor effects due to surface incommensurability are observed. A model involving a proliferation of surface vacancies gives a consistent description of the data.

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Currently, experimental information on the morphology of semiconductor surfaces near the bulk melting point is very limited, in spite of its evident importance in many growth processes. The Ge(111) surface has been reported to undergo a phase transition at a crystal temperature of about 1050 K, which is 160 K below the bulk melting temperature T_m (1210 K).[1-4] The nature of the transition remains controversial.[2-4] We have studied the Ge(111) surface using synchrotron x-ray scattering techniques with a glancing-angle scattering geometry. Our observations do not conform to any standard model of surface disordering. We believe that the structural change is not due to a phase transition, but rather reflects a continuous change of the surface morphology. We propose a model in which disorder is induced by surface vacancies which become abundant at about 160 K below T_m. The surface diffraction data can be understood quantitatively by use of kinematical diffraction theory.

At room temperature, a $c(2\times8)$ structure on the Ge(111) surface is stable.[5] Near 573 K the $c(2\times8)$ reconstruction converts to a (1×1) phase.[6] The (1×1) structure may not have an ideally terminated bulk structure; adatoms are believed to be present.[7] At higher temperatures a second structural transition of the Ge(111) surface was first suggested by Lever in 1968.[1] He found that the sticking coefficient of oxygen on Ge(111) dropped precipitously with increasing crystal temperature near 1050 K.[1] McRae and Malic recently studied this reported transition in a low-energy electron-diffraction (LEED) experiment.[2] The intensity of the surface diffraction peaks decreased rapidly near 1050 K saturating at a low but nonzero value. The results were interpreted on the basis of a heuristic model in which the outermost double layer of the Ge(111) consists of incommensurate crystalline islands surrounded by a disordered sea. Electron-energy-loss spectroscopy done on a Ge(111) single-crystal surface, as well as on liquid and amorphous Ge overlayers, suggested that the high-temperature disordered Ge(111) surface resembles an amorphous layer more than a liquid layer.[3] Ion scattering indicated that above ~1050 K there are local departures of surface atoms from their equilibrium lattice positions.[4]

Our experiments were performed on the IBM-MIT beam line X20A at the National Synchrotron Light Source at Brookhaven National Laboratory. A beam of 8.91-keV photons was focused onto the sample. The resolution function was set by slits. The longitudinal half width at half maximum (HWHM) was 0.0022 Å^{-1}. The transverse HWHM was 4.6×10^{-4} Å^{-1}. The sample and surface chamber were oriented in a grazing-incidence geometry such that the in-plane $(\frac{2}{2}\,\frac{2}{3}\,\overline{\frac{4}{3}})$ and $(\frac{4}{3}\,\frac{4}{3}\,\overline{\frac{8}{3}})$ nonspecular surface peaks as well as the in-plane bulk $(02\bar{2})$ peak were observable. In the LEED convention, which we will use for in-plane peaks for the rest of this work, these are respectively the (10), (20), and (11) peaks of the surface triangular lattice. The $\langle111\rangle$ direction was approximately perpendicular to the scattering plane. The incident and outgoing grazing angles were adjusted to maximize the detected intensity from the surface peaks. This condition is satisfied at the critical angle for total external reflection, which is 0.28°. X-ray measurements were performed on five samples with similar results. One sample was also mounted with its surface normal in the scattering plane to measure the temperature dependence of the bulk $(444)_{\text{cubic}}$ peak.

Our observations were made on Ge wafers (*n*-type, Sb doped, 1.0 Ω cm, $30\times6\times0.5$ mm^3) resistively heated inside a surface chamber which had a base pressure of 5×10^{-10} torr. The sample surface was prepared by ion bombardment [10^{16} Ar$^+$ ions/(cm^{2}sec), 700 eV, normal incidence] for 30 min at 970 K followed by a 1-h anneal at the same temperature. Auger-electron spectroscopy was done *in situ* to check surface cleanliness. The sample temperature was measured by two W5%Rh/W26%Rh thermocouples which were calibrated against the melting temperature of bulk Ge. The temperatures measured with these thermocouples were in agreement with those obtained with an optical pyrometer with an emissivity setting of 0.46.

Representative (10) scans at a series of temperatures bracketing 1070 K are shown in Fig. 1. It is evident that well-defined sharp peaks are observed up to temperatures near bulk melting; significantly, there is no important change in line shape throughout this temperature range. The integrated intensities of the (10) and (20) peaks are shown in Figs. 2(a) and 2(b), respectively. Both show pronounced minima at about 1070 K. By contrast, the (11) and (444) bulk peaks exhibit weak variations in their intensities throughout this temperature range with intensity variations consistent with the known bulk Debye-Waller (DW) factors.[8] The minimum in the (10) and (20) surface peak intensities thus reflects a change in the surface morphology around 1070 K, in qualitative agreement with the LEED experiments.[5]

We now discuss the significance of the (10) scans shown in Fig. 1. First, it is evident that the peaks are always commensurate to within 0.001 Å^{-1}. This immediately rules out any models for the surface metamorphosis based on a lateral compression of the surface layers.[5] Second, the peaks are quite sharp in both the longitudinal and transverse directions at all temperatures. Fits of the central portions of each of the (10) longitudinal scans with a Gaussian curve demonstrate that the peaks

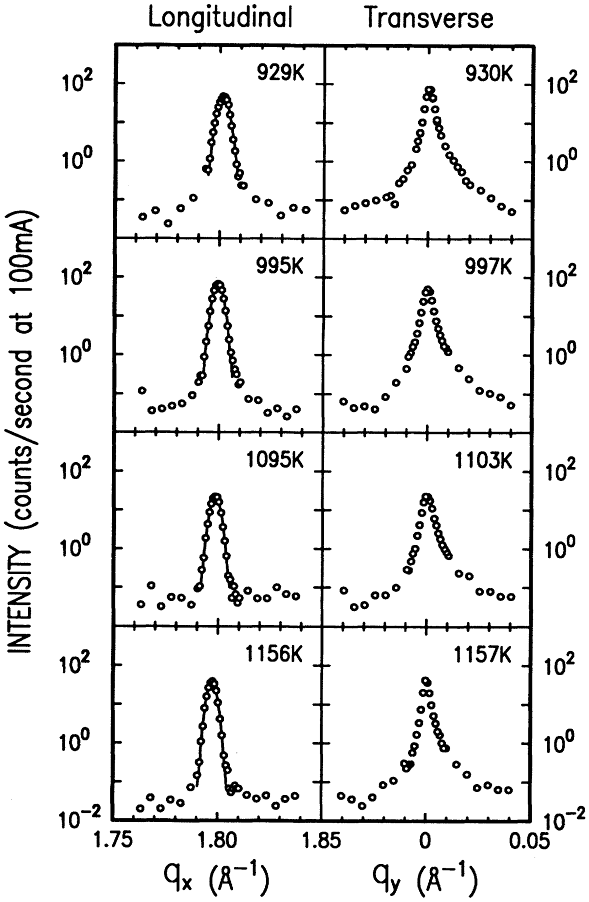

FIG. 1. Longitudinal and transverse scans through the (10) peak are shown for four different temperatures: 929, 995, 1095, and 1156 K. The central portion of each of the longitudinal scans is fitted with a Gaussian curve. All widths fall within ±10% of 0.0022 Å^{-1} HWHM.

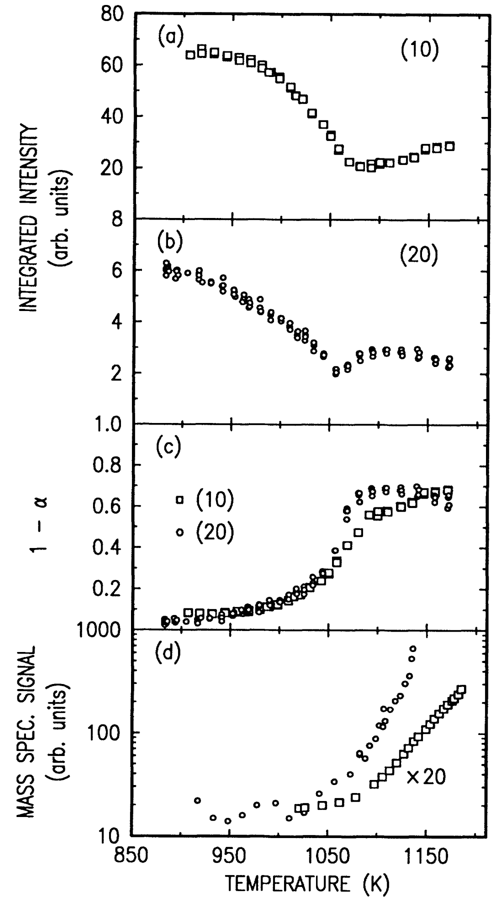

FIG. 2. The integrated intensities of the (a) (10) and (b) (20) peaks as a function of temperature. Although the overall vertical scales are arbitrary, the ratio between the scales reflects the ratio in peak intensities. (c) The data inverted according to the model outlined in the text. The vertical axis represents the vacancy fraction in the first bilayer for small fractions. (d) The ionization current of a mass spectrometer in arbitrary units as a function of temperature. The circles are the *in situ* data while the squares are the AT&T data. The ratio of signal in the observed mass channel to that in neighboring channels exceeds 5:1 in the AT&T data.

are resolution limited with a HWHM of 0.0022 ± 0.0002 Å^{-1}. We estimate that we are sensitive to a change of roughly twice the uncertainty in the width. Since Gaussian widths add in quadrature, this means that the intrinsic HWHM can be at most 0.0014 Å^{-1}. For finite-size domains the size is related to the HWHM by $L \simeq 2.8/\text{HWHM}$. Thus, the surface domains exceed 2000 Å in size throughout the measured temperature range. This in turn necessitates that there are no thermally generated single or double bilayer steps with a mean spacing much less than 2000 Å up to 1156 K; such steps take one from one fcc sublattice to another and thus would produce a broadening of the peak. Third, it is evident, especially from the longitudinal scans, that there is no significant diffuse scattering in the tails. This immediately rules out surface-roughening[9] and lattice-gas melting models[10] for a surface transition in this temperature range.

Our own model rests strongly on the above observations together with the unusual behavior of the (10) and (20) intensities shown in Fig. 2. Before discussing this model, we note that we searched without success for diffuse scattering indicative of a floating surface fluid layer. Such features either do not exist or were too weak to be detected. We also carried out an extensive survey to locate satellite structures around the (10) peak; no such features were found. This contrasts with the LEED measurements where weak satellite beams were typically observed. McRae and Malic[2] reported, however, that their satellite peaks were not reproducible with temperature cycling.

There are two principal features of the data in Fig. 2 which require explanation. First, the (10) and (20) peaks exhibit similar behavior. This immediately rules out models based on random strains or disorder since such effects produce strongly q-dependent behavior in the scattering. Second, in contrast to the behavior seen with LEED,[2] the (10) and (20) surface peak intensities actually *increase* above 1070 K. These observations severely constrain possible models of the surface structure and morphology. In fact, the only model that we have been able to construct which is consistent with our own x-ray data as well as the LEED data is one based on the proliferation of random vacancies in the surface bilayer. This model was originally suggested to us by sublimation data to be discussed later in this paper, but is in no way dependent on those data.

We now consider the effects of random vacancies on the bulk-forbidden surface scattering. The penetration length of x rays into a Ge crystal at the critical angle is about 190 Å. A bulk-forbidden surface peak like the (10) or (20) occurs when a periodicity in the surface layer is repeated with a phase shift in successive layers. The destructive interference and the finite penetration depth of x rays into the crystal yield a net scattering intensity of about one-third of the intensity expected from a single atomic layer of Ge(111). Because successive layers add out of phase, the net intensity is highly sensitive to the in-plane order in each of the uppermost layers. The structure factor of the (h0) peaks can be expressed by the following formulas:

$$I \propto S(q) = \left| \sum_{n=0}^{\infty} \alpha_{n+1}(q,T) e^{in\phi} e^{-n\varepsilon} \right|^2 , \qquad (1)$$

where I is the intensity, α_n is the q-dependent scattered amplitude from the nth bilayer for a particular surface periodicity, ϕ is the phase shift of this Fourier component between successive bilayers, and ε^{-1} is the extinction length in units of the bilayer separation. For the (h0) peaks of Ge(111), $\phi = 2\pi h/3$. At the critical angle for total external reflection, $\varepsilon = 0.0085$.

For simplicity, we assume that the surface bilayer disorders while all deeper layers do not. Then one has

$$I(q,T) = I_0 \{ \alpha_1^2 + A(\varepsilon) \alpha_{\text{bulk}} \alpha_1 + B(\varepsilon) \alpha_{\text{bulk}}^2 \} + I_{\text{bg}} , \qquad (2)$$

where α_1 is the scattered amplitude for the surface bilayer, α_{bulk} is the scattered amplitude for the remaining bulk layers, I_{bg} is the small measured background, and I_0 is a normalization constant. A and B are functions of the penetration depth alone. Thus, treated as a function of α_1, the corrected intensity has a minimum for $\alpha_1 = -A\alpha_{\text{bulk}}/2$; for physically relevant parameter values α_1 is approximately $\frac{1}{2}$ at the minimum. The intensity increases for sufficiently large surface bilayer disorder. It is evident that the measured variation of the scattered intensity with temperature can be well described as an interference effect caused by the independent disordering of the surface bilayer.

The key assumption of our model is that near 1000 K thermally generated random vacancies in the surface bilayer begin to proliferate. The effects of random site vacancies on a lattice with no subsequent distortion are to depress the scattered amplitude by multiplying it by the fractional occupancy, and to add weak diffuse scattered intensity throughout reciprocal space. This random vacancy model has two salient features: It produces an equal reduction of each surface peak amplitude by multiplying it by the fractional occupancy, and it produces no change in line shape. These characteristics are essential features of the data shown in Figs. 1 and 2. At each temperature we characterize the surface bilayer by a vacancy fraction and an enhanced mean-square deviation of surface atoms from their equilibrium lattice positions. Thus, we write $\alpha_1(\mathbf{q},T) = \alpha(\mathbf{q},T) e^{-M_1 T}$, and we hypothesize that $1-\alpha$ represents the vacancy fraction. We assume that the vacancies appear only in the first bilayer, and that both the first and second bilayers have DW factors enhanced over the bulk. For simplicity, we assume that the vacancy positions are entirely uncorrelated although inclusion of correlations up to distances of order 20 Å would have no important consequences for the predictions of the model.

The expression for the intensity [Eq. (1)] with these assumptions for $\alpha_1(\mathbf{q},T)$ and $\alpha_2(\mathbf{q},T)$ may then be easily inverted to extract $\alpha(\mathbf{q},T)$ from the data. The overall normalization constant I_0 is separately chosen for the (10) and (20) peaks to fix the value of the intensity at the minimum. We have used the established bulk DW factor[8] for the third and subsequent bilayers, and 2 and 1.5 times that value for the first and second bilayers, respectively. These represent reasonable vibration amplitudes, and are in rough agreement with general molecular-dynamics results.[11] The values of α, especially those obtained in the inversion of the (10) peak, are insensitive to the explicit values chosen for these surface DW factors as long as the vibration amplitudes lie in a reasonable range.

The results of this inversion for $1-\alpha(T)$ are shown in Fig. 2(c) for both the (10) and (20) peaks. Our analysis thus suggests that the surface vacancy concentration on Ge(111) under UHV conditions rises rapidly between ~950 and 1080 K and then saturates. It is clear that the results for $1-\alpha(T)$ in Fig. 2(c) satisfactorily explain the LEED data of Ref. 2 since the LEED intensities are determined primarily by the first bilayer. We expect our results for the vacancy concentration $1-\alpha(T)$ to be quantitatively correct in the dilute limit. The vacancy concentration appears to exceed 50% above 1080 K although our model is undoubtedly too simplistic in this regime. For these vacancy concentrations we certainly expect vacancies to appear in the second bilayer as well as local distortions of the surface-atom positions. It should be noted, however, that the close agreement of the $1-\alpha$ curves for both the (10) and (20) intensities implies that these distortions are small. We have also considered alternate models for the vacancy distribution between the layers. Our results turn out to be surprisingly restrictive. For example, structure-factor calculations demonstrate that vacancies in the first half-bilayer alone produce a monotonic increase in scattered intensity. The small fraction of a monolayer of adatoms involved in the $c(2\times8)$ reconstruction has little effect on the structure factor and has been ignored. We should note that we also considered in detail various models involving an increase in the adatom concentration with increasing temperature. No physically plausible adatom model can explain the data in Fig. 2. Further calculations demonstrate that the vacancy concentration must decay rapidly to interior layers to produce the observed dip and recovery in the (10) and (20) peak intensities. For exponential decay the characteristic length must be less than 1.5 times the bilayer separation distance.

Finally, we note that these experiments may have important implications for our understanding of evaporation from the Ge(111) surface. Figure 2(d) shows ^{74}Ge mass spectrometry data as a function of temperature. These were obtained in two different experiments, one *in situ* and one at AT&T Bell Laboratories on a separate sample. It is evident that the sublimation is readily observable and grows rapidly above ~1100 K. The change in slope below ~1100 K in the AT&T data appears to be real but this requires a more complete study. Evaporation is normally assumed to originate from steps (the so-called terrace-ledge-kink model) on surfaces. It is intuitively clear that a high surface vacancy concentration will also promote sublimation; our results suggest that such effects may be important for Ge(111) especially above 1100 K. To test this idea we are currently carrying out diffraction and sublimation studies of vicinal Ge(111) surfaces.

There is currently very little microscopic information in the literature on the structures and morphologies of semiconductor surfaces at high temperatures. Our data and analysis suggest that in this regime the surface bilayer on Ge(111) reaches a steady state with a large vacancy concentration. We find it particularly surprising that the Ge(111) surface remains atomically flat over distances exceeding 2000 Å for surface vacancy concentrations near 50%. We are not aware of any model of semiconductor surface structures in this regime which is consistent with our results.

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