A New Phase Transition at the Ge(111) Surface Observed by Low-Energy Electron Diffraction

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Observations on the (111) surface of Ge crystal at elevated temperatures have been made by low-energy electron diffraction with position-sensitive detection. The results indicate that the outermost few atom double layers lose lateral crystalline order in a continuous phase transition 150 K below the bulk melting temperature.

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The observation of a low-energy electron diffraction (LEED) pattern for a crystal surface is evidence that the laterally projected crystalline order of the substrate persists right up into the surface region sensed by LEED —i.e., the outermost few atom layers.[1] This is the case for clean surfaces of well-annealed crystals at low temperatures. With increasing crystal temperature approaching the bulk melting temperature, one expects that a crystal surface will disorder, and that the disordering will be observable as an attenuation of the LEED pattern more rapid than the Debye-Waller attenuation. Two relevant modes of disordering have been recognized: surface melting and surface roughening. With regard to surface melting, theoretical models,[2-4] simulations,[5] and observations on Pb(110)[6] and ice[7] surfaces all indicate a continuous transition with a critical temperature equal to the bulk melting temperature. All available results are consistent with the picture[2-4] in which melting begins in a thin surface layer whose thickness increases with temperature and diverges at the bulk melting temperature. With regard to surface roughening, there have been recent indications of roughening transitions on high-index Cu[8] and Ni[9] surfaces, as well as on the surfaces of Ar films[10] at temperatures below the bulk melting temperatures of these crystals. However, in the course of LEED observations on Ge(111) surface, we have observed a different mode of loss of lateral crystalline order in which a thin surface layer (no more than a few atom double layers) disorders reversibly at a temperature far below the bulk melting temperature, without any broadening of the specular beam, as would occur if the surface were roughened. This behavior has not been observed before for macroscopic crystals,[11] and does not conform to any existing model of surface disordering. In this paper we present evidence that this new phase transition resembles surface melting, and we speculate that the surface-melting temperature is depressed because of intrinsic lateral compressive stress at the Ge(111) surface.

Our observations were made on Ge crystal samples (*n*-type, Sb-doped, 0.01 Ω cm, $12 \times 6 \times 0.25$ mm^3) Ohmically heated in vacuum. The surface was prepared by sputtering (10^{17}Ne$^+$ ions/cm^2, 800 eV, 550 °C, normal incidence) and annealing (700 °C, 30 min) after which the room-temperature surface was found to be clean and well-ordered according to the usual criteria of Auger-electron spectroscopy (AES) and LEED. AES scans at temperature and after each data run showed no impurity above the AES detection limit (about 0.2% of a monolayer). The surface temperature was measured with an infrared pyrometer at emissivity setting 0.46. The accuracy and precision of this measurement are estimated to be ±10 and ±1 K, respectively. The LEED measurements were made with a conventional electron gun and a position-sensitive detector of the resistive anode type. Compared to previous applications to LEED,[12] the performance of the detector has been enhanced substantially by provision of improved position-computing electronics[13] and of an event-counting memory.[14] The detection rate was 100 kHz with (256×256)-channel resolution. The detector was positioned so that its active area subtended 14° at the sample. Each LEED spot of interest was made to impinge near the center of the detector, and edge-gating controls were used to limit the angular width of the effective area of detection to about 8°. The observed angular profile of each spot was a narrow peak (width $< 1°$) superimposed on a flat background due to the inelastically scattered electrons passed by the retarding grid of the detector. The reported peak intensity is the number of counts in the maximum channel, less background counts. The spot width is the full width at half height of the intensity profile. The counting time at each temperature was typically 120 s. The peak intensities were in the range $1 \times 10^3 - 20 \times 10^3$ and the background intensity was typically 150. Observations on one spot at a series of crystal temperatures were made for a fixed time and with fixed incidence conditions. Profile plots were made in a fixed direction across the spot. The scattering angle was 270°. The crystal was oriented with the $\langle 110 \rangle$ direction in the scattering plane. For observation of the (00) and (01) spots, the polar incidence angles relative to the crystal normal were respectively 45° and about 60° depending on the electron energy.

The main experimental result is illustrated in Fig. 1. With increasing crystal temperature, the nonspecular LEED spots weaken substantially relative to the specular

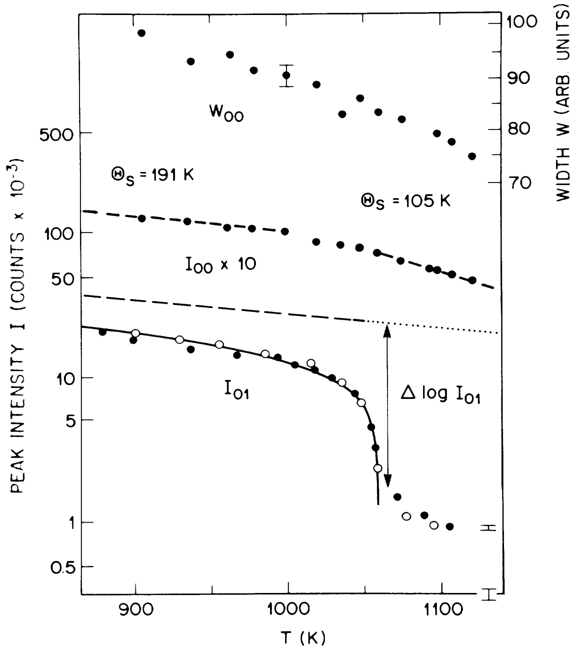

FIG. 1. Intensities I_{00} and I_{01} and width W_{00} of LEED spots from the Ge(111) surface as functions of crystal temperature T. The electron energy was 69 eV and the polar angles of incidence relative to the surface normal for observation of the (00) and (01) spots were 45° and 62°, respectively. Filled and open circles denote measurements with T increasing and decreasing, respectively. Bars at bottom right indicate estimated counting errors for the lowest observed intensity and for the (01) intensity linearly extrapolated to the bulk melting temperature. For W_{00} the error bar is that estimated from duplicate measurements. The broken lines are Debye-Waller lines with slopes corresponding to the values of surface Debye temperature θ_s indicated. The solid line represents a continuous phase transition [see text, Eq. (2)]. The arrow indicates the magnitude of the (01) intensity drop attributable to the transition.

or (00) spot, but do not die out completely, in a narrow interval above 150 K below the Ge crystal melting temperature (1210 K). The spots are not broadened with increasing crystal temperature.

Qualitatively similar results have been obtained for each of several sets of LEED incidence conditions. The results shown in Fig. 1 were obtained for a particular value of electron energy, 69 eV, near which preliminary observations of spot intensity versus energy showed a broad peak (width 25 eV) for both the (00) and (01) spots over the temperature range represented. This means that the results are not sensitive to the temperature dependence of Bragg peak positions, and so may be interpreted confidently in terms of surface ordering. As shown in Fig. 1, the (01) spot intensity drops reversibly by a factor of 10 in the interval 1025–1075 K. Outside this interval, it has a relatively slow temperature dependence similar to that exhibited by the (00) spot intensity throughout the range represented. The (00) intensity variation is like a Debye-Waller factor with different parameter values for temperatures below 1000 K and above 1060 K. The straight-line segments in Fig. 1 (broken lines) correspond to

$$I(T) \propto \exp(-2M'T), \tag{1}$$

where T denotes the crystal temperature, $M' = 1.0 \times 10^{-3}$ K^{-1} ($T < 1000$ K) and $M' = 3.3 \times 10^{-3}$ K^{-1} ($T > 1060$ K). The surface Debye temperatures θ_s calculated from these values of M' by a standard formula[1] are shown in Fig. 1. For temperatures below a critical value T_c near 1060 K, the (01) intensity varies as expected (within error) for a continuous transition,[15] namely,

$$I(T) = I(0)[(T_c - T)/T_c]^{2\beta} \exp(-2M'T), \quad T < T_c. \tag{2}$$

The solid line in Fig. 1 is given by Eq. (2) with $I(0) = 2.1 \times 10^5$, $M' = 1.0 \times 10^{-3}$ K^{-1}, $T_c = 1058$ K, and $\beta = 0.15$. The broken line with the dotted extension is the Debye-Waller line given by Eq. (2) with the same parameter values except for T_c indefinitely large. These decreases of intensity with increasing temperature are not accompanied by significant broadening of the spots for any value of electron energy; for the particular energy (69 eV) represented in Fig. 1, there is a slight narrowing as illustrated there for the (00) spot.[16]

The results summarized in Fig. 1 indicate that the Ge(111) surface undergoes an apparently continuous structural phase transition with a critical temperature T_c equal to 1058 ± 10 K. We interpret it as a loss of lateral crystalline order in a thin surface layer. The alternative interpretation, that the transition is between two ordered states with different Bragg-peak positions, may be ruled out on the basis of the preliminary observations of (01) intensity with respect to electron energy described above. The limitation of disordering to a thin surface layer is evidenced by the persistence of the (01) spot above T_c. We estimate the effective thickness of the layer from the observed drop of intensity (Fig. 1), using the experimental geometry and assuming that the inelastic mean free path for 69-eV electrons in the layer has the same value, 11 Å, as reported[17] for amorphous germanium. The estimated effective thickness is 9 Å. It corresponds to the disordering of two to three Ge(111) double layers.

Other properties of the surface layer may be inferred from observations on the (00) spot. Plots of (00) intensity versus electron energy, made at various temperatures both above and below T_c, all contain Bragg-type peaks attributable to layerlike ordering in the surface-normal direction.[18] As a surface region of depth 9 Å would contribute about 90% of the (00) intensity, we conclude that layerlike ordering is preserved right up to the surface. This is consistent with the observed absence of broadening of the spots with increasing temperature. If there were roughening or other marked disruption of layerlike ordering, the spots would be broadened instead of unchanged or even narrowed as observed (Fig. 1).

The observed temperature dependence of the (00) intensity indicates a pronounced softening of the surface layer near T_c. For $T < 1000$ K, the ratio of the surface to the bulk Debye temperatures[19] is 0.67, which is within the range of values clustered around 0.7 determined from LEED for several different crystals.[1] For $T > T_c$, the ratio is 0.36. This is so far below the normal range as to suggest that the surface layer more nearly resembles liquid than solid Ge. For example, the assumption of a solid surface layer for $T > T_c$ would imply unrealistically large mean square displacements of surface atoms from their equilibrium positions. A standard formula[1] relating mean square displacement to Debye temperature would indicate a mean square surface-normal displacement of Ge(111) surface atoms an order of magnitude greater than the mean square displacement in bulk Ge crystal at its melting temperature. All available facts are consistent with an assignment of the observed transition to surface melting. However, unlike those of other relevant experiments on different crystals,[6,7] our results do not conform qualitatively to existing theories[2-4] or simulations[5] of surface melting; all of these theories and simulations predict a critical temperature equal to instead of substantially below the bulk melting temperature. We speculate that the depression of the Ge(111) surface melting temperature 150 K below the bulk value is caused by intrinsic lateral compressive stress in the outermost few double layers—a factor not included in any model of surface melting.

Since liquid Ge is more dense than the solid, compression lowers the melting temperature. The existence of intrinsic lateral compressive stress at Ge(111) surface has been inferred from an observed correlation between surface reconstruction and surface strain.[20] No estimate of stress at Ge(111) surface is available, but calculations for the analogous case of Si(111) indicate a lateral stress equivalent to a pressure of 54 kbar.[21] A hydrostatic compression of 54 kbar lowers the bulk Ge melting temperature by more than 150 K.[22]

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