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Temperature-dependent electronic excitations of the Ge(111)-2×1 surface

J. E. Demuth, R. Imbihl, and W. A. Thompson
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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The temperature dependence of the surface-state electronic transition for cleaved Ge(111)-2×1 is reported and compared to previous results on Si(111)-2×1. Ge(111)-2×1 shows an almost linear dependence of the surface-state band gap between 30 and 295 K, varying between 535 and 415 meV, respectively. Cleaved Ge(111)-2×1 shows little evidence for the defect-induced states usually found, even on excellent single-domain 2×1 cleaves of Si(111).

The coupling of phonons to the electronic states in bulk semiconductors is generally understood.[1] Recent interest in such interactions at the surfaces of semiconductors has been stimulated by the observation of striking temperature-dependent alterations of the surface electronic structure.[2-4] Such coupling between surface vibrations and electronic states has important implications concerning semiconductor surface reconstruction,[5] epitaxy and growth processes,[6] as well as surface superconductivity,[7] particularly if electron-phonon coupling is stronger at the surface than in the bulk. Although this latter point is not theoretically resolved,[8,9] the temperature-dependent shifts of the surface-state band edges on Si(111)-7×7 and -2×1 surfaces appear to be comparable or larger than in the bulk.[2,10] Enhanced electron-phonon coupling at surfaces would not be surprising since the reduced symmetry at the surface will allow new phonon modes and electronic states to exist which are not possible in the bulk.

The Si(111)-2×1 surface electronic structure has been studied recently to investigate such temperature-dependent effects[10-12] since its geometric structure is well established,[13-15] and it has a relatively simple electronic structure.[13] In particular these studies examined the temperature dependence of the Si(111)-2×1 surface-state gap, which was originally observed at room temperature using electron-energy-loss spectroscopy (EELS)[16,17] and optical-absorption methods.[18-21] One of the conclusions of these optical studies was that cleaved surfaces can exhibit additional surface states in the gap which can be attributed to defects.[20] These "defect states" were found not only on multidomain cleaves but also they occurred on 90% of all excellent single-domain 2×1 cleaves.[10] Recent scanning tunneling microscopy studies of cleaved Si(111)-2×1 revealed irregularities in the π-bonded chains structure approximately every 100 Å, which from bias-dependent measurements would correspond to these defect states in the gap.[15] Such irregularities on cleaved Si(111)-2×1 may also influence other properties on this surface and, in part, may account for the different temperature dependence of the surface-state gap found in other optical results.[11,12]

Here, we present the first temperature-dependent measurements of the surface electronic transitions of the cleaved Ge(111)-2×1 surface using EELS. The Ge(111)-2×1 surface, while not as widely studied, appears to be similar in many respects to Si(111)-2×1 and has a π-bonded chain structure.[11,13,18,21] We find an unusually large temperature-dependent shift in the Ge(111)-2×1 surface-state band gap and no evidence for the type of defect gap states observed on Si(111)-2×1. These combined features make the Ge(111)-2×1 surface an ideal system for the further understanding of such temperature-dependent effects. For these reasons, we have performed detailed measurements of the variation of the Ge(111)-2×1 surface-state gap with temperature and compare these results to earlier measurements on Si(111)-2×1.

All experiments were performed in a turbo- and ion-pumped ultrahigh vacuum system with which base pressures of 4×10^{-11} Torr could be routinely achieved. Details of the experimental apparatus are described elsewhere.[22] For high-resolution EELS a set of two hemispherical analyzers was used, typically allowing a resolution of 8 to 10 meV. All EELS measurements were carried out under specular conditions ($\theta_i=\theta_0=45°$) with a beam energy of 11.7 eV. To allow for EELS measurements while the sample was held at constant temperature, the heating current was pulsed on and off at 14 Hz so that the EELS signal could be monitored during the off heating cycles.

The data we report were obtained on three different single-domain cleaves of a Ge(111) bar (3×3 mm^2) with nearly intrinsic doping. The samples were cleaved along the [2$\bar{1}\bar{1}$] direction at room temperature using a single 14° wedge, and exhibited sharp one-domain 2×1 pattern in LEED. LEED intensity-energy measurements were

also recorded at room temperature and at 30 K but are not reported here. However, no evidence for a temperature-dependent structural transition is found. In the EELS measurements the scattering plane of the electrons was set along the $[0\bar{1}\bar{1}]$ direction which is parallel to the chains in a chain model of the surface reconstruction.

In Fig. 1 are shown loss spectra representative of cleaved Ge(111)-2×1 surfaces at $T=295$ and 30 K. These spectra were obtained from the same cleaved sample and taken sequentially with the same spectrometer settings. As found previously,[17] the scattered elastic beam is broadened at room temperature, and we find that it significantly narrows at low temperatures. While this elastic beam broadening is similar to that found on Si(111)-7×7,[2,23] the inelastic background on Ge(111)-2×1 is only weakly temperature dependent. This allows the onset to the surface-state transition to be readily established over a wide temperature range. Similar low backgrounds and sharp onsets were observed on *all* the cleaved Ge(111) surfaces studied—each of which were also single domain cleaves.

The detailed shape and position of the peak for the electron excited surface-state transitions have been considered by Ritz, Spitzer, and Luth.[17] This peak depends on several experimental factors such as the beam energy and angular resolution which selects the range of $\Delta q_{\parallel}$ sampled experimentally. The measured EELS loss peak thereby differs from the optical peak which corresponds to $\Delta q_{\parallel}=0$ transitions *only*.[18-21] Since the detailed unoccupied and occupied surface-state band topologies for the Ge(111)-2×1 surface are not known, we do not analyze the shape of the EELS loss peaks, but instead focus on the onsets. For the π-bonded chain structure, these onsets correspond to the minimum gap of those surface-state transitions at the $\bar{J}$ point of the surface Brillouin zone.[13]

In Fig. 2 we show these electronic transition onsets derived from EELS measurements at several temperatures. The error bars at high and low temperatures provide a measure of the uncertainites involved, which are largely associated with defining the onset. We also show the room-temperature gap measured directly by Olmstead and Amer[21] using a photothermal displacement method. The uncertainties in defining a gap from these optical measurements arise from the noise in the optical data and the necessity to extrapolate to energies below 0.43 eV, where their data stops. For our results we obtain this band edge by taking a linear extrapolation of onset, as shown in Fig. 1. The overall agreement between the onsets we derived in this way, and those measured optically[18,19,21] provide evidence that our procedures are relatively accurate.

The temperature-dependent change in the surface-state gap between 30 and 300 K corresponds to 125 meV and is significantly larger than the 90 meV found for the Si(111)-2×1 surface.[10] This is also larger than the 80 meV variation in the bulk band gap of Ge found over this temperature range.[1] Recent optical measurements on Si(111)-2×1 (Ref. 12) confirm the relatively large variation in the surface optical gap on Si(111)2×1 originally found by EELS.[10] Thus, both Si(111)-2×1 and Ge(111)-2×1 surfaces appear to show larger temperature-dependent surface-state gap changes than does the bulk. There is currently no explanation for these larger values and all surface theories of this electron-phonon coupling predict smaller shifts than occur in the bulk.[8,24] However, the near linear dependence of the gap on temperature, shown in Fig. 2, is consistent with the approximately linear

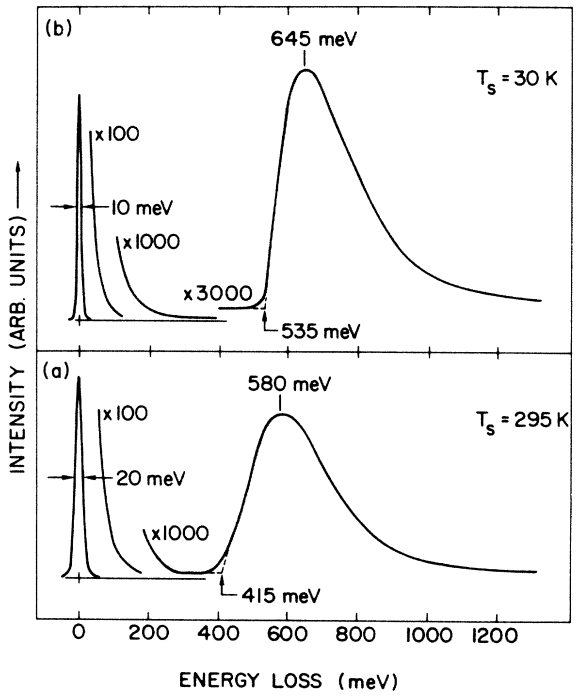

FIG. 1. Electron-energy-loss spectra of Ge(111)-2×1 at (a) $T=295$ K and (b) 30 K. The incident beam energy is 11.7 eV.

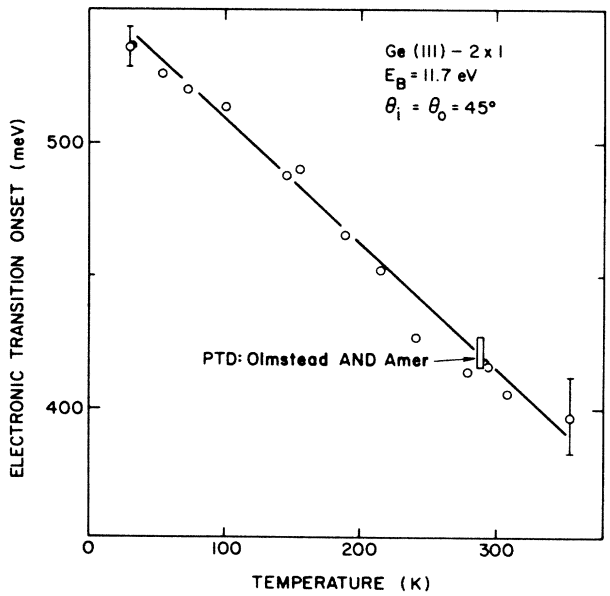

FIG. 2. The temperature dependence of the onset for the surface electronic transition of Ge(111)-2×1. Also indicated is the photothermal deflection measurement of the onset as measured by Olmstead and Amer (Ref. 21).

dependence found in one surface calculation[24] and which occurs in the bulk.[1]

In conclusion, the detailed temperature dependence of the surface-state gap of Ge(111)-2×1 surface has been measured and found to be larger than in bulk Ge or observed for Si. This together with the property that cleaved Ge(111) exhibits negligible cleavage-induced defects makes this an ideal system to theoretically analyze to understand electron-phonon coupling at semiconductor surfaces.

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