Metal-Insulator Transition on the Ge(001) Surface

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High-resolution angle-resolved photoemission studies of the Ge(001) surface are reported which clearly indicate the existence of a metallic surface state whose emission is observed over a narrow range of parallel momenta near the center of the surface Brillouin zone. The state slowly disappears as the temperature is lowered from room temperature to 77 K. This metal-insulator transition is coincident with a recently predicted and observed transition from a disordered to an ordered $c(4\times2)$ structure.

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Clean semiconductor surfaces and their various reconstructions have been the subject of intensive investigation by a variety of experimental and theoretical techniques. The success of these efforts is indicated by the profound improvements in our understanding of the most complex semiconductor surfaces in the past few years.[1-3] Recently, self-consistent total-energy calculations have been coupled to renormalization-group techniques to investigate the various stable reconstructed phases of the Si(001) and Ge(001) surfaces.[3] A result of these calculations has been the prediction[4] and subsequent observation[5] of an order-disorder transition on Ge(001) below room temperature. We show here direct evidence using angle-resolved photoemission (ARP) that this transition is accompanied by a metal-insulator transition. Exceptional energy and momentum resolution were required for an accurate characterization of this transition since the observed metallic surface state has a natural energy width $\Delta E \leq 100$ meV, and is in addition observable over a narrow momentum range.

The (001) surfaces of germanium and silicon are generally thought to reconstruct to form a nominal (2×1) surface unit cell by asymmetric dimerization of nearest-neighbor surface atoms.[6] Higher-order reconstructions sometimes observed on these surfaces[5,7-9] have been attributed to different arrangements of neighboring dimers. It is our purpose in investigating the electronic structure of the Ge(001) surface to search for a possible electronic driving force for transformations between different reconstructions.[10-12]

Experiments were performed at the National Sychrotron Light Source at Brookhaven National Laboratory utilizing a photoemission spectrometer and 6-m toroidal-grating monochromator which have been described elsewhere.[13,14] The operating energy resolution was < 100 meV at all photon energies, while the angular resolution was 0.9° full width at half maximum. An n-type (30 Ω cm) Ge crystal was polished to within $\frac{1}{2}°$ of the (001) axis, chemically etched in 5% bromine in methanol, and inserted in the vacuum system. Following a few cycles of neon-ion sputtering (5 μA/cm, 10 min) and annealing (800 K, 5 min) a clean and well-ordered surface was produced.

Several room-temperature energy distribution curves (EDC's) collected for emission normal to the surface are shown in Fig. 1. Most aspects of these curves are similar to those reported elsewhere.[15] A significant difference is the presence of a weak but very sharp feature at or near the Fermi level which is clearly visible at all photon energies where an intense bulk feature does not interfere ($h\nu \geq 19$ eV in Fig. 1). The observed width of ~ 150 meV is unusually small for semiconductor surfaces. We estimate a natural width of $\Delta E \leq 100$ meV. This state is exceptionally sensitive to contamination. At our pressure during experimentation [$(1-2)\times10^{-10}$ Torr] the peak disappeared in 20–30 min. A gentle flash (400 °C, 1 min) would regenerate the metallic peak, implicating hydrogen as the probable contaminant. This observation along with the state's energy position in the bulk band gap leads us to conclude that, at room temperature, Ge(001) posseses a metallic or nearly metallic surface state. Our experimental energy resolution and the natural energy width of the peak preclude ruling out semimetallic or very narrow-band-gap (20–30 meV) semiconductive behavior. Further studies of the infrared frequency response of this surface will shed light on this question.[2,16] It is important to note that on Si(001) no such feature has been observed,[17] indicating that a more detailed investigation of the state's temperature and angular behavior is in order.

The left panel of Fig. 2 shows EDC's of the Fermi-level region, expanded from Fig. 1 at $h\nu = 20$ eV, for various sample temperatures

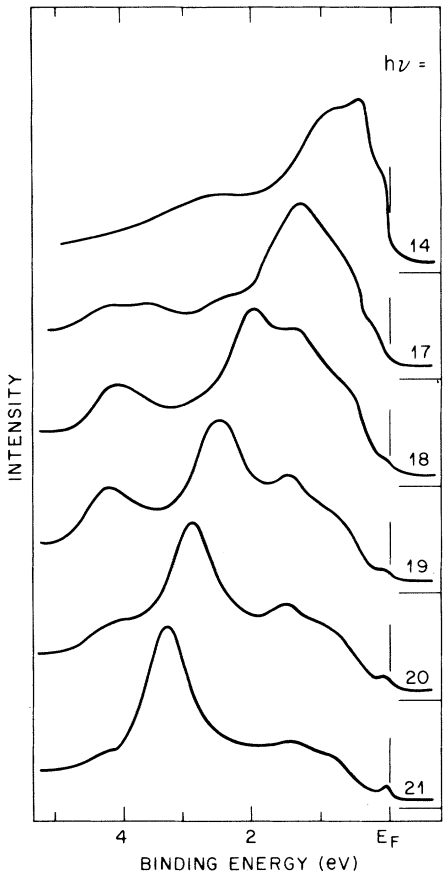

FIG. 1. EDC's of the Ge(001) valence band at various photon energies for emission normal to the surface. The metallic state is seen as a small peak for $h\nu \geq 19$ eV.

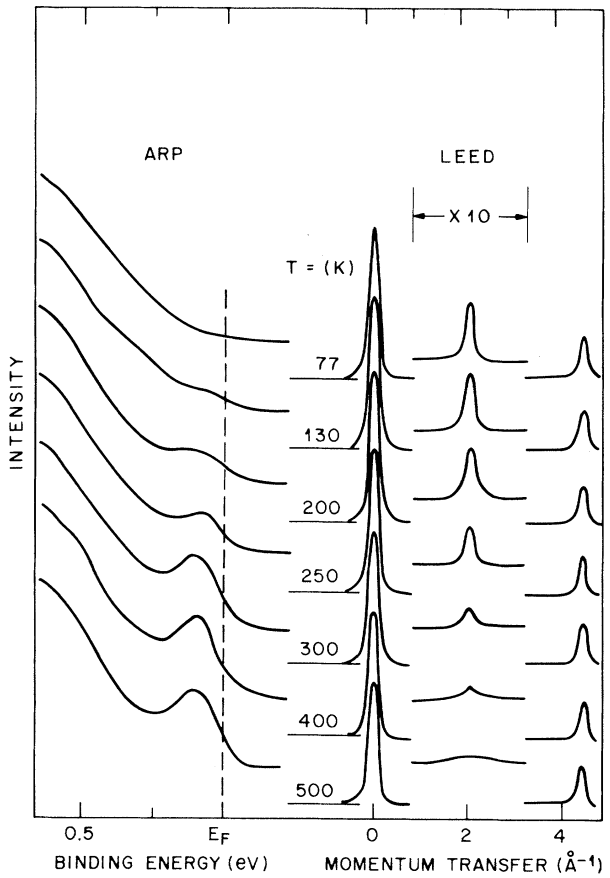

FIG. 2. Left half: EDC's of the Fermi-level region of the Ge(001) valence band at normal emission, $h\nu = 20$ eV, for various sample temperatures. The metallic state is seen to disappear gradually as the temperature decreases. Right half: LEED profiles extending from the (0,0) beam to the $(1,\frac{1}{2})$ beam at the same temperatures. The gradual appearance of a peak at 2.2 Å^{-1} is indicative of the transition to an ordered $c(4\times2)$ structure.

between 77 and 450 K. The metallic state is clearly seen to disappear smoothly as the temperature decreases, with no apparent change in energy position or peak shape, nor with any discontinuity in intensity. At the same time the nominal (2×1) room-temperature low-energy electron-diffraction (LEED) pattern gradually converts to a $c(2\times4)$ as the temperature is lowered. This result is shown in the right panel of Fig. 2, where the corresponding temperature-dependent LEED profiles extending from the (0,0) beam to the $(1,\frac{1}{2})$ beam are shown. The appearance and sharpening of a beam at the $(\frac{1}{2},\frac{1}{4})$ position (momentum transfer ~ 2.2 Å^{-1}) is indicative of the transition to a well-ordered $c(4\times2)$ surface structure at low temperature. The substantial scattering intensity at this position at higher temperatures indicates that as predicted[4] this phase is actually a disordered $c(4\times2)$ rather than a (2×1) structure. Indeed, there really is no distinct transition observed in either the LEED[5] or the photoemission results shown in Fig. 2; both show a gradual evolution with changing temperature. This observation, along with the lack of any energy shift of the metallic state with temperature, rules out an electronic instability driving force as proposed for other systems.[10-12] The observed changes are in addition completely reversible without any hysteresis on our time scale. A more precise analysis of these temperature-dependent data will be presented in a forthcoming publication.[18]

As a final experimental result, we present in Fig. 3 the angular dependence of the room-temperature metallic surface-state intensity. At 300 K, the emission intensity has an angular half-width of $\pm 2°$ in all of the several azimuths we checked. This range is temperature dependent, increasing to $\pm 4°$ at 500 K. In addition, the peak does not appear to

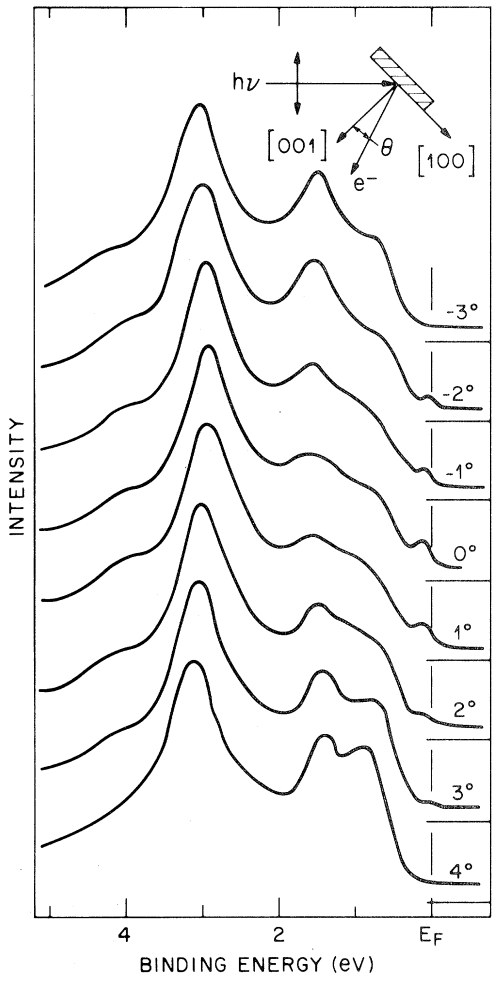

FIG. 3. EDC's of the Ge(001) valence band at $h\nu = 20$ eV for small angles of emission in the ($\Gamma \rightarrow \bar{J},\bar{J}'$) azimuth.

disperse in energy over this narrow range; rather, the intensity diminishes smoothly away from normal emission, again without any apparent change in peak shape.

The moderate-range $c(4\times2)$ ordering of the surface at higher temperatures implied by the LEED results of Fig. 2 indicates a probable origin for the metallic peak we observe. Since photoemission is a moderate-range probe, one would expect to see the $c(4\times2)$ result throughout the temperature range we studied. This prediction is supported by the lack of spectral changes away from E_F observed as a function of temperature in these studies and elsewhere.[15] The metallic peak must be related to the disorder itself. As the temperature is lowered, the disorder-induced defects disappear and, as is observed, the metallic peak slowly vanishes without preceptibly changing its energy position. The angle-dependent intensity data shown in Fig. 3 yield information on the real-space character of these hypothesized defects. An isolated defect would have a fairly isotropic intensity distribution reflecting its broad frequency spectrum. The other extreme is an ordered array of "defects" which would then form a band and, at a given energy, be observable at only one angle. The metallic state seen here is somewhere between these extremes. At higher temperature, correlation between neighboring dimers becomes more and more short range, leading to a broader intensity distribution. At low temperatures, the number of defects decreases and the range of their correlation increases so that the peak decreases in intensity and sharpens its intensity distribution in momentum space. A more complete analysis of this temperature-dependent ordering will be given elsewhere.[18]

A rough estimate of the angular width of the emission intensity is provided by an analogy to the N-slit problem, when the metallic state is spread coherently over N unit cells. Each dimer or unit cell corresponds to a slit separated by the lattice spacing $d = 4.0$ Å. The angular width of the principle diffraction maximum is given by

$$\Delta^{\theta} = \lambda / Nd,$$

where λ is the de Broglie wavelength of the outgoing electron. At higher temperatures, our data yield $N \sim 3$, which corresponds roughly to inverting one dimer in the $c(4\times2)$ structure to yield three aligned dimers. In this sense, the low-energy excitations of the $c(4\times2)$ structure can be thought of as simple dimer inversion, corresponding to spin flips and magnons in the antiferromagnetic case. The calculation in Ref. 3 neglected these low-energy excitations, a fact which might explain why a sharp order-disorder transition was predicted but a gradual onset of ordering is observed. Our N-slit analogy is simplistic, and a more accurate analysis will be required for a quantitative estimate of these effects.

In summary, we have observed a metal-insulator transition on Ge(001) between 77 and 450 K in the form of a gradual disappearance of a metallic surface state. It was argued that the source of the metallic state was from disorder-induced defects present on the surface at high temperatures. An unusually sharp momentum-space intensity pattern was noted, and was interpreted in terms of short-range correlations of the surface dimers in the disordered state.

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