

Strain-induced metal-insulator transition of the Ge(111) surface

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The Ge(111) surface was observed to be metallic under compressive strain, while normally it is semiconducting in the fully annealed state. The compressive strain was produced by the lattice mismatch between Ge and Si for epitaxial Ge films of Si(111). When the strain is relieved, the metallic surface became semiconducting.

The study of the response of electronic properties of bulk solids to strains and high pressures is a fairly mature field.¹ Yet there has been very little work done on surfaces. The reason lies simply in the experimental difficulties in producing a sizable strain field in surfaces under conditions suitable for surface spectroscopies. This paper reports an experimental observation of the metal-insulator transition of the Ge(111) surface induced by strain.

A clean Ge(111) surface can be prepared in a strained state by molecular-beam epitaxial (MBE) growth of Ge on Si(111) under suitable conditions.² The compressive strain at the surface, caused by the lattice mismatch between Si and Ge, is generally quite small, yet it can cause noticeable changes in the surface properties of Ge(111). Gossmann *et al.* recently reported the observation of a (7×7) reconstruction on the strained Ge(111) surface,² which normally exhibits the nominal *c*(2×8) reconstruction in the fully annealed state.³ In this paper, we report an experimental determination of the surface electronic properties in this system. In particular, the strained (7×7) surface was found to be metallic, while the annealed *c*(2×8) surface is semiconducting.⁴⁻⁶ The metallic surface can be made to undergo a transition to the semiconducting state upon thermal annealing to relieve the strain. We will compare the surface electronic states observed in Ge(111)-(7×7) with those found in Ge(111)-*c*(2×8), Si(111)-(7×7), and the (5×5) surface of a Si-Ge alloy.

The surface electronic properties were probed by photoemission in our experiment, which was performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison. A three-meter toroidal-grating monochromator was used to disperse the synchrotron radiation; the photoelectrons were analyzed by a double-pass cylindrical-mirror analyzer. The Fermi level of the substrate, serving as the binding-energy reference, was determined by measuring the position of the Fermi edge of a gold foil in electrical contact with the substrate. The sample cleanliness and surface atomic composition were verified by Auger spectroscopy and photoemission from the Si 2*p* and Ge 3*d* core levels. The surface quality and surface reconstruction were determined by grazing-angle high-energy electron diffraction (HEED). All photoemission samples were prepared *in situ* under ultrahigh-vacuum conditions with no transfer in air involved. The Si(111)-(7×7) substrates and a single-crystal Ge(111)-*c*(2×8) sample were prepared in the usual manner.⁴ MBE growth of Ge on Si(111) substrates was performed by deposition at various sample temperatures at a rate of 0.1–0.5 Å per second. The

sample temperature was measured and monitored with an infrared pyrometer.

At a growth temperature of above about 500 °C, a chemically graded Ge-Si interface is formed;^{5,7,8} in the present experiments the range of intermixing was observed to extend beyond 1000 Å, depending on the temperature. By choosing a low growth temperature of about 500 °C, the sample surface can become chemically pure for overlayer thickness greater than about 200 Å, while the mismatch strain is not totally relieved at the surface. Several strained Ge(111)-(7×7) samples with different Ge layer thicknesses corresponding to different degrees of surface strain were prepared in this manner.² Upon annealing to high temperatures, the (7×7) surface could be converted to one exhibiting the *c*(2×8) reconstruction. For even lower growth temperatures, the surface quality became inferior as judged from HEED. Interestingly, at even lower growth temperatures such as 350 °C, Ge(111)-*c*(2×8) could be produced; these samples showed a relatively rough growth. Evidently, a proper growth temperature is important, and atomic intermixing at the interface with a resultant graded junction, which provides a means to relieve most of the 4% mismatch between Si and Ge gradually, might be an important factor in the smooth uniform growth of a continuous film. For growth at lower temperatures, the degree of intermixing was not sufficient to relieve the strain gradually, and many gross defects were formed.

Several Si-Ge alloy surfaces were also produced by depositing a relatively thin layer of Ge on Si(111) at 500–600 °C. With sufficiently high Ge concentration, the surface reconstruction was (5×5).^{5,7,8} Recent low-energy electron diffraction studies indicated that the (5×5) reconstruction has a very similar atomic structure to the (7×7) surface of Si(111) with the major difference being just the size of the surface unit cell.⁹ Thus, the (5×5) surface provides another interesting system for comparison of the electronic properties.

Figure 1 shows angle-integrated photoemission spectra from Ge(111)-(7×7), Ge(111)-*c*(2×8), Si(111)-(7×7), and Si(111)-Ge(5×5) (alloy of Ge and Si) taken with a photon energy of 55 eV. These spectra show essentially the density of states. The photoelectron escape depth is of the order of 5 Å; thus the spectra contain significant contribution from the surface density of states as well as contribution from the bulk density of states. Features that were sensitive to dirt adsorption and/or surface quality are indicated by arrows in Fig. 1; these are assigned as surface-state emission peaks. These surface states are also evident in

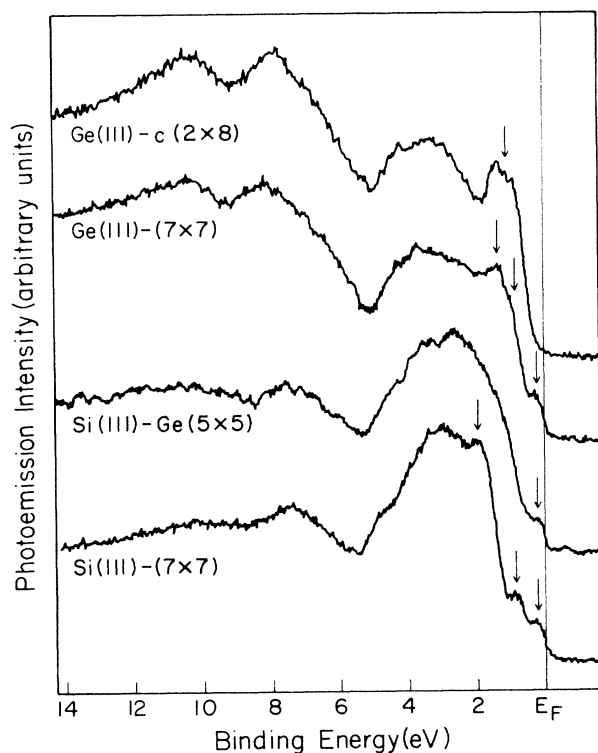


FIG. 1. Angle-integrated photoemission spectra from Ge(111)- $c(2 \times 8)$, Ge(111)- (7×7) , Si(111)-Ge (5×5) , and Si(111)- (7×7) taken with a photon energy of 55 eV. The binding-energy scale is referred to the Fermi level at E_F .

spectra taken with other photon energies including 70 and 35 eV. For Ge(111)- (7×7) , three surface features are indicated in Fig. 1. The middle one is, however, not as pronounced as the other two; therefore, its assignment is somewhat uncertain.

Note that all these samples except Ge(111)- $c(2 \times 8)$ showed noticeable density of valence states right up to the Fermi level at E_F . The somewhat rounded edge near E_F is mainly due to instrumental broadening. The presence of this Fermi edge is direct evidence that the Ge(111)- (7×7) surface as well as the Si(111)- (7×7) and Si(111)-Ge (5×5) surfaces are metallic. Since the bulk substrate materials in these cases are semiconductors, the density of states near E_F must be derived from surface electronic states. Indeed, the spectral features are surface sensitive as mentioned above, consistent with the surface-state assignment. For comparison, the Ge(111)- $c(2 \times 8)$ surface is semiconducting; the spectrum in Fig. 1 indicates that the sample surface was actually p type.

The Ge(111)- (7×7) surface could be converted to one exhibiting the $c(2 \times 8)$ reconstruction by either thermal annealing or further MBE growth to large thicknesses to relieve the strain at the surface. In any case, the Fermi edge in the photoemission spectrum disappeared after the transition to the $c(2 \times 8)$ state, and the photoemission spectra obtained after the transition were just like the one for bulk single-crystal Ge(111)- $c(2 \times 8)$ shown in Fig. 1. Thus, the

metal-insulator transition is tied to the transition in surface reconstruction.

Ge and Si are in the same column of the periodic table, and exhibit the same bulk crystal structure. Scanning tunneling microscopy has shown that Ge(111)- (7×7) and Si(111)- (7×7) have qualitatively similar surface atomic corrugation.³ Although the exact surface and subsurface atomic coordinates are not known in these systems, it is natural to speculate that the surface electronic properties of Ge(111)- (7×7) are similar to those of Si(111)- (7×7) . For Si(111)- (7×7) , it is known that there are three surface-state bands corresponding to the three surface-sensitive features indicated in Fig. 1.⁴ It appears that the surface features in Si(111) are also present in Ge(111)- (7×7) but with different binding energies. For Ge(111)- (7×7) , the energy separation between the two more deeply bound states is significantly smaller than in the case of Si(111)- (7×7) . It is likely that the middle state in Ge(111)- (7×7) is partially obscured by the more intense deeper state. This may explain the experimental observation that the middle state in Ge(111)- (7×7) does not appear as pronounced as in the case of Si(111)- (7×7) .

For comparison, the (5×5) surface of the alloy, known to have a similar surface atomic structure to that of the Si(111)- (7×7) surface,⁹ shows only one surface feature near the Fermi level. The Ge(111)- $c(2 \times 8)$ surface has quite different surface electronic states. It has three surface-state bands,⁴⁻⁶ they are not resolved and correspond to the broad surface feature shown in Fig. 1.

Comparing the spectra for these four related systems, we can conclude that, overall, the surface electronic states of Ge(111)- (7×7) are fairly similar to those of Si(111)- (7×7) . The binding energies of these surface states are, however, different for these two systems; these differences might be related to differences in details of the surface and subsurface atomic coordinates. Reliable and/or accurate theoretical calculations of the electronic properties of these surfaces are not yet available for comparison with our experimental findings.

In summary, we have observed a metal-insulator transition induced by strain on the Ge(111) surface. The compressive strain was produced by the lattice mismatch between Ge and Si for MBE-grown Ge films on Si(111).

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