RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 17 15 JUNE 1988-I

Unoccupied surface-state band on Si(111) 1×1–Ge

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(Received 6 April 1988)

Angle-resolved inverse photoemission studies of the Si(111) 1×1–Ge surface reveal an unoccupied surface-state band induced by the germanium overlayer. The band exhibits very little energy dispersion along the major symmetry directions of the surface Brillouin zone. The results are explained in terms of a disordered Si(111) 2×1–Ge surface.

A crucial problem in the physics of semiconductor-semiconductor interfaces is to know how the two semiconductors accommodate their lattice mismatch. Different lattice parameters are responsible for strained interfaces and play a big role in determining the electronic and structure properties[1,2] of the strained regions. Silicon and germanium (111) planes have a lattice mismatch of 4%, and the Si(111)/Ge interface is a good example to observe strain-induced effects. They could be the reason that explains the Si(111) 5×5–Ge reconstructed surface[3,4] prepared by depositing a small amount of Ge onto a Si(111) 7×7 surface and annealing at higher temperatures. The conversion of the Si(111) 7×7 into the more strained 5×5–Ge surface, due to dissolution of Ge atoms in the silicon matrix, was taken[3] as a proof that surface strain plays a substantial role in the appearance of the 7×7 reconstruction on cleaved and annealed Si(111) surfaces.

Chemical reactions do not occur when the Si/Ge interface is prepared by Ge deposition at room temperature.[5–10] The interface is abrupt,[5–10] and a 1×1 low-energy electron-diffraction (LEED) pattern is usually observed for nominal Ge thicknesses below two monolayers[6,9] (ML). A well-ordered $\sqrt{3}\times\sqrt{3}R30°$ reconstruction has also been reported[9] for Ge coverages of the order of $\frac{1}{3}$ ML. Above two monolayers, the LEED pattern disappears and, possibly, island formation occurs.[3,8] Electron-energy-loss and photoemission experiments[5–7] on Si(111) 1×1–Ge revealed the existence of Ge-induced states in the valence band. The results were compared to tight-binding calculations of the surface energy bands[5] assuming a monolayer coverage with Ge atoms placed on onefold (on-top) or threefold (hollow) positions. Recent total-energy calculations have shown[11] that these geometrical arrangements are unstable with respect to the formation of 2×1 Seiwatz chains. The Seiwatz chains are directly derived from the on-top model for one monolayer by allowing the interaction of Ge atoms to form Ge–Ge bonds along chains similarly to Si or Ge atoms on the reconstructed Si or Ge(111) 2×1 surfaces.[12,13]

Both theoretical calculations[5,6,11] predict a pair of π-bonded surface-state bands in the gap region, which differ in their energy dispersion along the main symmetry directions. While for the on-top- or hollow-site models, a large energy dispersion of the empty surface bands is predicted,[5] a nearly flat-band situation is found for the Seiwatz-chain model.[11]

Here we present angle-resolved inverse-photoemission results of the Si(111) 1×1–Ge surface obtained by *in situ* evaporation of one monolayer of germanium on Si(111) 2×1 cleaved surfaces held at room temperature. The Ge coverage was monitored by a quartz-crystal microbalance. The ⟨111⟩-oriented Si rods (p-doped, ~0.3 Ω cm) were cleaved along the bulk ⟨$\bar{2}$11⟩ direction in a vacuum better than 5×10^{-10} Torr. The flat 4×5 mm^2 surfaces exhibited single-domain (111) 2×1 LEED patterns. After the *in situ* cleavage and Ge evaporation, the sample was transferred to the spectrometer chamber (base pressure better than 1×10^{-10} Torr) to perform angle-resolved inverse photoemission measurements with incident electrons emitted from a custom-built electron gun, impinging upon the sample surface at given polar (θ) and azimuthal (ϕ) angles. For more details see Ref. 14. Outcoming photons were filtered at $h\nu=9.5$ eV and detected by a Geiger-Müller-type counter. The photon intensity versus primary-electron energy monitored at given θ and ϕ produced spectra as shown in Figs. 1 and 2. The overall (electron and photon) energy resolution $\Delta E=0.35$ eV and the position $E_F\equiv0$ of the Fermi energy were determined from the Fermi-level onset of a tantalum foil interchangeable with the Si sample. LEED was used to align the clean and Ge-covered sample surface along the two main directions of the surface Brillouin zone (SBZ), which are the $\bar{\Gamma}$–$\bar{K}$ and $\bar{\Gamma}$–$\bar{M}$ symmetry directions of the Si(111) 1×1 surface.

In Fig. 1, we report the inverse-photoemission data along the $\bar{\Gamma}$–$\bar{M}$ direction. The dashed curve represents the normal-incidence spectrum of cleaved Si(111) 2×1, in agreement with our earlier measurements.[15] The structure at $E_F+0.9$ eV belongs to a surface-state band, which becomes more pronounced and exhibits a strong energy dispersion in going away from the $\bar{\Gamma}$ point.[15] Covering the clean surface with a monolayer of Ge so that the 2×1 LEED pattern transforms into a 1×1 periodicity profoundly modifies the inverse-photoemission spectrum (cf. Fig. 1), in particular its part near E_F. The surface-state feature of the clean Si(111) 2×1 surface at 0.9 eV is replaced by two new features denoted S_1 and S_2. Peak S_1 is well resolved and falls inside the silicon bulk band gap,[16] while the shoulder S_2 is superimposed onto bulk conduction-band states. The new Ge-induced surface state S_1 is clearly visible throughout the SBZ, i.e., for all θ, and its energy position $E_F+0.35$ eV remains nearly constant. The weaker feature S_2 at $E_F+1.65$ eV coin-

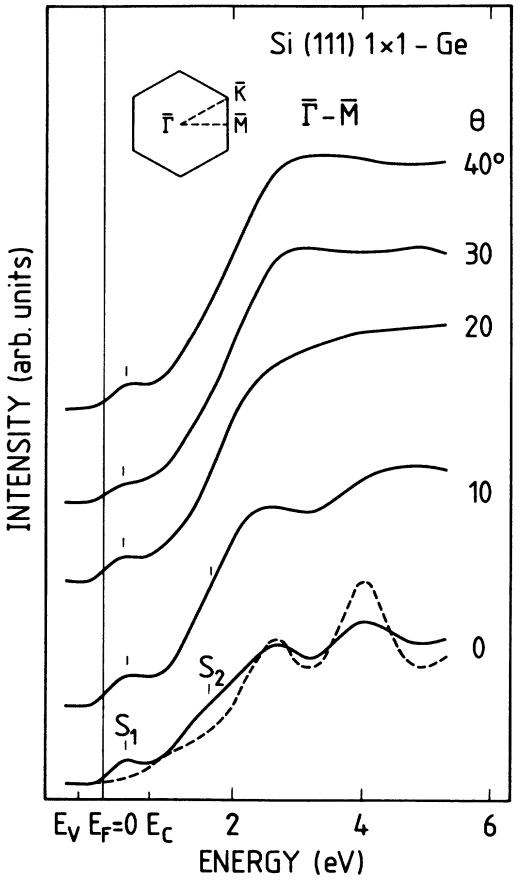

FIG. 1. Angle-resolved inverse photoemission spectra at $h\nu$=9.5 eV of Si(111)1×1-Ge for different polar angles θ along the $\bar{\Gamma}$-$\bar{M}$ azimuth. The dashed curve belongs to the clean Si(111)2×1 surface. Note the change of the spectral shape of the Si bulk features at 2.3 and 4 eV with Ge coverage. The tick marks indicate the positions of the surface-state emission peaks S_1 and S_2 and were obtained from different curves with a Si(111)1×1-Ge surface exposed to activated hydrogen as illustrated in Fig. 2. The inset represents the surface Brillouin zone.

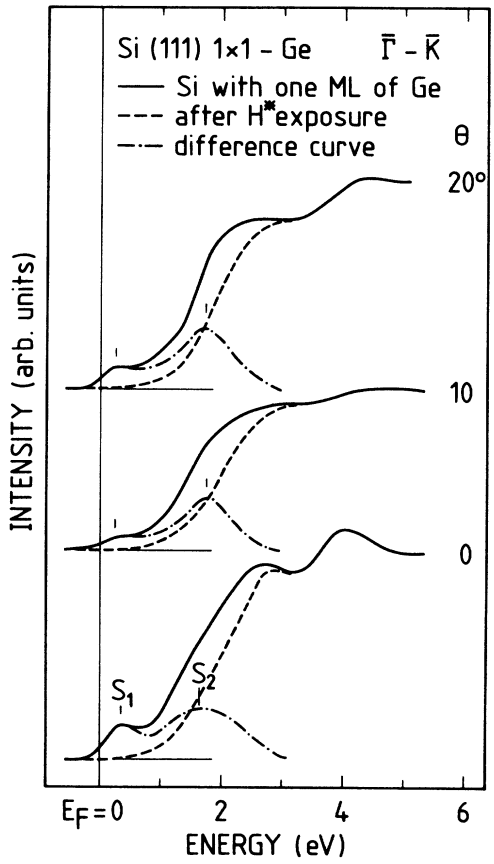

FIG. 2. Inverse photoemission spectra as in Fig. 1, but along the $\bar{\Gamma}$-$\bar{K}$ azimuth together with spectra obtained when the Ge-covered surface was exposed to activated hydrogen. The resulting difference curves allow determination of the peak positions of the surface-state features S_1 and S_2.

cides with electronic bulk states and represents a surface resonance. The surface-state character of both peaks S_1 and S_2 can be inferred from their sensitivity to activated hydrogen as demonstrated in Fig. 2 for spectra taken along the $\bar{\Gamma}$-$\bar{K}$ direction. The surface was exposed to 1×10^{-6} Torr of activated hydrogen (H^*) for ten minutes in the vicinity of a hot filament. The presence of peak S_2 becomes clear in the difference curves taken between spectra of clean Ge/Si(111) and H^*-exposed Ge/Si(111) surfaces. With increasing θ, some uncertainty in the position of S_2 arises from possible modifications of the bottom of the bulk conduction band by the hydrogen exposure. Also in Fig. 2 (as well as in data not shown), a small energy dispersion of S_1 may be discerned with minimum and maximum positions of 0.25 and 0.45 eV within the range of polar angles ($\theta \leq 30°$) measured.

The energy dispersion curves $E(k_\parallel)$ of S_1 and S_2, where $k_\parallel$ denotes the wave vector parallel to the surface, are plotted in Fig. 3 along the main symmetry directions as deduced from Figs. 1 and 2 and data not shown. We hesitated to reproduce the surface-state bands calculated for the on-top- and hollow-site models[5] or the Seiwatz-chain model[11] also in Fig. 3, since their absolute energy positions are not meaningful within the local-density formalism used. Furthermore, in the on-top-site model,[5] the two predicted surface-state bands merge at $\bar{\Gamma}$ and the lower bands exhibit a rather strong energy dispersion, while the Seiwatz-chain model[11] provides two flat bands with an energy gap of 0.18 eV at the $\bar{\Gamma}$ point. Both these results disagree with the measured bands S_1 and S_2 shown in Fig. 3. Their dispersions are flat with an energy gap at $\bar{\Gamma}$ of 1.3 eV. Since the ordered arrangement of Ge atoms in on-top- or hollow-site positions is the most natural one, the above findings raise the question, whether the Si(111)1×1-Ge surface is ordered at all. Looking at the bottom curve of Fig. 1, we notice that the two bulk features at 2.3 and 4 eV are reduced by the Ge deposition (compare solid and dashed curves in Fig. 1). Usually this is taken as evidence for an increased k broadening at the surface. Since at the same time the surface periodicity changes from 2×1 to 1×1, i.e., fewer surface wave vectors, we conclude that the Ge monolayer is not ordered and the 1×1 structure represents the Si(111) substrate. A similar effect occurred for the laser-annealed

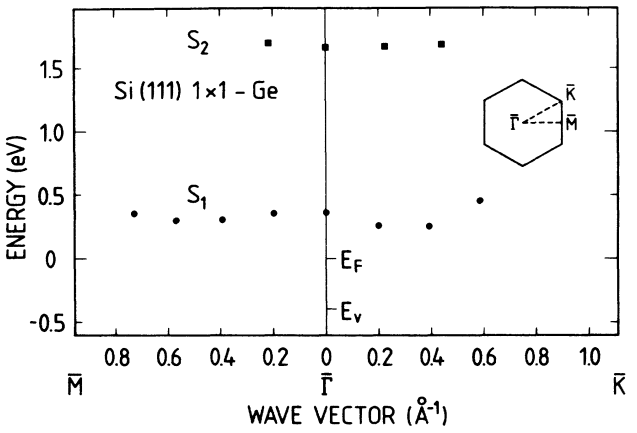

FIG. 3. Plot of the peak positions of the surface-state features S_1 and S_2 as function of the wave vector $k_{\parallel}$ along the $\bar{\Gamma}$-$\bar{K}$ and $\bar{\Gamma}$-$\bar{M}$ directions.

Si(111) 1×1 surface. It was found[17] that the Si(111) 1×1 exhibited a very similar electronic structure like the Si(111) 7×7 surface. This strong similarity was interpreted[17] as being due to similar local-bonding geometries of the two reconstructed surfaces, but different long-range orders involving geometrical arrangements that are only a perturbation on the average local-bonding geometry.

For Si(111) 1×1-Ge, the Seiwatz-chain model[11] predicts flat surface-state bands within the bulk energy gap, as we did indeed find experimentally, but it would require a 2×1 reconstruction which is in contradiction to the observed 1×1 LEED pattern. It is probable that in the submonolayer regime the Ge atoms do not interact with each other and give rise to the observed (Ref. 9) $\sqrt{3}\times\sqrt{3}R30°$ reconstructed surface. The increasing Ge-Ge interaction with increasing Ge coverage could be responsible for local Seiwatz-chain formation which determines the electronic properties of the surface, i.e., flat surface-state bands. The dispersionless behavior suggests that the Ge-Ge π-bonding interaction within the Seiwatz-chain model is much weaker than that occurring in the π-bonded chain model[12,13] proposed for the Si and Ge (111) 2×1 surfaces with an energy dispersion which was measured[15] to be much larger (~1 eV). In such an interpretation the Si(111) 1×1-Ge surface is only a disordered Si(111) 2×1-Ge surface with the 1×1 LEED pattern being due to the substrate underneath.

We conclude that in the beginning of the Si(111)-Ge interface formation, strain could be responsible for the breaking of the initial Si(111)$\sqrt{3}\times\sqrt{3}R30°$-Ge surface,[9] giving rise, for Ge coverages of the order of one monolayer, to a different local ordering. A local Seiwatz-chain arrangement could explain[11] our angle-resolved inverse photoemission results showing a surface-state band in the energy gap which is flat along the main symmetry directions.

We thank M. Tschudy for his help with the experiments.

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