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Si(111)7×7-Ge and Si(111)5×5-Ge surfaces studied with angle-resolved photoemission

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Angle-resolved photoelectron spectroscopy has been used to study the surface electronic structure of Si(111)7×7-Ge and Si(111)5×5-Ge surfaces. For the Si(111)7×7-Ge surface, three surface-state structures were observed at energies −0.20 eV (A_1), −1.0 eV (A_2), and ∼−1.4 eV (A_3) relative to the Fermi level. For the Si(111)5×5-Ge surface, two surface-state structures were identified at −0.12 eV (B_1) and ∼−1.2 eV (B_3), respectively. The A_3 and B_3 surface states show a downward initial-energy dispersion along the $\bar{\Gamma}$-$\bar{K}$ line in the 1×1 surface Brillouin zone, with an observed bandwidth of ∼0.35 eV. The results are compared with those obtained for the clean Si(111)7×7 surface.

Several experimental techniques have been applied to the study of the atomic and electronic structure of Si(111)7×7 surfaces, and a large number of models have been proposed to explain the experimental data.[1] Recently it has been possible, by using scanning tunneling microscopy (STM), to investigate the atomic structure of the outer layers of the 7×7 surface in real space.[2] Ion-scattering experiments[3,4] have provided evidence of a significant rearrangement of atoms in the underlying layers, interpreted in terms of a surface stacking fault.[5] Based on the results from transmission electron diffraction experiments, Takayanagi, Tanishiro, Takahashi, and Takahashi[6] have suggested a new model [dimer adatom stacking fault (DAS) model] for the 7×7 reconstruction which accounts for the STM and ion-scattering experiments. Further experiments and theoretical calculations are, however, required in order to fully determine the atomic structure of the Si(111)7×7 surface.

Recent experiments show that by evaporating a few monolayers of germanium on a Si(111)7×7 surface, a 5×5 or a 7×7 reconstruction is obtained, depending on the amount of Ge and on the annealing temperature.[7-10] Since electron diffraction experiments[8,10] show similarities between the patterns for the two Ge-covered surfaces and those for the clean 7×7 surface, a close relationship might exist between these surfaces. Becker, Golovchenko, and Swartzentruber[11] have studied the Si(111)5×5-Ge surface with the STM technique and compared the results with previously reported STM data on the clean 7×7 surface.[2] The tunneling images show that the two surfaces closely resemble each other and that a model similar to the DAS model for the clean 7×7 surface can be applied to describe the 5×5-Ge surface.

In this paper we present an angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) study of Si(111) 7×7-Ge and Si(111)5×5-Ge surfaces. These surfaces are found to have electronic structures *qualitatively* similar to that of the clean Si(111)7×7 surface.

Angle-resolved photoemission spectra were recorded in an ultrahigh-vacuum chamber at a pressure of less than 5×10^{-11} Torr. Monochromatized 10.2-eV radiation from a hydrogen discharge lamp was used. The estimated total energy resolution as determined by the analyzer voltages and the monochromator slit widths was ∼100 meV and the angular resolution of the analyzer was ±2°. All ARUPS spectra presented in the present paper were recorded along the [10$\bar{1}$] azimuthal direction, which corresponds to a $\bar{\Gamma}$-$\bar{K}$ line in the 1×1 surface Brillouin zone (SBZ), but spectra have also been recorded along the [11$\bar{2}$] and [2$\bar{1}\bar{1}$] directions.

In a separate vacuum chamber equipped with an electron- beam-heated source for Ge evaporation and facilities for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), we have studied the preparation of Si(111)5×5-Ge and Si(111)7×7-Ge surfaces by annealing of thin Ge deposits on clean Si(111) surfaces.[12] From the attenuation of the 92-eV Si *LVV* Auger line we have estimated the Ge content in the outer layers of these surfaces, either assuming a homogeneous alloy within the probe depth (λ∼4.4 Å) or assuming a pure Ge overlayer. The 5×5 reconstruction was observed on surfaces with a Ge content of 40–70%, which corresponds to an overlayer of 1.3–3.0 ML Ge (1 ML=7.8×10^{14} atoms/cm^2). This is in agreement with the results of previous studies.[7,10] A 7×7 reconstruction was observed on surfaces containing up to 30% of Ge, or, alternatively, up to 1.0 ML of Ge. The exact distribution of this Ge cannot be determined, but since the present study of the electronic structure of the 7×7-Ge surface shows significant quantitative differences with the electronic structure of the clean 7×7 surface, substantial amounts of Ge must be present in the 7×7-Ge surface.

The presented ARUPS spectra for the clean Si(111) 7×7 surface were recorded from a heavily *n*-doped, mirror-polished single crystal ($\rho\sim70$ mΩcm, $N_D\sim2\times10^{17}$ cm^{-3}). Before insertion into the vacuum chamber, the sample was degreased and etched according to the procedure by Henderson.[13] In ultrahigh vacuum it was thoroughly outgassed at ∼500 °C, heated to ∼950 °C for 10 min, and then annealed at ∼700 °C for 5 min. This procedure gives clean surfaces showing sharp 7×7 LEED patterns.

The presented spectra for the Si(111)7×7-Ge surface were recorded from a surface obtained by evaporating ∼4

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ML of Ge onto a clean 7×7 surface (prepared according to the procedure described above) followed by approximately 15-min annealing at 770 °C. This produced a surface with a sharp 7×7 LEED pattern with low background and no traces of 5×5 spots. The annealing temperature was chosen to be rather low in order to obtain a 7×7 surface with the largest possible Ge content. The 5×5-Ge surface was obtained by evaporating ~4 ML of Ge onto a clean 7×7 surface [prepared by repeated cycles of Ar-ion sputtering (1000 eV) and annealing at 750 °C] followed by approximately 5-min annealing at 690 °C, resulting in a sharp 5×5 LEED pattern with low background. In both cases the samples were lightly *n*-doped, mirror-polished single crystals ($\rho \sim 5\ \Omega$cm, $N_D \sim 1\times10^{15}$ cm^{-3}). Ge was evaporated from thoroughly outgassed tungsten filaments at a rate equivalent to ~1 ML/min, as monitored with a quartz microbalance.

ARUPS spectra have been recorded for several 5×5-Ge and high-coverage 7×7-Ge surfaces, obtained for somewhat different initial amounts of Ge, and the results show that the electronic structure of these surfaces are quite reproducible. Because of differences in band bending, the bulk peaks in the spectra recorded for the Ge-covered surfaces were observed to be shifted ~0.2 eV toward higher initial energy as compared to the corresponding peaks for the clean 7×7 surface.

Figure 1 shows spectra recorded for the clean 7×7 surface. The structures S_1, S_2, and S_3 are due to emission from previously reported surface states.[14-16] The nondispersing states S_1 and S_2 are observed at ~0.15 and ~0.8 eV below E_F, respectively. The surface state S_3 shows a downward dispersion for angles of emission $\theta_e > 35°$ with an observed bandwidth of ~0.35 eV and a maximum initial energy of ~1.5 eV below E_F. Due to overlap with bulk emission, it is not possible to clearly identify S_3 for $\theta_e < 35°$.

Figure 2 shows ARUPS spectra obtained for the Si(111)7×7-Ge surface. Three surface-state structures (A_1, A_2, and A_3) are identified. The surface state A_1 is observed at an energy of ~0.20 eV below E_F. The state A_2 is observed at ~1.0 eV below E_F, and, due to overlapping with A_3, it is resolved only for large angles of emission (as a shoulder). No significant initial-energy dispersion is observed for the A_1 and A_2 surface states. The A_3 state has, as S_3, a downward dispersion with an observed bandwidth of ~0.35 eV, but the maximum in initial energy is slightly higher (~1.25 eV below E_F).

In Fig. 3 spectra recorded for the Si(111)5×5-Ge surface are shown. In these spectra it is possible to identify two surface states, B_1 and B_3. The nondispersing surface state B_1 is observed at an energy of ~0.12 eV below E_F. The state B_3 has a downward dispersion, with maximum initial energy at ~1.05 eV below E_F and an observed bandwidth of ~0.35 eV. The behaviors of B_1 and B_3 are

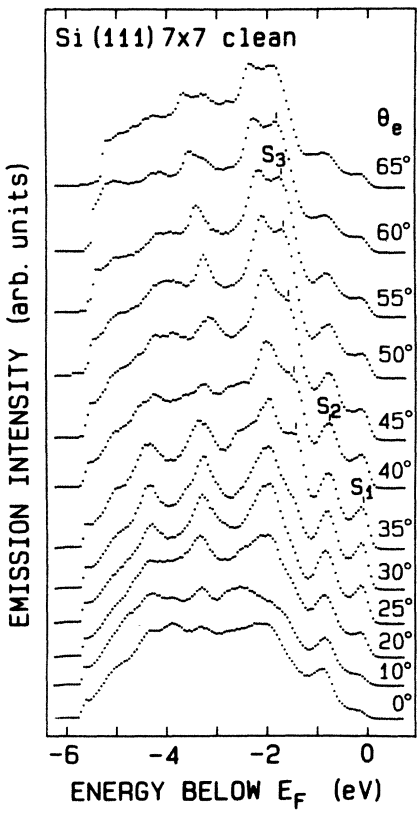

FIG. 1. Photoemission spectra recorded for Si(111)7×7 with 10.2-eV photon energy for various angles of emission along the [10$\bar{1}$] azimuthal direction. The angle of incidence is $\theta_i = 60°$ except for $\theta_e = 60°$ and 65°, for which $\theta_i = 50°$.

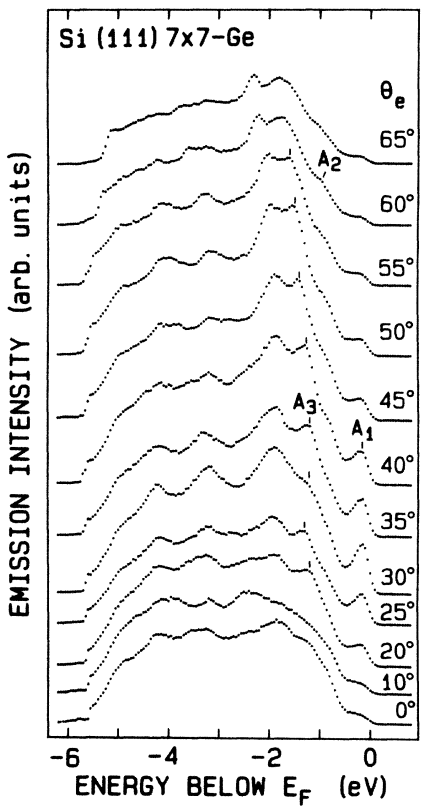

FIG. 2. Photoemission spectra recorded for Si(111)7×7-Ge with 10.2-eV photon energy for various angles of emission along the [10$\bar{1}$] azimuthal direction. The angle of incidence is $\theta_i = 60°$ except for $\theta_e = 60°$ and 65°, for which $\theta_i = 50°$.

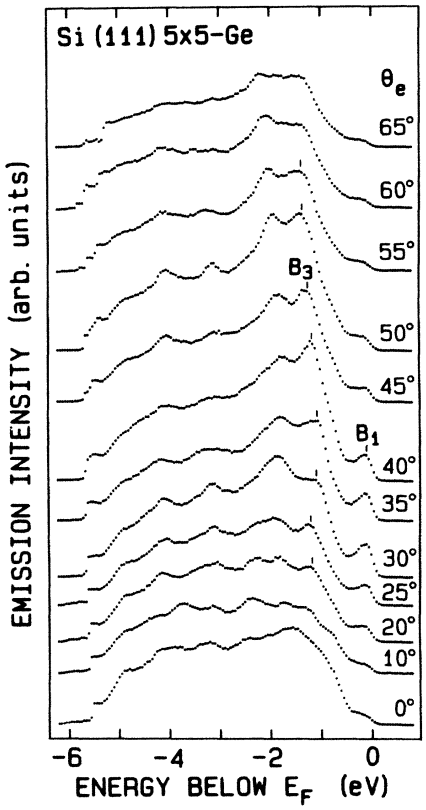

FIG. 3. Photoemission spectra recorded for Si(111)5×5-Ge with 10.2-eV photon energy for various angles of emission along the [10$\bar{1}$] azimuthal direction. The angle of incidence is $\theta_i = 60°$ except for $\theta_e = 60°$ and 65°, for which $\theta_i = 50°$.

quite similar to those of S_1, A_1 and S_3, A_3, respectively. Along the [10$\bar{1}$] direction, no structure B_2 corresponding to S_2 and A_2 is observed.

The surface states A_1, A_2, A_3, B_1, and B_3 all show strong p_z character and are sensitive to oxygen contamination, as previously reported with regard to the surface states S_1, S_2, and S_3.[16] The states S_1, A_1, and B_1 are clearly observed all along the $\bar{\Gamma}$-$\bar{K}$ line, and they all show maxima in emission intensity at $\theta_e = 30°$, which corresponds to probing these states at a corner in the SBZ of a 2×2 unit mesh. That the maximum for the S_1 emission from the clean Si(111)7×7 surface occurs near the boundary of a 2×2 SBZ has been established previously in photoemission experiments using different photon energies.[14-16] This may well be related to the fact that the protrusions found in STM studies of the clean 7×7 surface[2] form a quasi-2×2 lattice. The present results support this hypothesis since the same angular dependence of the emission from the Fermi-level surface state is found on the 5×5-Ge surface, for which the STM studies[11] also show a quasi-2×2 symmetry for the protrusions.

From the spectra described above it is clear that the surface states S_1, S_2, and S_3 present on the clean Si(111)7×7 surface have their counterparts in structures A_1, A_2, and A_3 on the 7×7-Ge surface and that the electronic properties of these surfaces closely resemble each other, although there are differences in initial energy of the surface states. For the Si(111)5×5-Ge surface, the B_1 and B_3 surface states are the counterparts of S_1, A_1 and S_3, A_3, respectively. A puzzling feature of the ARUPS spectra recorded for the 5×5-Ge surface along the [10$\bar{1}$] direction is the absence of a B_2 state related to S_2 and A_2. Since there is a gradual increase in the initial energy of the lowest surface state going from the clean 7×7 via the 7×7-Ge to the 5×5-Ge surface, it is possible that, for the 5×5-Ge surface, any B_2 emission along the [10$\bar{1}$] direction is obscured by the overlap with emission from B_3. This hypothesis is supported by the fact that ARUPS spectra recorded for large angles of emission along the [11$\bar{2}$] and the [2$\bar{1}\bar{1}$] directions reveal the presence of a shoulder that could be related to a B_2 state. Further ARUPS measurements with different photon energies are in progress for the purpose of gaining more information about this possible B_2 state.[12]

In a recent electron-energy-loss spectroscopy (EELS) experiment on the 7×7-Ge and 5×5-Ge surfaces,[9] the presence of a loss peak at ~1.4 eV for both surfaces was reported. In EELS experiments on the clean Si(111)7×7 surface, a loss peak has been observed at ~1.7 eV,[9,17-19] and the filled state responsible for this transition has been suggested to be either S_2 (Ref. 18) or S_3.[19] The present ARUPS spectra show that the energy positions of the state A_2 and the possible B_2 state are shifted ~0.2 eV toward *lower* initial energies as compared to S_2. On the other hand, the energy positions of states A_3 and B_3 are shifted ~0.25 and ~0.45 eV toward *higher* initial energy as compared to S_3. These last shifts have the correct sign and appropriate magnitudes to be consistent with the ~0.3-eV energy difference between the loss peak for the clean 7×7 surface and the loss peaks for the Ge-covered surfaces. This would indicate that the energy loss peaks at ~1.7 eV on Si(111)7×7 surfaces, and ~1.4 eV on 7×7-Ge and 5×5-Ge surfaces are due to transitions from the filled surface states S_3, A_3, and B_3, respectively.

In a very recent angle-integrated photoemission experiment on the Si(111)5×5-Ge surface,[20] one surface state, at the Fermi level, was observed. This state corresponds to the above-reported B_1 state. The main peak in the angle-integrated spectrum in Ref. 12 is rather broad and no clear feature that corresponds to the presently reported B_3 state or to any B_2 state can be identified.

To summarize, we report three measured surface-state bands for the Si(111)7×7-Ge surface that are similar to those corresponding to the Si(111)7×7 surface, the major difference being an increased overlap between the two lower-lying surface states. For the 5×5-Ge surface there are two surface-state bands that resemble those corresponding to the two 7×7 surfaces. There is some evidence of a third surface state, but further studies are required in order to confirm the existence of this state.

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