Occupied and unoccupied surface states on the single-domain Si(100):Sb-2×1 surface

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Angle-resolved photoelectron spectroscopy and k-resolved inverse photoemission have been used to study the electronic structure of the Si(100):Sb-2×1 surface. For both techniques, one occupied and one unoccupied surface-state band has been mapped along the [010] and [011] directions. The surface shows semiconducting behavior with an estimated minimum band gap of 1.45 eV along the [010] direction.

INTRODUCTION

The importance of group-V elements such as Sb and As as dopants in semiconductor technology has, recently, prompted interest in their interaction with Si and Ge crystal surfaces. In particular, the interaction of such group-V adsorbates with Si(100)2×1 surfaces has been the subject of continuous research in recent years.[1–10] Scanning-tunneling microscopy (STM) experiments by Nogami, Baski, and Quate[6] and by Richter and coworkers[7,8] have shown that by evaporating a few monolayers of antimony on a Si(100)2×1 surface kept at 375 °C and further annealing at a temperature of 550 °C produces a 2×1 reconstruction. In this case the 2×1 reconstruction consists of symmetric Sb dimers with a degree of disorder higher than for the clean silicon surface.

In the present work we have studied the electronic properties of the Si(100):Sb-2×1 surface with angle-resolved inverse- and direct-photoemission spectroscopy (KRIPES and ARUPS, respectively). ARUPS and KRIPES spectra along the [010] and [011] directions show a semiconducting behavior with the presence of one dispersive filled and one empty band. An optical surface band gap of 1.45 eV is derived.

EXPERIMENT

The experiments reported here were performed in a two-chamber ultrahigh-vacuum (UHV) system described elsewhere.[11] The base pressures in the chambers were in the 10^{11}-mbar range. The KRIPES experiments were carried out in the isochromat mode, detecting 9.5-eV photons with an overall energy resolution of 0.35 eV and wave-vector resolution of 0.1 Å.$^{-1}$ The ARUPS experiments were performed with unpolarized He I light ($h\nu=21.2$ eV) and an overall energy resolution of 0.1 eV. The Fermi-level position of a tantalum foil was taken as the energy reference, $E_F=0$. Such a Fermi-level position was taken several times during the whole experiment in order to monitor any possible variation.

The samples were highly n-doped Si(100) single crystals ($\rho=4-8$ mΩ cm, arsenic, from Wacker Chemitronic), cut 4° off the [100] direction, tilting towards [011]. The use of such vicinal sample is a well-known method for obtaining Si(100) surfaces with a single-domain 2×1 reconstruction.[12] Before insertion into UHV, the samples were cleaned by a chemical etching method.[13] Then *in vacuo* the samples were outgassed at about 600 °C and cleaned by resistive heating at 850 °C for several minutes. Subsequently, good single-domain 2×1 low-energy electron diffraction (LEED) patterns were observed. The surface cleanliness was checked by studying the emission intensity of the contamination-sensitive dangling-bond surface state in ARUPS.

Antimony was evaporated from a thoroughly outgassed oven at a rate equivalent to 0.5 ML/min as monitored with a quartz microbalance. One monolayer (1 ML) of Sb is defined as the site density for the unreconstructed surface which is 6.8×10^{14} atoms/cm^2. The 2×1-Sb surface was obtained by evaporating 4 ML of Sb onto a clean 2×1 surface followed by approximately 20 min annealing at 550 °C, resulting in a clear 1×1 LEED pattern with diffuse, one-domain 2×1 spots and a high background indicating some kind of disorder at the surface. All temperatures were measured with an infrared pyrometer. Pressures during Sb deposition and sample heating did not exceed 1.0×10^{-9} mbar. ARUPS and KRIPES spectra have been recorded for several 2×1-Sb

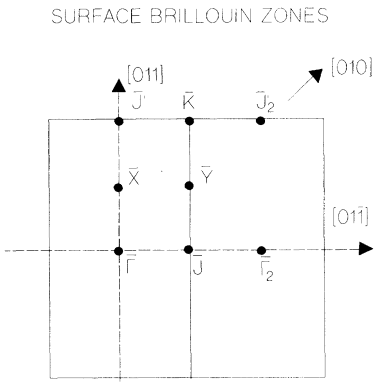

FIG. 1. The surface Brillouin zone of the single-domain Si(100)2×1 surface in the repeated zone scheme. Symmetry points are indicated in the figure.

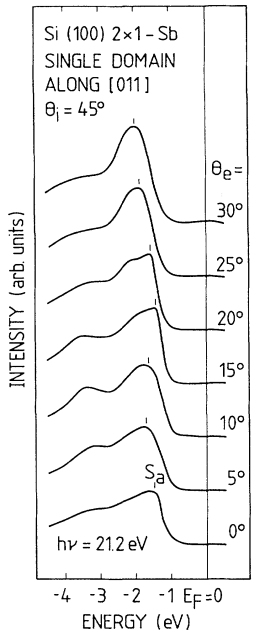

FIG. 2. ARUPS spectra recorded from Si(100):Sb-2×1 for various angles of emission along the [011] azimuthal direction. The angle of incidence is $\Theta_i = 45°$.

surfaces, obtained for somewhat different initial amounts of Sb, and the results show that the electronic structures are quite reproducible.

All the incidence angles shown in the angular series of KRIPES and ARUPS spectra (Figs. 2–5) refer to the surface normal for the vicinal samples while the measured dispersions (Fig. 6) refer to the [100] direction.

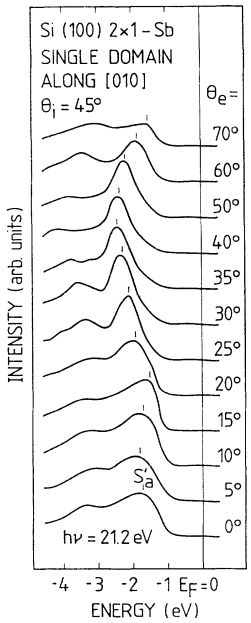

FIG. 3. ARUPS spectra recorded from Si(100):Sb-2×1 for various angles of emission along the [010] azimuthal direction. The angle of incidence is $\Theta_i = 45°$.

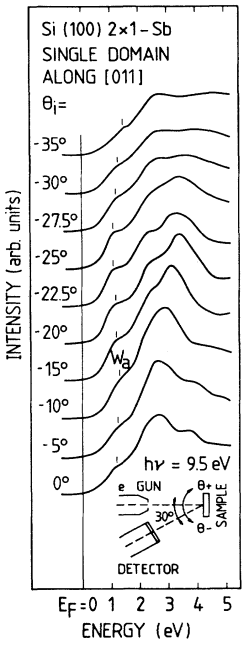

FIG. 4. KRIPES spectra recorded from Si(100):Sb-2×1 for various angles of incidence along the [011] azimuthal direction. The inset shows the geometry of a KRIPES experiment. The electron gun and the detector are kept at a fixed angle with respect to each other. The electron incidence angle (Θ) is defined negative when turning the sample downwards (towards the detector).

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the surface Brillouin zones (SBZ's) of the single-domain surface in the repeated zone scheme. Symmetry points are indicated in the figure. Mirror

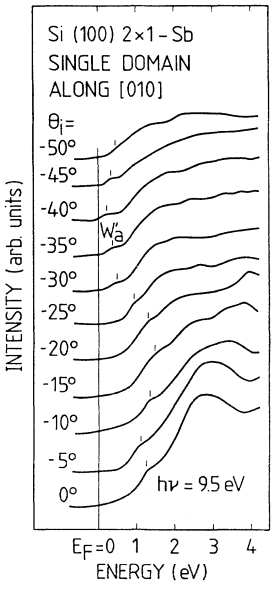

FIG. 5. KRIPES spectra recorded from Si(100):Sb-2×1 for various angles of incidence along the [010] azimuthal direction.

planes of the surface are indicated with broken lines.

Figure 2 shows ARUPS curves recorded from the Si(100):Sb-2×1 surface for various angles of emission along the [011] direction. The spectra are dominated by a prominent peak (S_a). This structure is identified in normal emission around 1.7 eV below E_F with a small upward dispersion (0.2 eV) with maximum energy at $\Theta_e = 15°$ (X point of Fig. 1) and then a downward dispersion (0.45 eV) for larger angles of emission.

Figure 3 shows ARUPS curves recorded from the Si(100):Sb-2×1 surface for various angles of emission along the [010] direction. Also the spectra obtained along the [010] direction are dominated by a single peak (S_a'). This structure is identified in normal emission at 1.75 eV below E_F with a small upward dispersion (0.4 eV) with maximum energy at $\Theta_e = 15°$ (around the Y point of Fig. 1) and then a downward dispersion (0.95 eV) for larger angles of emission. After the minimum at the J_2' point ($\Theta_e = 37°$) the state disperses again upward.

Figures 4 and 5 show KRIPES data recorded from the Si(100):Sb-2×1 surface for various angles of emission along the [011] and [010] directions, respectively. The spectra obtained along the [011] direction (Fig. 4) are dominated by a single structure (W_a) which is located at 1.15 eV above E_F in normal emission showing a downward dispersion (0.2 eV) with minimum energy at $\Theta_i = -22.5°$ (X point of Fig. 1) and then an upward dispersion (0.3 eV) for larger angles of emission.

The spectra obtained along the [010] direction (Fig. 5) exhibit a single structure (W_a') which is located at 1.1 eV above E_F in normal emission showing an upward dispersion (0.4 eV) with maximum energy at $\Theta_i = -15°$ around the Y point of Fig. 1) and then a downward dispersion (1.25 eV) for larger angles of emission with a minimum energy of 0.2 eV above E_F at $\Theta_i = -40°$.

We have derived the experimental energy dispersions of the different spectral features of Figs. 2–5 and plot them in Fig. 6.

Since all the Sb-induced structures are not present for the clean surface and only a small part of them lies within the projected bulk band gap,[14] we assign them to Sb-induced surface states. The surface-state assignment is further supported by the periodicity of the dispersions along the probed lines in the surface Brillouin zone (see, for example, structure S_a' of Fig. 3, which shows a symmetric dispersion around the J_2' point).

The dispersion of the filled surface states (S_a and S_a') is very similar to ARUPS results on the Si(100)2×1-As surface[2,3] where a symmetric dimer model [predicted by theoretical calculations and observed by STM (Ref. 15)] can account for the surface-state band dispersion. In that ARUPS study[2,3] the dispersion of the filled band along the [010] direction shows a maximum at $k_\parallel = 0.33$ Å and then disperses downward toward the J_2' point with a bandwidth of 0.8 eV. For the S_a' structure we have observed the same kind of dispersion (maximum at $k_\parallel = 0.39$ Å^{-1}) with a similar bandwidth (0.95 eV); the only difference is in the absolute energy position which depends on the bonding between the different kind of atoms involved (As or Sb in our case). A similar result is also obtained in the comparison along the [011] direction. Since symmetric dimers have been observed by STM also on this 2×1-Sb surface we expect that calculations based on symmetric dimers will fully describe our observed band structure.

The fact that no emission at the Fermi level is observed in either ARUPS or KRIPES clearly shows that the Si(100):Sb-2×1 surface is semiconducting. By combining the ARUPS and KRIPES results in Fig. 6 we can assign possible optical transitions to precise points of the SBZ. Before making such a comparison we have to take into account our limited energy and $k_\parallel$ resolution of 0.35 eV and 0.1 Å^{-1}, respectively. The energy position in KRIPES of the surface-state peak at the Y and X points in the SBZ may be closer to E_F than measured.[16,17] It was

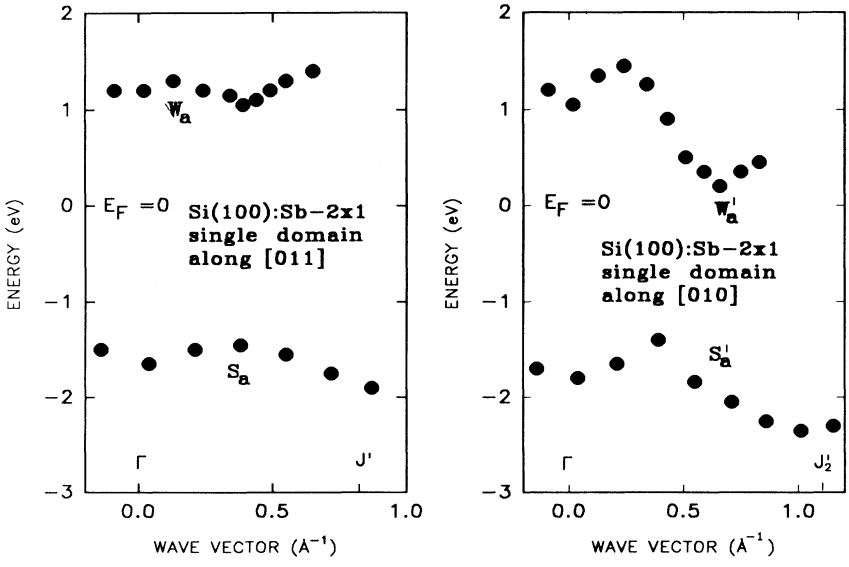

FIG. 6. Experimental energy dispersion of filled and empty surface states for the Si(100):Sb-2×1 surface along the [011] and [010] azimuthal direction.

shown in several simulations in Refs. 16 and 17 that the measured position should be 0.15 eV higher in energy than it had been measured. Taking this into account, the minimum optical gap is 1.45 eV at the points around $k_{\parallel}-0.5$ Å^{-1} along the [010] direction which corresponds to the border line of the SBZ (Y point in Fig. 1). Another optical transition at 2.5 eV is expected around the points with $k_{\parallel}=0.4$ Å^{-1} along the [011] direction (X point in Fig. 1). At Γ an optical transition around 2.8 eV is expected.

SUMMARY

We have performed angle-resolved direct and inverse photoemission studies of the Si(100):Sb-2×1 surface. The dispersion of one occupied and one unoccupied surface-state band has been determined along the high symmetry lines in the surface Brillouin zone. The surface shows a semiconducting behavior with a possible minimum optical gap of 1.45 eV along the [010] direction.

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