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Surface electronic structure of GaAs(110)1×1-Sb studied with angle-resolved photoelectron spectroscopy

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The ordered 1×1 overlayer of Sb on GaAs(110) has been studied with angle-resolved photoemission. The experimentally determined energy dispersions of three surface-state bands are compared with the results of previously reported theoretical calculations based on a surface model favored by low-energy electron diffraction analysis. Although there is a qualitative agreement between experiment and theory, the results suggest that a modification of the model is needed in order to obtain a better description of the GaAs(110)1×1-Sb surface.

The adsorption of group-III and -V elements on the (110) surfaces of III-V compound semiconductors has been the subject of several experimental and theoretical investigations.[1] One of the most interesting cases is the adsorption of antimony on GaAs(110) since thermal desorption,[2] elastic low-energy electron diffraction (ELEED),[2,3] and photoemission experiments[4,5] have shown that a very stable and ordered adsorbate structure with the same symmetry as that of the clean surface is formed for a coverage of approximately one monolayer (1 ML).[6]

Duke *et al.*[3] have proposed a full structural model for the GaAs(110)1×1-Sb surface that gives a good agreement between measured and calculated ELEED intensities. In the model, chains of Sb atoms reside upon a nearly unrelaxed GaAs(110) substrate as shown in Fig. 1. Using this model, Bertoni, Calandra, Manghi, and Molinari[7] have made a self-consistent pseudopotential calculation of the surface electronic structure of GaAs(110)1×1-Sb. The energy positions of several occupied and unoccupied surface states were determined in high-symmetry points of the surface Brillouin zone (SBZ). Recently, Mailhiot, Duke, and Chadi[8] made an extensive study of the surface electronic structure for an energy minimized surface geometry of the same type as the geometry suggested by the ELEED analysis. These authors calculated the surface-state energy dispersions along the major symmetry lines of the SBZ and discussed the orbital character of the surface states. The limited photoemission data that have been available so far[5,9] seem to be consistent with the calculated surface electronic structure, but extensive angle-resolved photoemission studies are needed for a better understanding of the surface structure.

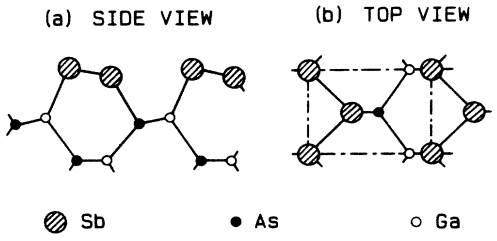

FIG. 1. Schematic diagram of the surface geometry for GaAs(110)1×1-Sb. (a) Side view. (b) Top view.

In this paper we present an angle-resolved photoemission study of the GaAs(110)1×1-Sb surface. In the region of the bulk valence-band edge two surface states have been identified and the energy dispersions of these states have been mapped along the major symmetry lines of the surface Brillouin zone. A third surface state, located in the upper part of the large central gap of the bulk bands, has been mapped along the edge of the SBZ. The experimentally obtained surface-state dispersions are compared with the results obtained in the theoretical calculations of Bertoni *et al.*[7] and of Mailhiot *et al.*[8]

Angle-resolved photoemission spectra were recorded with a VG ADES 400 spectrometer using polarized synchrotron radiation from the DORIS II storage ring at Hamburger Synchrotronstrahlungslabor, Deutsches Elektronen-Synchrotron.[10] All spectra presented in this paper have been recorded with the polarization vector of the light parallel to the plane in which the electrons were analyzed. The angle of incidence of the light θ_i and the emission angle θ_e are defined according to the inset of Fig. 2. The azimuthal angle φ is defined to be 0° for the azimuth of the Ga dangling bond on the clean surface. The total energy resolution (analyzer and monochromator) is in all spectra better than 0.20 eV. The angular resolution is ±2°. The position of the Fermi level was determined to an accuracy of ±0.05 eV

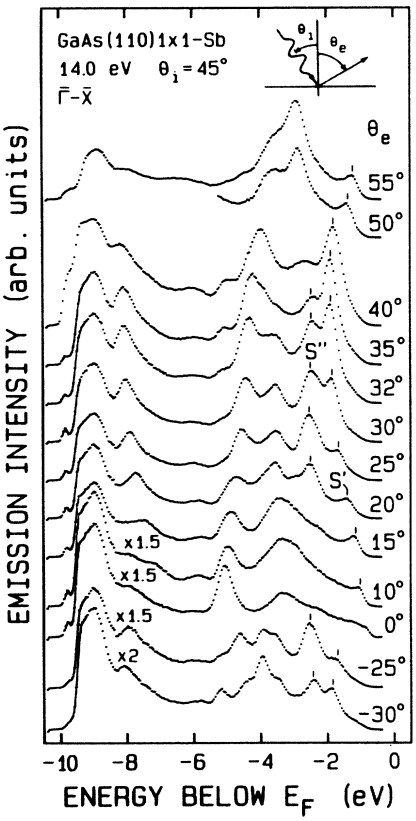

FIG. 2. Photoemission spectra recorded with 14.0-eV photon energy for various angles of emission θ_e along the $\bar{\Gamma}$-$\bar{X}$ symmetry line in the SBZ ($\varphi = 90°$).

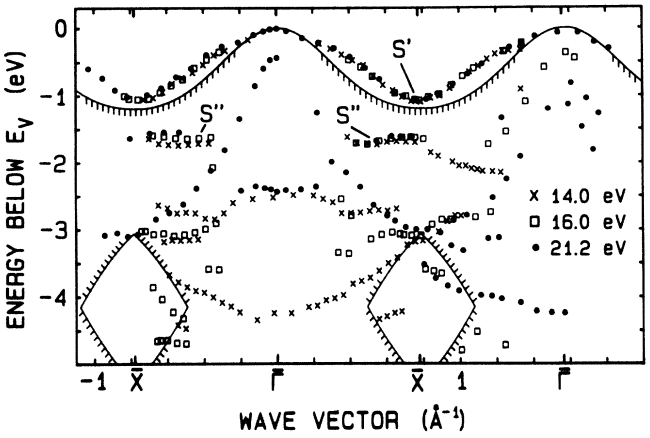

FIG. 3. Initial-energy positions for the different structures that are observed in the spectra recorded with 14.0-eV (×), 16.0-eV (□), and 21.2-eV (●) photon energy for various angles of emission θ_e along the $\bar{\Gamma}$-$\bar{X}$ symmetry line in the SBZ. The shaded regions show the edge of the projected bulk bands according to the theoretical calculation of Bertoni *et al.* (Ref. 7).

by emission from the metallic sample holder. A very lightly n-doped GaAs(110) single-crystal bar ($\sim 5\times10^{15}$ carriers per cm^3) was cleaved along a ⟨111⟩ crystal direction using the standard knife and anvil technique. Antimony was evaporated from an effusion cell at a rate equivalent to ~ 2 Å/min. The background pressure in the ultrahigh vacuum chamber was better than 2×10^{-10} Torr, and the pressure never exceeded 1×10^{-9} Torr during evaporation. Since thermal desorption and LEED studies[2] have shown that the 1×1-Sb overlayer on GaAs(110) is stable up to temperatures of ~ 500 °C, whereas any excess Sb desorbs at temperatures of 250°–350 °C, the GaAs crystal was heated to ~ 300 °C during the evaporation and exposed to the equivalent of ~ 2.5 ML of Sb. Before cleaving, the crystal had been thoroughly outgassed at ~ 550 °C. After completion of the photoemission experiment the Sb-covered surface was studied with LEED and a clear 1×1 pattern with low background was observed.

Figure 2 shows a selected set of photoemission spectra recorded for various angles of emission θ_e along the $\bar{\Gamma}$-$\bar{X}$ line (the longer axis) in the SBZ for 14.0-eV photon energy. In Fig. 3 the initial-energy positions E_i of the features observed in photoemission spectra recorded at 14.0-, 16.0-, and 21.2-eV photon energy are plotted as functions of the wave vector parallel to the surface, $k_\parallel$. A value of 0.8 eV was used for the energy difference between the Fermi level E_F and the valence-band maximum E_V.[4] For the structures S' and S'' (defined in Fig. 2) there is good agreement between the initial-energy dispersions obtained with different photon energies, and these structures are therefore interpreted as due to emission from surface states or resonances.[11]

The experimental data in Fig. 3 are shown relative to the projected bulk bands obtained by Bertoni *et al.*[7] since those are in better agreement with the data than the ones obtained by Mailhiot *et al.*[8] Several features are seen for one photon energy only and these are therefore interpreted as due to emission from bulk states. The central gap obtained by Mailhiot *et al.* is considerably larger than that obtained by Bertoni *et al.* and many of the bulk dispersions fall within this larger gap. There are, however, features that are located also within the smaller gap from Bertoni *et al.* The origin of these features is not fully understood and further studies are required in order to interpret them correctly.

In Figs. 4(a) and 4(b) spectra recorded for $\theta_e = 30°$, $\varphi = 90°$, and 14.0-eV photon energy are shown. The angle of incidence θ_i of the photons is 0° for the spectrum in Fig. 4(a), while it is 45° for the spectrum in Fig. 4(b). It is clear that the surface states S' and S'' are excited by the component of the polarization vector that is perpendicular to the surface, indicating that these states have p_z character.

Measurements were also made on the clean GaAs(110) 1×1 surface in order to identify bulk contributions in the spectra. However, a comparison between spectra obtained for the clean and for the overlayer surface may not be straightforward since the Sb overlayer can also affect the bulk contributions as discussed by Myron, Anderson, and Lapeyre.[9] In Fig. 4(c) a spectrum recorded for the clean GaAs(110) surface is shown. The same geometry was used as for the spectrum in Fig. 4(b), obtained for the Sb-covered surface. The two peaks near −4 eV in both spectra have similar polarization and angle dependencies for both surfaces and are therefore interpreted as due mainly to bulk emission. The peaks Z_1 and Z_2 are unique for the clean surface and are therefore interpreted as due to emission from surface states on the clean surface.[12,13]

Photoemission spectra have also been recorded for various angles of emission along the $\bar{\Gamma}$-$\bar{X}'$ and the $\bar{X}$-$\bar{M}$-$\bar{X}'$ lines in the SBZ. Details of these measurements will be

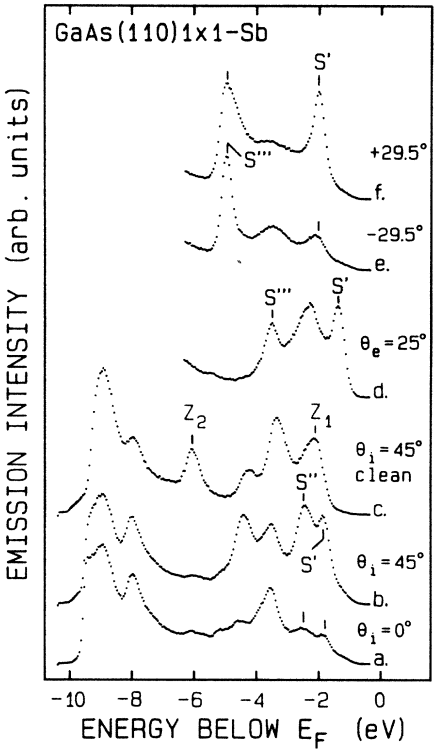

FIG. 4. Angle-resolved photoemission spectra obtained for (a) $\bar{\Gamma}$-$\bar{X}$(φ=90°), θ_e=30°, θ_i=0°, 14.0 eV; (b) $\bar{\Gamma}$-$\bar{X}$(φ=90°), θ_e=30°, θ_i=45°, 14.0 eV; (c) $\bar{\Gamma}$-$\bar{X}$(φ=90°), θ_e=30°, θ_i=45°, 14.0 eV, clean surface; (d) $\bar{\Gamma}$-$\bar{X}'$(φ=0°), θ_e=25°, θ_i=45°, 16.0 eV; (e) $\bar{\Gamma}$-$\bar{M}$(φ=125.3°), θ_e=−29.5°, θ_i=45°, 21.2 eV; (f) $\bar{\Gamma}$-$\bar{M}$(φ=125.3°), θ_e=+29.5°, θ_i=45°, 21.2 eV.

lished elsewhere.[14] Along the $\bar{\Gamma}$-$\bar{X}'$ direction of the SBZ the surface state S' is clearly visible, whereas the state S'' is visible only close to the $\bar{X}'$ point (as a weak shoulder). A spectrum recorded for θ_e=25°, φ=0°, θ_i=45°, and 16.0-eV photon energy is shown in Fig. 4(d). In this spectrum a strong structure S''' is present at ~3.5 eV below E_F. This structure disperses downwards in initial energy going from $\bar{X}'$ to $\bar{\Gamma}$ in the SBZ. It is situated in the large central gap of the bulk bands and shows the same dispersion for the different photon energies used, suggesting that it is due to emission from a surface state. The dependence of the emission intensity from the state S''' on the angle of incidence of the light indicates that S''' does not have p_z character.

For 21.2-eV photon energy, the dispersion of S''' has been mapped along the $\bar{X}'$-$\bar{M}$-$\bar{X}$ line in the SBZ. Close to the $\bar{X}'$ point the emission intensity from S''' is rather low, but it increases as the $\bar{M}$ point is approached. In Figs. 4(e) and 4(f) we show two spectra obtained with 21.2-eV photon energy, θ_i=45° and φ=125.3°. The emission angle is θ_e=−29.5° for spectrum (e) and θ_e=+29.5° for spectrum (f), which means that the state S' is probed at two $\bar{M}$ points. The peak at ~−5 eV in spectrum (f) is broadened broadened towards the low binding energy side due to interference with a peak that we interpret as due to emission from a bulk state. In Fig. 4(e) this bulk emission is suppressed leading to a very narrow peak that is interpreted as the pure S''' surface-state emission.

In Fig. 5 the experimentally determined initial-energy dispersions $E_i(k_\parallel)$ of the surface states S', S'', and S''' are

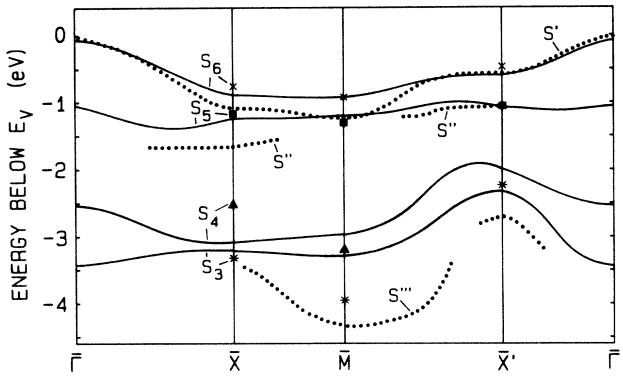

FIG. 5. Experimentally determined initial-state energy dispersions for the three states S', S'', and S''' (dotted lines that have been fitted to the experimental points). Also shown are the theoretical predictions from the calculations of Bertoni *et al.* (Ref. 7) (symbols) and of Mailhiot *et al.* (Ref. 8) (solid lines).

shown together with the results from the calculations of Bertoni *et al.*[7] (symbols) and of Mailhiot *et al.*[8] (solid lines). A qualitative agreement between theory and experiment is found by associating the experimentally observed states S', S'', and S''' with the theoretically predicted states S_6, S_5, and S_3, respectively.

Mailhiot *et al.* have shown that the uppermost surface state can be associated with the bond between Sb atoms and Ga atoms of the substrate. The total experimental dispersion along $\bar{\Gamma}$-$\bar{X}$ is ~1.05 eV, which is somewhat larger than the value of ~0.8 eV obtained by Mailhiot *et al.*[8] The difference in energy between the $\bar{X}'$ and the $\bar{M}$ point is ~0.65 eV in the experiment as compared to the value of ~0.3 eV obtained by Mailhiot *et al.*[8] and the value of ~0.4 eV obtained by Bertoni *et al.*[7]

According to the two calculations the state S_5 is degenerate with the bulk bands in a large part of the SBZ. This gives a possible explanation for the difficulty in observing the state S'' in the photoemission spectra. According to the calculation in Ref. 8 this state can be associated with the Sb—As bond. The experimentally obtained difference in initial energy between the $\bar{X}'$ and the $\bar{X}$ point is ~0.6 eV, whereas the calculations give < 0.2 eV.

Although there are discrepancies between Refs. 7 and 8 concerning the interpretation of the origins of the different surface states, both groups report that the two uppermost states S_6 and S_5 should have dangling-bond character. This is in agreement with the experimentally observed p_z character of S' and S''.

For the large central gap state S''' the experimentally obtained difference in initial energy between the $\bar{X}'$ and the $\bar{M}$ point is ~1.6 eV. This is in good agreement with the value of ~1.55 eV obtained by Bertoni *et al.*, while Mailhiot *et al.* obtained a value of only ~0.95 eV. The experimentally obtained polarization dependence of the emission from the state S''' supports the interpretation of Mailhiot *et al.* that this state is a mainly p_x,p_y derived state associated with the Sb—Sb bond in the overlayer.

The surface-state initial energies obtained in the self-consistent pseudopotential calculation of Bertoni *et al.*[7] are in better agreement with the experimental results than those obtained in the empirical tight-binding calculation of Mailhiot *et al.*[8] There are, however, some details in the experi-

mental surface-state dispersions that are not well described by any of the calculations, and therefore it seems that a modification of the model suggested by the ELEED analysis of Duke *et al.*[3] is needed in order to get a satisfying agreement between experiment and theory.

Maani, McKinley, and Williams[15] have studied the adsorption of Sb on the cleaved InP(110) surface. By comparing angle-resolved photoemission spectra for the clean and the Sb-covered surface they have identified two surface states at the $\bar{M}$ point in the SBZ showing strong similarities with the corresponding states S' and S''' in the present study of Sb on GaAs.

To summarize, in an angle-resolved photoemission study of the GaAs(110)1×1-Sb surface three surface states have been identified and their energy dispersions along the major symmetry lines in the surface Brillouin zone have been determined. The dispersions are in fair agreement with previously reported theoretical calculations. The polarization dependence of the emission from the surface states supports the interpretation of the origins of the Sb derived surface state bands given by Mailhiot *et al.*

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