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Photoemission study of the surface electronic structure of InSb(110)

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Angle-resolved ultraviolet photoemission has been applied to the investigation of the surface electronic structure of InSb(110). Strong emission from surface states has been observed at $k_{\parallel}$ values around $\bar{X}$ at ~ 1 and ~ 3.1 eV binding energy and for $k_{\parallel} = \frac{1}{2} k_{\bar{X}\bar{M}}$ at ~ 0.9, ~ 2.7, and ~ 5 eV with respect to the top of the valence band. The experimentally determined dispersion of the surface states is in reasonable agreement with scattering-theoretical-model calculations of the relaxed InSb(110) surface.

I. INTRODUCTION

The determination of the electronic surface structure of the nonpolar (110) cleavage face of the zinc-blende-type compound semiconductors has been the subject of long-standing interest due to their technical as well as their scientific importance.[1] Among the variety of surface-sensitive spectroscopies, elastic low-energy electron-diffraction[2–4] (ELEED) and angle-resolved ultraviolet photoemission spectroscopy[5–8] (ARUPS) have been the most powerful techniques for investigating the atomic and electronic structures of semiconductor surfaces.

Energy-minimization calculations by Chadi[9] and dynamical calculations of ELEED experiments led to the so-called rotational relaxation model, which is now the commonly accepted relaxation for the (110) surface of the whole group of zinc-blende semiconductors. In this model the cations move from the surface towards the bulk while the anions move outward resulting in an angle ~27° between the anion and cation bond directions.

Most of our knowledge about the surface structure of zinc-blende-type compound semiconductors arises from experimental and theoretical studies carried out on GaAs. Despite a lot of similarities between GaAs and other group III-V semiconductors, there are differences in the bulk and surface electronic properties which make a detailed investigation of these III-V semiconductors worthwhile. The surface core excitons, for instance, are bound states in the gap of GaAs but are found to lie above the gap in InSb as resonant conduction-band states.[10] Recently several theoretical groups have started to study the electronic structure of a few In—group V semiconductors in more detail.[11–13] The most advanced calculations used a tight-binding Hamiltonian to determine the bulk band structure. This provided parameter values for calculating surface electronic structure by the scattering-theoretical method[1,14] (STM). Due to the local changes in the surface binding configuration, occupied anion dangling bonds and empty cation dangling-bond states appear in the band gap. A cation-derived s-like band appears in the stomach-gap region of the projected bulk band structure and an anion-derived s-like state near the upper part of the bulk anion s-like band around 10-eV binding energy.[11]

Relaxation of the (110) surface, which also includes some charge transfer between the dangling and back bonds, pushes cation dangling bonds towards the conduction band and lowers the anion dangling bonds close to the top of the valence band. New p-like surface states appear around 3-eV binding energy due to the lowering of the cation surface layer. Photoelectron yield experiments[10] detected cation-derived empty surface states about 0.2 eV above the bottom of the conduction band of InSb but did not locate unoccupied surface states within the band gap. The present work reports angle-resolved photoemission experiments of InSb(110) and compares the results with theoretical predictions of the surface electronic structure based on calculations of the ideal and relaxed InSb(110) surface.[11,13]

II. EXPERIMENTAL DETAILS

Crystal plates of 7×7-mm^2 and 1.2-mm thickness of InSb oriented with the [110] axis perpendicular to the face of the plate were brought to mirror finish by mechanical polishing. Crystal damage due to the cutting and polishing as well as surface contamination could be removed by sputtering with Ar^+ ions of 500-eV energy at temperatures around 300 °C. After several hours of cleaning a well-developed streak pattern was obtained by reflection of high-energy electron diffraction (RHEED). The cleanliness of the sputter-annealed InSb(110) surface was monitored by two methods. Measuring the $4d$ core line spectra of In and Sb gave a rough indication of the oxide removal. Since the oxide formation is beyond the limit seen as well-resolved oxide structures in the core-line spectra,[15] we have also measured the surface cleanliness indirectly by comparing the intensity of surface-sensitive structures in the valence-band photoemission spectra. As will be discussed in the next section, there are features in the spectra near the surface—Brillouin-zone boundary which are very sensitive to small amounts of contaminants.

The photoemission experiments have been carried out in a Vacuum Generators ADES-400 angle-resolved photoemission spectrometer which had a base pressure of $\sim 10^{-10}$ Torr. Photoemission spectra were taken with photons from a differentially pumped rare-gas discharge lamp in the energy range $h\nu = 11$–48 eV. The photon incidence angle was held constant at $\theta_i = 45°$ relative to the surface normal. The electron spectrometer was operated with an angular resolution of $\Delta\theta = 1.5°$ and an energy resolution of $\Delta E = 65$ meV.[16] With these parameters the maximum uncertainty of the parallel component of the electron momentum was $\Delta k_{\parallel} \sim 0.06$ Å^{-1} for regions near the first-surface Brillouin-zone boundary.

III. RESULTS AND DISCUSSION

Due to the small escape depth $\lambda_e \sim 10$–20 Å of photoexcited electrons, photoemission spectra generally exhibit a superposition of structures arising from the bulk and surface bands of solids. A recent review of the ARUPS technique and the interpretation of experimental results is given in Refs. 17 and 18.

Placing the analyzer at an angle θ relative to the sample normal determines $k_{\parallel}$ for each structure in the spectrum by

$$k_{\parallel} = \left[\frac{2m}{\hbar^2} (h\nu - E_B - e\phi) \right]^{1/2} \sin\theta \; .$$

E_B is the binding energy measured relative to the Fermi level, $e\phi$ the work function of the sample, and $h\nu$ the photon energy.

Determining the $k_{\parallel}$ component of a peak in the photoemission spectra restricts its bulk initial states to a line of $k_{\perp}$ in the bulk Brillouin zone (BBZ) as shown in Fig. 1. It has been demonstrated in different ARUPS experiments[5,18,19] that $k_{\perp}$ can be determined by using a modified free-electron-like final-state dispersion.

Photoemission valence-band spectra of InSb(110) excited with $h\nu = 21.2$ eV are shown in Fig. 2 as a function of the polar angle θ. It can be seen immediately that there is considerably more structure in the spectra than expected from the three bulk valence bands present in this energy range. We have shown in a preliminary work[19] that most of the structures seen in the normal emission spectra ($k_{\parallel} = 0$) could be explained by direct transitions into free-electron final-state bands in an inner potential $V_0 \sim 9$ eV. The contribution of the secondary-cone emission, which is usually an order of magnitude smaller than the primary emission, is much more pronounced in the zinc-blende-type semiconductors. With the relatively simple analysis outlined in Refs. 17 and 18 we determined the experimental band structure from normal emission spectra of the InSb (001), (110), and (111) surfaces.[19–21]

Moving the analyzer out of the normal so that $k_{\parallel}$ increases along the [110] direction (as indicated in the inset of Fig. 2) shows additional structures and a strong downward dispersion of the top of the valence band. As mentioned above, photoemission spectra generally contain surface structures which depend only on $k_{\parallel}$ and three-dimensional bulk structures which disperse with $k_{\parallel}$ and $k_{\perp}$. Since bulk-band structures are usually only calculated along high-symmetry lines in the BBZ [and not in the hatched area of the BBZ shown in Fig. 1(c) which contributes to the bulk emission for $\theta > 0$], we are left with the problem of distinguishing experimentally between surface and bulk structures.

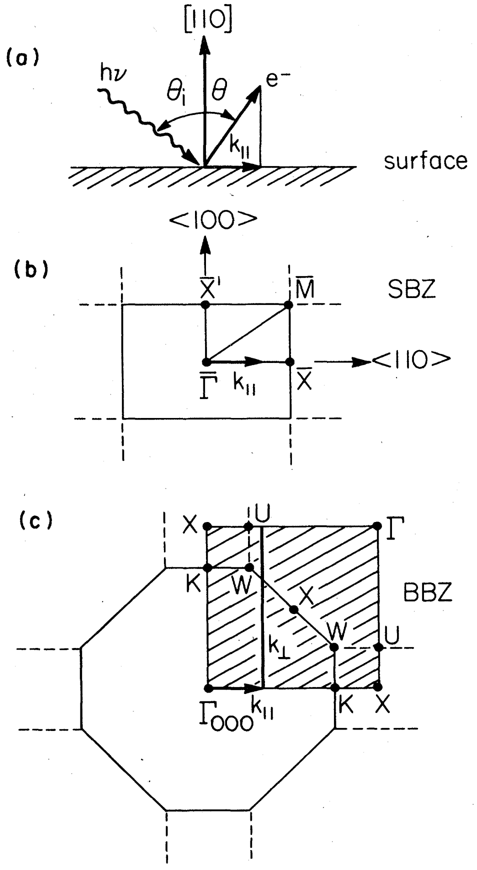

FIG. 1. (a) Geometrical arrangement of the experiment. The photon direction is 45° from the normal and in the plane of the surface normal and the emitted electrons. (b) Surface Brillouin zone (SBZ) of the (110) surface, with $k_{\parallel}$ along ⟨110⟩. (c) Cut through the bulk Brillouin zone (BBZ) with $k_{\parallel}$ along ⟨110⟩. Bulk transitions are along a vertical line $k_{\perp}$.

A commonly employed method is to quench surface-state emission by adsorbing small amounts of foreign atoms on the surface.[22,23] This technique seems to work well for hydrogen and oxygen adsorption but has to be handled more carefully for adsorption of metal atoms. Surface states of GaAs(110) have been quenched by Au overlayer[24] but were not significantly influenced by Pd adatoms.[10] Another very powerful method is based on the fact that surface states are nondispersive with $k_{\perp}$. Using different photon energies and setting the analyzer at angles θ so that $k_{\parallel}$ is fixed usually leads to dispersion of bulk states (because the final states are changed with $h\nu$) but should not influence the position of the surface states.[6]

We have employed both methods to determine the surface-state emission. The effect of quenching the surface states by an Sn overlayer on the InSb(110) surface is shown in Fig. 3. Films of Sn have been grown by molecular-beam epitaxy (MBE) using a Knudsen effusion cell at a temperature ~ 1200 °C. Growth rates have been determined with a calibrated quartz-crystal oscillator to be ~ 0.1 Å/sec. The growth mode was monitored by re-

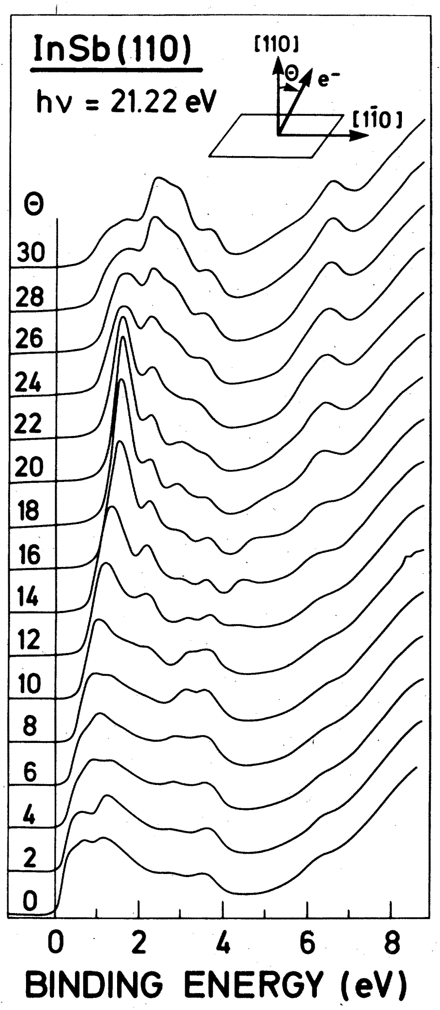

FIG. 2. Valence-band photoemission spectra of InSb(110) obtained at $h\nu=21.22$ eV for different azimuthal angles θ.

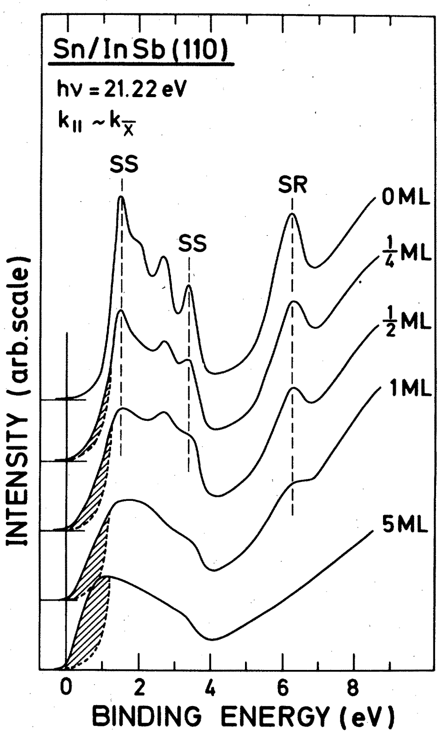

FIG. 3. Valence-band photoemission spectra of InSb(110) at $k_{\parallel} \sim \bar{X}$ with different Sn coverages. Spectra with 0, $\frac{1}{4}$, and $\frac{1}{2}$ monolayer Sn coverage have been measured with $k_{\parallel}$ along $\langle 112 \rangle$ whereas for 1 and 5 ML Sn $k_{\parallel}$ is along $\langle 110 \rangle$. (ML denotes monolayers.)

flection of high-energy electron diffraction (RHEED). The valence-band spectra were taken at an angle θ so that $k_{\parallel}$ of the strong peak ~ 1.5-eV binding energy was at the $\bar{X}$ point of the SBZ shown in Fig. 1(b). Small amounts of Sn reduce the intensity of the structures at ~ 1.5, ~ 3.4, and ~ 6 eV considerably and shift the top of the valence band closer to the Fermi level. The latter effect is most probably not due to the creation of new interface gap states but can be explained by the formation of the α-Sn bulk band structure[25] with increasing film thickness. The epitaxial layer growing of α-Sn (which is a diamond-structure zero-gap semiconductor), on top of different InSb surfaces has been demonstrated recently using different techniques.[19–21,26,27]

Since we observed the same spectral features for comparable $k_{\parallel}$ values by changing the excitation energy to $h\nu=16.85$ eV, we ascribe the structures *SS* at ~ 1.5 and ~ 3.4 eV binding energies to emission from surface states. The peak at ~ 6 eV can be explained as a superposition of a surface resonance and bulk emission associated with the critical point L_6 in the bulk band structure of InSb.[26] We should note that weak nondispersive features seen around 6.7 eV in the valance-band spectra of GaAs and InSb have been discussed as emission from critical points in the one-dimensional density of states.[8,21] We believe, however, that most of the intensity of this peak is due to surface effects because of the strong damping with increased Sn coverage. If the main contribution to the peak at ~ 6 eV came from indirect bulk band-structure transitions we would expect a slight shift towards higher binding energies due to the modified α-Sn band structure,[21] rather than a strong suppression.

The method of tracing surface-state emission by employing different photon energies and setting the analyzer angle so that $k_{\parallel}$ for a given spectral feature is kept constant is shown in Fig. 4. The valence-band spectra were taken with photon energies of 21.22 16.8, and 11.83 eV. The $k_{\parallel}$ component is along the [211] azimuth as indicated in the inset of Fig. 4. The polar angles θ are chosen so that $k_{\parallel} \sim \frac{1}{2} k_{\bar{X}'\bar{M}}$ for a spectral feature ~ 1.2 eV. Binding energies are referenced to the Fermi level which is pinned at the bottom of the conduction band.[20] The intensity of the nondispersive structure labeled *SS* in Fig. 4 does also decrease with a thin overlayer of Sn indicating that it is most likely a surface-state emission. By using different sets of polar angles θ other surface-sensitive structures have also been identified at ~ 2.9 and ~ 5.2 eV for the same $k_{\parallel}$ point in the surface Brillouin zone.

Surface-state emission *SS* is reduced in intensity and exhibits a slight dispersion for values of $k_{\parallel} < \overline{\Gamma X}$ as

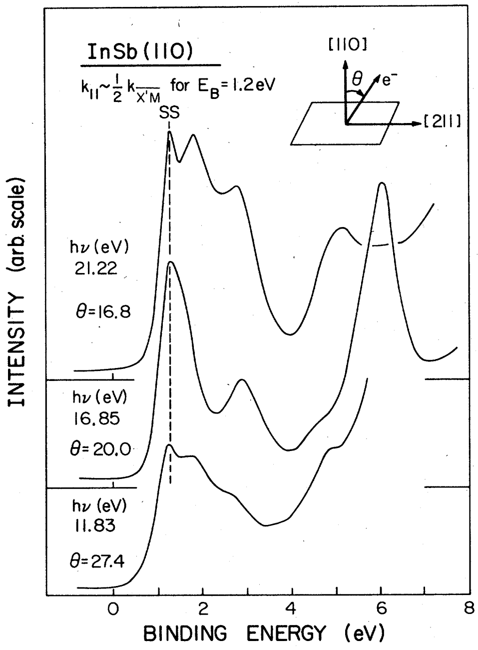

FIG. 4. Valence-band photoemission spectra of InSb(110) obtained with different photon energies. Polar angles θ are chosen so that $k_{\parallel}\sim\frac{1}{2}k_{\overline{X'M}}$ for a spectral structure ~1.2 eV.

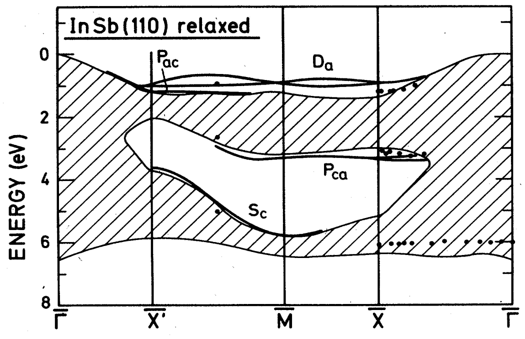

FIG. 5. Comparison of the experimentally obtained surface band structure (circles) with a calculation for the relaxed InSb(110) surface from Ref. 14. The hatched area indicates the regions of the projected bulk bands. The energy zero is referenced to the top of the valence band. D_a refers to the anion d-like surface band, S_c to the cation s-like surface band, and P_{ca} to the p-like mixed anion and cation-derived surface bands.

shown in Fig. 5. For $k_{\parallel}\le\frac{2}{3}\,\overline{\Gamma X}$ surface states cannot be distinguished from bulk band-structure transitions. The experimentally determined surface states agree quite well with a recent STM-band-structure calculation by Schmeits *et al.*[11] (hereafter referenced as SMP). The hatched area in Fig. 5 shows the upper part of their projected bulk band structure. This calculation used a realistic empirical tight-binding Hamiltonian fitted to experimental data of the optical-gap and valence-band spectra. The solid lines show the dispersion of surface states which have been calculated for the relaxed InSb(110) surface. The energy zero is referenced to the top of the valence band. The position of the anion dangling bond D_a in the band gap around the $\overline{X}$ point is ~0.25 eV higher than the experimental data. Measurements with $k_{\parallel}=\frac{1}{2}k_{\overline{X'M}}$ also showed emission related to the dangling bond D_a as well as to the p-like cation and anion states $P_{ca}\sim 2.7$ eV and the s-like cation states $S_c\sim 5$ eV. The predicted spin-orbit splitting of the D_a band of ~0.3 eV for $k_{\parallel}=\frac{1}{2}k_{\overline{X'M}}$ was not observed in our experiments. The surface resonance (SR) at ~6 eV is in general agreement with calculations by Beres *et al.*[13] (hereafter referenced as BAD) but does not show the dispersion for $k_{\parallel}$ along the line $\overline{\Gamma X}$.

The latter calculation, which was also based on an ETB method, results in a somewhat different bulk band structure than those reported by SMP.[11] In particular, the top of the valence band shows a 0.45-eV smaller dispersion around the $\overline{X}$ point, whereas the top of the stomach gap is ~0.75-eV higher and extends much further in k space towards the $\overline{\Gamma}$ point. Since the bulk band-structure parameters are important in determining the surface electronic structure, it is not surprising that the calculated surface-state dispersion differs to some extent for the two calculations.

Dangling-bond states appear as surface resonances around $\overline{X}$ in the calculation of BAD (Ref. 13) whereas SMP (Ref. 11) calculate real surface states which are well separated from bulk valence-band states. The surface-state emission around the $\overline{X}$ point at ~3 eV agreed quite well with the p-like *SS* calculated by SMP (Ref. 11) but cannot be explained with the calculation by BAD (Ref. 13).

It is not clear yet whether a slightly modified relaxation model would lead to a further improvement between theory and experiment. Both calculations used a somewhat different relaxation model. BAD (Ref. 13) assumed a cation bond direction which was rotated by 27.3° with respect to the ideal surface plane, whereas SMP (Ref. 11) based their calculation on a 25.7° rotation which was adopted from an energy-minimization calculation by Chadi.[9] Dynamical calculation of ELEED data,[4] on the other hand, have shown that the most probable surface structure of InSb(110) is one with a 28.8° rotation and a 0.05 Å relaxation of the bond length towards the substrate.

The experimental method of separating bulk and surface structures by quenching surface states through adsorbates, or by tracing peak positions versus $k_{\parallel}$ and watching for nondispersive structures, is certainly not sensitive enough to give a complete picture of the surface electronic structure along high-symmetry lines of the SBZ. A better comparison between out-of-normal ARUPS data and surface band-structure calculations will be possible with the availability of bulk band structures calculated along certain directions $k_{\perp}$ down in the BBZ for specified $k_{\parallel}$ values of the SBZ.

IV. CONCLUSIONS

Surface-state emission has been observed around the $\overline{X}$ point of the SBZ at ~1 and ~3.1 eV and at the point $k_{\parallel}=\frac{1}{2}k_{\overline{X'M}}$ at ~0.9, ~2.7, and ~5 eV with respect to the top of the valence band. Those states are in reasonable agreement with STM calculations of the relaxed (110) surface.[11] The spin-orbit splitting of the anion dangling-bond surface state which was calculated to be ~0.3 eV was not seen in our investigation. Spectral features around 6-eV binding energy show contribution of emission of surface resonances which have been predicted recently.[13]

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