Polarization-dependent angle-resolved photoemission study of a surface state on GaSb(110)

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Using polarization-dependent, angle-resolved photoemission, a prominent nondispersive structure in the normal emission spectra from GaSb(110) has been identified as being due to transitions from the Sb-derived dangling-bond surface state. The atomic-orbital character of the surface state was confirmed to be mainly p_z-like, and the dispersion of the surface state along the $\bar{\Gamma}\bar{X}$ direction in the surface Brillouin zone was observed. Using symmetry selection rules, an accurate determination of Γ_8^v, the valence-band maximum (VBM), was made. The surface state was found to be 150 ± 100 meV above the VBM, showing that the surface state is indeed an intrinsic intergap surface state.

I. INTRODUCTION

A central question in studies of surface states of III-V semiconductors is whether there are intrinsic surface states in the fundamental band gap. Theoretical calculations of surface states on the (110) surfaces of GaAs, InSb, and InP indicate that surface states are pushed out of the band gap by surface relaxation,[1-3] but, for GaP, the Ga dangling-bond surface-state band remains in the band gap even if surface relaxation is taken into account.[4] These calculations are in agreement with experimental results.[3,5-7] In the case of GaSb(110), early measurements of photoemission[8] and contact potential differences[6] showed no empty surface states in the band gap. Recently, however, Manzke *et al.*[9] reported evidence of an intrinsic occupied surface state on GaSb(110) being 190 meV above the valence-band maximum (VBM). Identification of the surface state was based on a weak nondispersive structure in normal emission spectra and the dispersion of this structure along the $\bar{\Gamma}\bar{X}'$ direction in the surface Brillouin zone (SBZ). Hansson and Uhrberg[10] have given an alternative interpretation to the spectra of Manzke *et al.*; they suggested that emission from the proposed surface state could arise from the heavy-hole valence states, while the valence band as identified by Manzke *et al.* might be the light-hole valence band. The observed dispersion along the $\bar{\Gamma}\bar{X}'$ direction of the proposed surface state was ascribed to indirect transitions from the projected bulk edge along the Γ-L direction in the bulk Brillouin zone. They consequently considered that the existence of an intergap surface state on GaSb(110) had not yet been finally established.

In the present study, this controversial surface state of GaSb(110) was examined by polarization-dependent, angle-resolved photoemission, which has proved to be a powerful technique in studies of surface electronic structure of solids. Polarization effects have previously been exploited to assist in the determination of surface states as follows: (1) a study of polarization effects in photoemission from W(100) has confirmed a theoretical prediction that surface photoemission vanishes if the exciting light is polarized parallel to the emitting surface;[11] (2) using polarization-dependent angle-resolved ultraviolet photoemission spectroscopy (ARUPS), Martensson, Cricenti, and Hansson,[12] in their study of surface states on Si(111) 2×1, observed that when the light was normally incident on the sample, transitions from the surface states vanished almost completely, indicating the p_z character of the surface states. Surface states on GaAs(110) have also been studied using polarization-dependent ARUPS, and the parity of the surface states has been determined.[13] Additionally, using mirror plane selection rules, Plummer and Eberhardt[14] identified two surface states on the Ni(100) surface which are superimposed on bulk states of opposite symmetry.

GaSb has the face-centered-cubic zinc-blende structure with a lattice constant $a=6.10$ Å. The surface structure of GaSb(110) is shown from the top view in Fig. 1(a) and from the side view in Fig. 1(b). In the top view, a rectangular surface unit cell is chosen conventionally, leading to a rectangular surface Brillouin zone [see Fig. 1(c)]. Important dimensions of the surface Brillouin zone are $\bar{\Gamma}\bar{X}=0.73$ Å^{-1}, $\bar{\Gamma}\bar{X}'=0.515$ Å^{-1}, and $\bar{\Gamma}\bar{M}=0.893$ Å^{-1}. Surface relaxation of the GaSb(110) surface is characterized by a movement of the Sb atoms out of the surface plane and of the Ga atoms into the crystal. This relaxation gives rise to a bond rotation. The angle of this bond rotation has been measured by mass-resolved Rutherford backstattering to be approximately 29° [see Fig. 1(b)].[15] On GaSb(110), the only symmetry element is a mirror plane containing the sample normal and the [001] azimuth direction. The Ga dangling bonds (or the Sb dangling bonds) are within the mirror plane. In the present study, the polarization vector of the light was chosen in three different orientations relative to the mirror plane to investigate the origin of observed transitions.

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II. EXPERIMENTAL DETAILS

Polarization-dependent, angle-resolved photoemission measurements on GaSb(110) were made on the TGM-4 beam line at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) synchrotron. This beam line provides linearly polarized radiation with photon energy variable from 9 to 120 eV. The photoelectron analyzer, which has been detailed elsewhere,[16] is a toroidal analyzer capable of simultaneously measuring photoelectrons over 180° of emission angle. The angular resolution of the analyzer is about 2°, while the combined energy resolution of the beam line and the analyzer was kept below 100 meV during the measurements. The GaSb(110) surface was produced by cleaving in vacuum with a blade and anvil mechanism, and its quality was checked by low-energy electron diffraction. The sample preparation and photoemission measurements were performed at a base pressure of 2×10^{-10} Torr.

In order to explore the origin of observed transitions, energy distribution curves of electrons were measured in three different polarizations, which were obtained by changing the incidence angle of the light and by rotating the sample around the surface normal. At normal photon incidence, the polarization vector was either in the mirror plane or perpendicular to it (these will be referred to as the $A_{\parallel}$ and the $A_{\perp}$ geometries). In both cases, the polarization vector was parallel to the sample surface. The third geometry used a higher angle of incidence, 45°, and the measured azimuthal direction was set to $[1\bar{1}0]$, which is perpendicular to the mirror plane. With this geometry, both components of the polarization vector were equally available parallel to the sample normal and perpendicular to the mirror plane. This orientation of the polarization vector made it possible to excite all initial states regardless of symmetry.

III. RESULTS AND ANALYSIS

Normal emission spectra obtained with light incident at 45° are shown in Fig. 2 for photon energies from 12 to 25 eV. A photon-energy-independent (nondispersive) structure, marked with a dashed line can be seen at −4.5

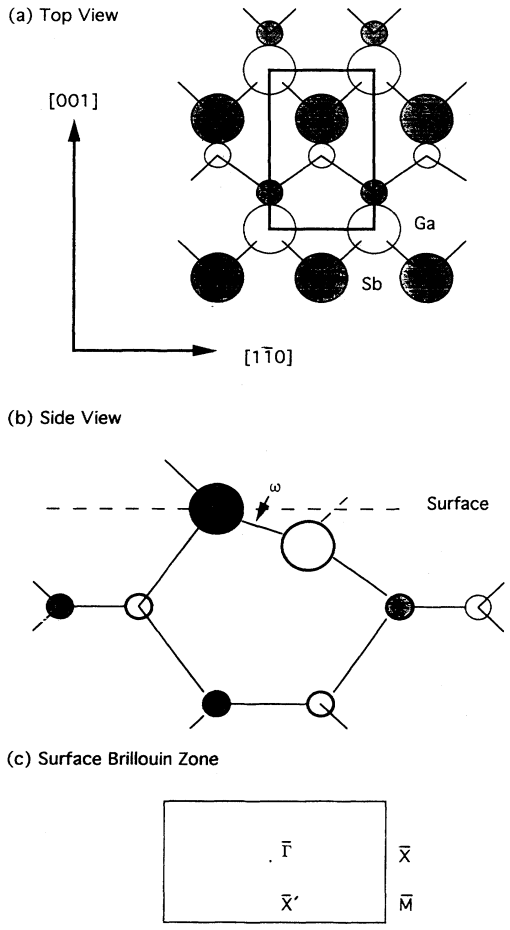

FIG. 1. The surface atomic structure and the surface Brillouin zone of GaSb(110). The shaded and open circles represent Sb and Ga atoms, respectively. Large circles indicate the atoms in the top layer, while small circles indicate atoms in underlying layers. (a) Top view of the surface structure. (b) Side view of the surface structure. (c) The surface Brillouin zone.

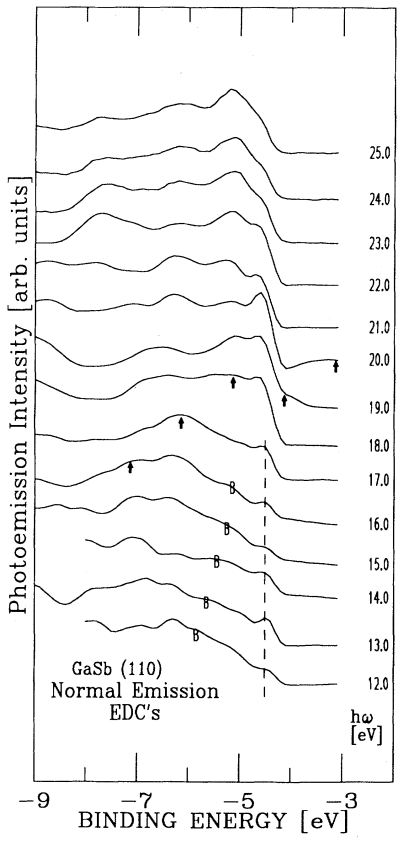

FIG. 2. Normal emission spectra from GaSb(110) obtained with light incident at 45°. The binding energy is with reference to the vacuum level. Transitions from the Ga 3*d* core level are indicated by arrows, while the dashed line marks the nondispersive structure of interest at −4.5 eV. A dispersive feature is labeled *B*.

eV binding energy for photon energies between 12 and 17 eV (here the binding energy is with reference to the vacuum level). Compared to the nondispersive structure observed by Manzke *et al.*,[9] this structure is more prominent and extends to lower photon energies. We also observed a dispersive feature labeled with the letter *B* in these spectra. Other clearly observed features are associated with bulk band dispersions and are not of relevance to the present study. Peaks indicated by arrows in the spectra were identified as transitions from the Ga 3*d* core level excited by the second-order harmonic of the light.

To examine whether the nondispersive structure is due to bulk transition from the heavy-hole band, as proposed by Hansson and Uhrberg,[10] we determined the values of momentum k for each peak observed in the nondispersive structure and in feature *B*, using a free-electron final state model. For normal emission, the value of k (in Å^{-1}) for an observed transition is given by

$$k = 0.51(E - V_0)^{1/2} \quad (1)$$

where E is the kinetic energy of the electron in eV and V_0 is the inner potential. In a previous ARUPS study of the valence bands of GaSb,[17] the inner potential with respect to valence-band maximum was determined to be -6.92 eV. The results are shown in Fig. 3 together with a calculated heavy-hole band from a tight-binding calculation. The valence-band maximum was determined to be at -4.65 eV (the determination of the VBM will be discussed later in this section). It can be seen from Fig. 3 that the feature *B* is in agreement with the calculated heavy-hole band, while the nondispersive structure of interest has a binding energy about 0.5–1.5 eV towards lower binding energy from the heavy-hole band. This suggests that the nondispersive structure is not due to transitions from the heavy-hole band.

The photon-energy-independent structure indicates that the initial states associated with it do not disperse with $k_\perp$ since a variation in photon energy necessarily leads to a change in $k_\perp$. This suggests that these initial states are likely to be surface states. To determine whether they are extrinsic surface states, e.g., cleavage-induced surface states or not, the off-normal behavior of the initial states has been studied. In Fig. 4, the off-normal spectra for a photon energy of 14 eV are shown over a range of polar angles from 0° to 25°. It can be seen that the peak at -4.5 eV in normal emission disperses to higher binding energies as the emission angle increases from the sample normal. At 16° the dispersion is about 0.3 eV. This indicates that the initial states of interest are dispersive with $k_\parallel$ in the $\bar{\Gamma}\bar{X}$ direction in the SBZ (Manzke *et al.*[9] observed the off-normal dispersion along the $\bar{\Gamma}\bar{X}'$ direction). Because the initial states are dispersive with $k_\parallel$, they are unlikely to be extrinsic surface states since such surface states show no dispersion in three-dimensional k space.

According to theoretical calculations of surface states III-V semiconductors, there is an occupied anion-derived dangling-bond state, mainly p_z-like, near the valence-band maximum.[1] In order to investigate if the nondispersive structure observed here is due to transitions from the occupied Sb-derived dangling -bond state, the atomic orbital character of the transitions was examined using different polarization geometries. Normal emission spectra at 16 eV photon energy for both 45° and 0° incidence angles of the light are shown together in Fig. 5 for comparison. It is found that the peak at -4.5 eV disappears when the incidence angle is changed from 45°to 0°. This indicates that the observed transition is excited by the normal component of the polarization vector, suggesting that the peak at -4.5 eV binding energy is due to a transition from a p_z-like initial state (z axis pointing along the sample normal). This initial state is most likely the Sb-derived dangling-bond surface state.

Based on its energy position, dispersion behavior, and atomic orbital character, the photon-energy-independent structure at -4.5 eV in the normal spectra shown in Fig. 2 can therefore be identified as due to transitions from an intrinsic surface state on the GaSb(110) surface.

The position of the surface state relative to the VBM is critical in this study since it relates to the question as to whether the surface state is an intergap state or not. There are different methods in the literature for determining the VBM in ARUPS.[18] Quite frequently, the VBM is obtained by a linear extrapolation of the leading edge of the valence-band emission, while some groups identify the VBM as the bulk emission peak (belonging to a dispersive structure) with the lowest binding energy in normal emission spectra as observed over a wide range of photon energies. If one determines the VBM to be the leading edge of the spectra in Fig. 2, the surface state would be a surface resonance since the position of the nondispersive structure is below the leading edge. This method is affected by the presence of surface states, which would change the apparent value of the VBM. Manzke *et al.* determined the VBM to be the peak with

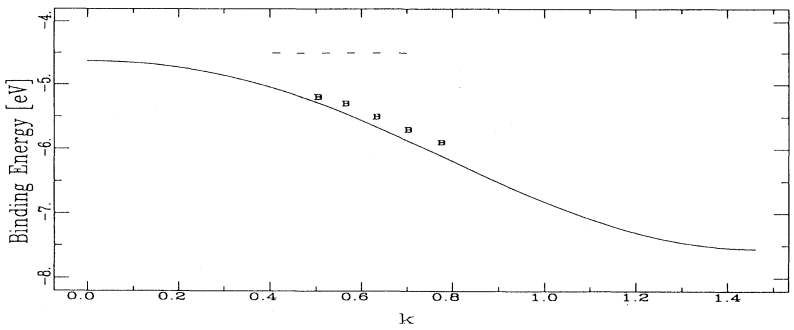

FIG. 3. The nondispersive structure (—) and the dispersive feature *B* are plotted in the format of binding energy vs k (in Å^{-1}) with the calculated heavy-hole band based on a tight-binding approximation. The values of k for the observed transitions were determined by a free-electron final-state model with an inner potential of -6.92 eV with respect to valence-band maximum.

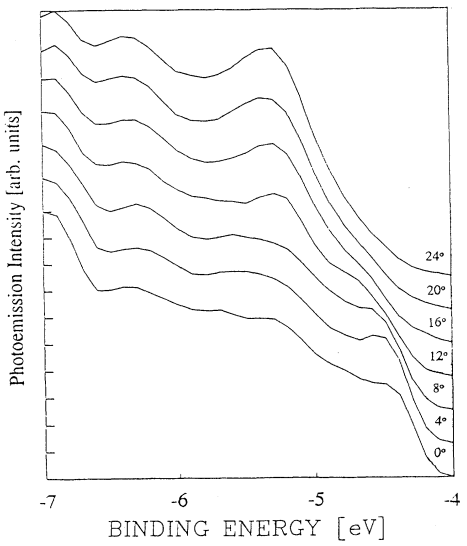

FIG. 4. The off-normal spectra from GaSb(110) obtained with the light incident at 45° for a photon energy of 14 eV. The binding energy is with reference to the vacuum level.

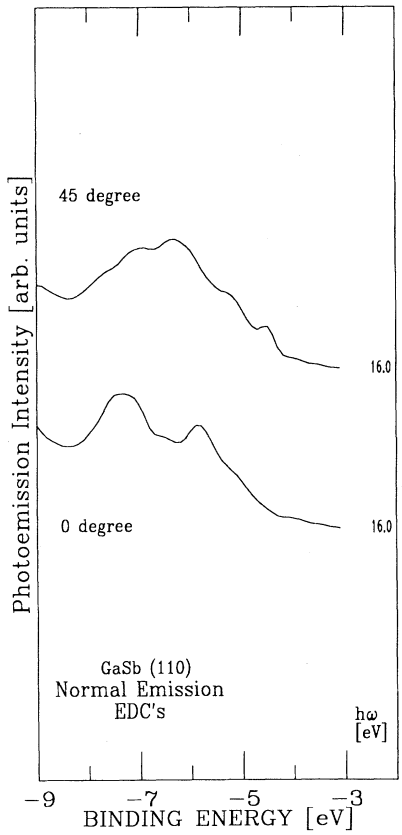

FIG. 5. Normal emission spectra from GaSb(110) at 16 eV photon energy for 45° and 0° incidence angles of the light.

the lowest binding energy in their spectrum at 23 eV photon energy, leading to the conclusion that there is an intergap surface state in the band gap of GaSb. In the present study, using symmetry selection rules for dipole transitions, the Γ_8^v point of GaSb can be determined, leading to a correct determination of VBM.

Dipole transitions between a final state $\langle \phi_f |$ and an initial state $|\phi_i\rangle$ are described by a matrix element $\langle \phi_f | \mathbf{A}\cdot\mathbf{P} | \phi_i \rangle$, where $\mathbf{A}\cdot\mathbf{P}$ is the dipole operator. For an allowed transition, the direct product of the irreducible representations of the initial state (Γ_i), final state (Γ_f), and the dipole operator (Γ_{AP}) must contain the unity representation.[19] This implies that $\Gamma_i \times \Gamma_{AP}$ must contain Γ_f. For GaSb, the VBM lies at a Γ_8 point. At the Γ point, the representation of the dipole operator belongs to Γ_{15} for all polarizations of electric field.[20] Since $\Gamma_8 \times \Gamma_{15} = \Gamma_6 + \Gamma_7 + \Gamma_8 + \Gamma_8$, transitions from Γ_8 are allowed into final states with Γ_6, Γ_7, and Γ_8 symmetry. According to our free-electron final-state model discussed previously, there is a free-electron final state at the Γ point about 24 eV above the VBM. This final state, containing two Γ_6, two Γ_7, and four Γ_8 representations,[20] is an allowed final state for dipole transitions from Γ_8^v. Based on the above analysis and taking into account the broadening of free-electron final states, polarization-independent transitions from the VBM are expected to be observed in the spectra between 23 and 25 eV photon energy.

A number of normal emission spectra obtained under the $A_\parallel$ and the $A_\perp$ geometries are shown in Fig. 6 for photon energies from 20 to 26 eV. For the $A_\parallel$ geometry [see Fig. 6(a)], the peaks located between -4 and -5 eV are prominent in the spectra at 23 and 24 eV photon energies. In the spectra at 22 and 26 eV, the peaks in this binding energy region become less prominent, and they disappear in the spectra at 21 and 20 eV. On the other hand, in the case of $A_\perp$ [see Fig. 6(b)], peaks are present between -4 and -5 eV for all photon energies. In other words, the peaks in the spectra at 23 and 24 eV are prominent for both geometries, while the intensity of the peaks in the spectra at 20, 21, 22, and 26 eV photon energy changes dramatically with the polarization orientations. This is in agreement with the theoretical prediction that, when the photon energy is between about 23 and 25 eV, polarization-independent transitions from the VBM can be observed for both geometries. The VBM can thus be determined by the peak at -4.65 eV in the spectra at 23 or 24 eV photon energy.

This determination of the VBM can be further supported by investigating the origin of the polarization-dependent emission in the spectra at $h\nu = 20$, 21, 22, and 26 eV in Fig. 6. The polarization-dependent intensity can be interpreted in terms of the mirror plane symmetry of the transition matrix. For an allowed transition, the transition matrix element must be invariant under reflection of the mirror plane. The mirror plane symmetry of the transition matrix is determined by the symmetry of initial states, final states, and the photon operator. Since, for normal emission, the mirror plane symmetry of the final states is always even,[21] normal emission can only

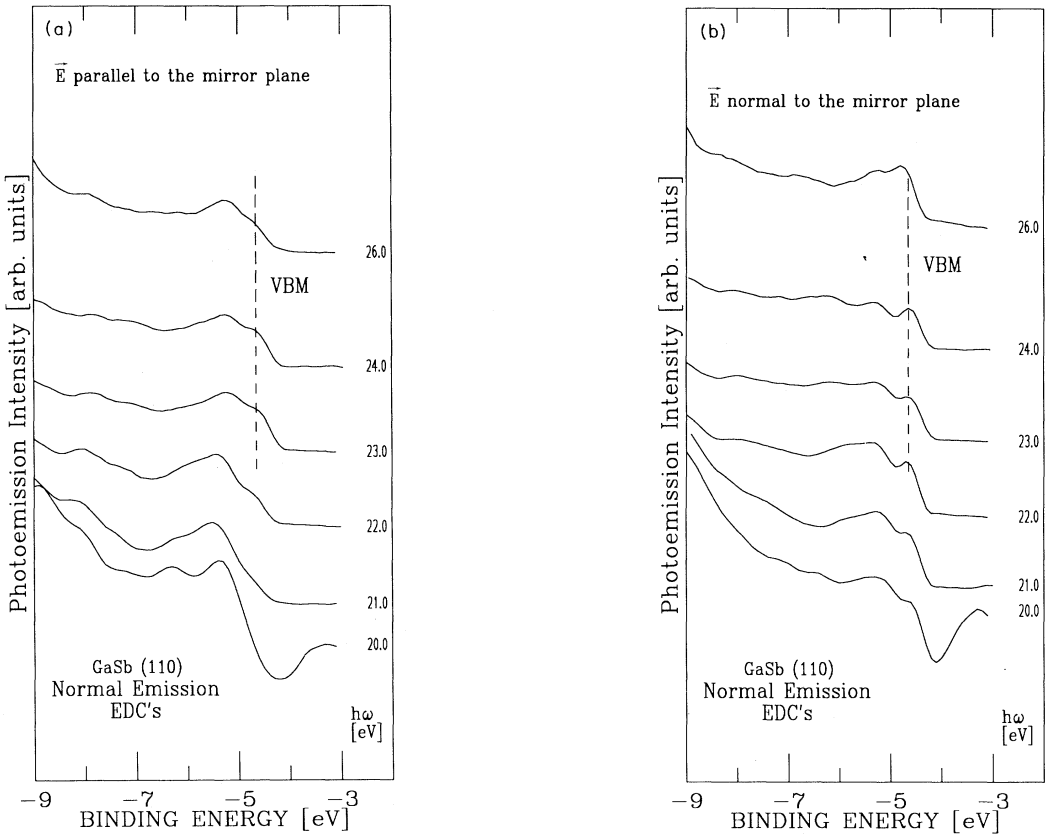

FIG. 6. Normal emission spectra from GaSb(110) obtained under normal incidence of the light. (a) **E** parallel to the mirror plane. (b) **E** normal to the mirror plane.

arise from initial states with symmetry identical to that of the photon operator. When the polarization vector is set to be parallel (perpendicular) to the mirror plane, the photon operator has even (odd) parity.[22] Under the $A_{\perp}$ geometry, the photon operator has odd parity, thus the presence of the peaks between -4 and -5 eV for all photon energies in Fig. 6(b) indicates that the associated initial states have odd parity. This can be confirmed by the fact that the peaks disappear at 20 and 21 eV photon energy in the case of $A_{\parallel}$ since transitions from odd initial states are not allowed in this case (the weak peaks for photon energies of 22 and 26 eV probably arise from allowed transitions from the VBM due to the broadening effect of the free-electron final state at the Γ point). These odd initial states belong to the upper valence band because the upper valence band has odd parity while the light-hole band and the spin-orbit split-off band have even parity.[23] Based on the above analysis, the peaks between -4 and -5 eV in the spectra of 20, 21, 22, and 26 eV in Fig. 6(b) can be identified as transitions from the upper valence band. This identification supports the determination of the VBM by the peak at about -4.65 eV in the spectrum at 23 or 24 eV because it indicates that the determined VBM relates to the identified upper valence band.

In order to show the position of the surface state relative to the VBM, the spectrum for $h\nu=23$ eV from Fig. 6 is plotted in Fig. 7 together with the spectrum for $h\nu=16$ eV from Fig. 1. It can be seen from Fig. 7 that the surface state is above the VBM by 150 meV. Therefore, the observed Sb-derived dangling-bond state can be confirmed to be an intergap surface state as initially proposed by Manzke *et al.*

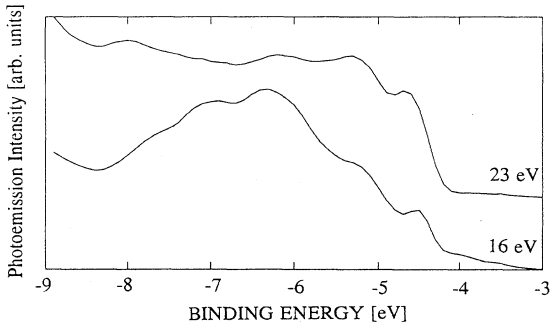

FIG. 7. Normal emission spectra showing the position of the surface state relative to the VBM. The rightmost peaks in the spectra at 16 and 23 eV represent the positions of the surface state and the VBM, respectively.

IV. CONCLUSION

Using polarization-dependent, angle-resolved photoemission, a prominent nondispersive structure in the normal emission spectra from GaSb(110) has been identified as being due to transitions from the Sb-derived dangling-bond surface state. The dispersion of the surface state along the $\bar{\Gamma}\bar{X}$ direction in the surface Brillouin zone was observed, and atomic orbital character of the surface state was confirmed to be mainly p_z-like. Using symmetry selection rules, the Γ_8^v (VBM) was determined, and the surface state was found to be 150 ± 100 meV above the valence-band maximum, showing that the surface state is indeed an intrinsic intergap surface state.

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