Unoccupied surface states of (1×1) Sb overlayers on GaAs(110) and InP(110)

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Unoccupied electronic states of an ordered (1×1) Sb overlayer on cleaved GaAs(110) and InP(110) surfaces are studied by angle-resolved inverse photoemission. A well-ordered overlayer is obtained by thermal annealing after room-temperature deposition of Sb onto freshly cleaved surfaces. At $\bar{\Gamma}$ we observe a clearly resolved Sb-derived surface resonance at 2.1 eV above the valence-band maximum for GaAs as well as for InP. An upward dispersion of the Sb state of 0.2 eV is found towards $\bar{X}$.

Metal-semiconductor interfaces are an essential part of microelectronic components. A thorough understanding of their microscopic electronic behavior is therefore not only of fundamental interest but also highly relevant for the development of sophisticated semiconductor devices. The most widely studied and perhaps best understood compound semiconductor surfaces are the (110) cleavage surfaces of GaAs and InP. Thus, they are good model surfaces to investigate metal adsorption. Group-III and -V overlayers on III-V semiconductor (110) surfaces have been probed by various experiments[1-9] but a detailed theoretical description of the observed electronic properties is often plagued by a complex interface chemistry (in particular for group-III elements) which smears out the interface and obscures the basic physical processes. In the case of Sb, however, a well-ordered (1×1) structure can be formed on clean GaAs(110) and InP(110) surfaces at monolayer (ML) coverage under appropriate experimental conditions leading to a sharp and well-defined interface.[1-9] This is the only (1×1) overlayer structure known for III-V semiconductors and, therefore, represents a simple model for understanding III-V semiconductor-metal interfaces from first principles. Auger electron[1] and core-level photoemission spectroscopy[2] have revealed no signs of Sb-substrate reaction or interdiffusion as observed for the adsorption of group-III metals.[3,4] The atomic geometry of the Sb overlayer has been determined from a dynamical analysis of low-energy electron diffraction intensity data for Sb/GaAs(110) (Ref. 5) and Sb/InP(110) (Ref. 6) and is in agreement with the results of a total energy minimization calculation.[10] The adsorbed Sb forms zigzag chains bonded to the substrate in quasicontinuation of the bulk crystal structure and saturates both anion and cation dangling bonds. Thereby the topmost substrate (110) layer assumes nearly bulklike atomic positions. The Sb chains, however, are tilted because of the two different bonding sites. The simplicity of this interface is especially suited for a theoretical investigation and several calculations of the electronic interface band structure have recently been performed.[10-12] Experimentally, the changes in the electronic structure at the surface due to the interface formation can be studied by photoemission techniques which are very surface sensitive in the vacuum-ultraviolet regime. Occupied Sb-induced surface states have been observed in several photoemission studies for Sb on cleaved GaAs(110) (Refs. 2, 3, 7, and 8) and InP(110) (Refs. 4 and 9) surfaces. Unoccupied Sb states are calculated near the conduction-band minimum.[10-12] These states are located below the vacuum level and can be detected by the inverse (time-reversed) photoemission technique[13] with high surface sensitivity.[14] Our results using this technique exhibit a clearly resolved unoccupied Sb-induced state at $\bar{\Gamma}$ for a well-ordered adsorbate overlayer on GaAs(110) and InP(110).

The experiment was performed with a high-resolution inverse photoemission spectrometer[15] that simultaneously detects photons in the 8–30-eV range via multichannel plates. High-purity Sb was evaporated from a thoroughly outgassed evaporator onto freshly cleaved surfaces (*p*-type GaAs, *n*-type InP) at room temperature (RT) in a separate preparation chamber. The pressure at the sample stayed below 1×10^{-9} torr during the evaporation (at rates of 0.02 ML/s as monitored with a quartz microbalance) and was about 6×10^{-11} torr in the spectrometer chamber. The Sb overlayer structure was confirmed by the *I-V* characteristics of the low-energy electron diffraction (LEED) pattern. The samples were mounted on a heatable holder to allow annealing up to 300 °C.

Inverse photoemission spectra for an annealed and well-ordered (1×1) Sb overlayer on GaAs(110) and InP(110) surfaces are shown in Fig. 1. Spectra from the as-cleaved clean (110) surfaces have been included for comparison. For Sb on GaAs (left panel) a new strong peak (arrow) is observed at 2.1 eV above the valence-band maximum $E_{\rm VBM}$ at $\bar{\Gamma}$ (i.e., for $k_{\parallel}=0$). The shoulder seen near 2 eV for clean GaAs is due to an intrinsic surface state of the relaxed (110) surface. Note that the bulk related features above 4 eV are almost unaffected indicating a sharp interface and an ordered overlayer structure. In contrast, they are strongly altered by (reactive and disordered) transition-metal adsorption of comparable thickness ($\simeq2.5$ Å).[16] A similar behavior is observed for InP (right panel), although the intensity of the Sb state is lower.

For an unannealed RT-deposited Sb (1-ML) film on GaAs(110) the Sb-induced peak is considerably

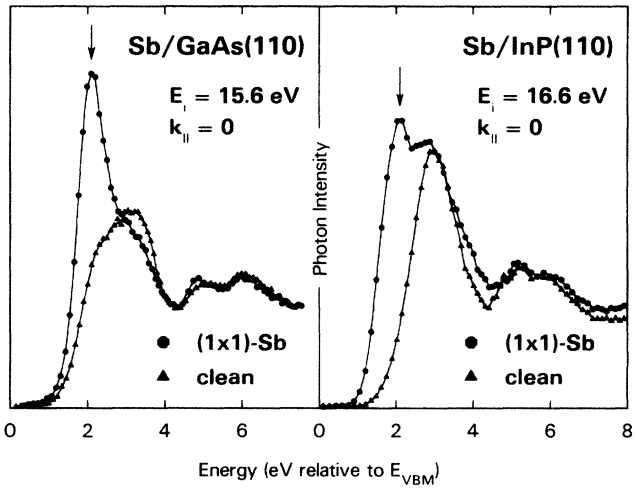

FIG. 1. Inverse photoemission spectra from clean cleavage surfaces (triangles) and an ordered (1×1) Sb overlayer (dots) for GaAs and InP. Sb-induced states are marked by arrows. The peaks above 4 eV are derived from bulk states and are unaffected by the Sb adsorption. The pronounced shoulder near 2 eV for clean GaAs is due to an intrinsic surface state of the relaxed GaAs(110) surface.

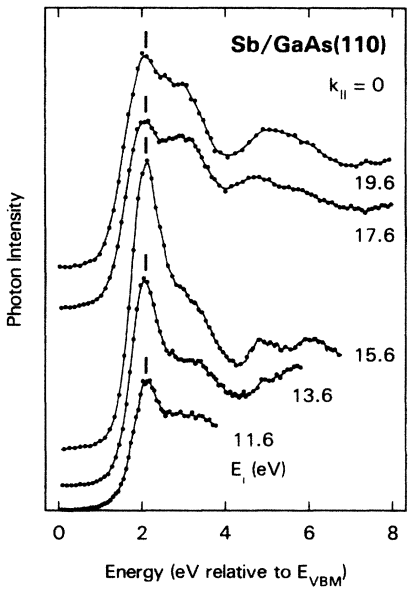

FIG. 2. E vs $k_\perp$ band dispersion measured via energy-dependent inverse photoemission at normal electron incidence. The energy of the Sb state (tic marks) relative to E_{VBM} is constant for varying electron energies E_i confirming its two-dimensional character. All other states disperse, indicating their bulk character.

broadened compared to the annealed film. In addition, the band bending at the Sb(1 ML)/GaAs interface is reduced by 150 meV after annealing at about 200–300 °C. This is in agreement with a recent photoemission study of thermal annealing effects on the Sb/GaAs interface. Schäffler *et al.*[7] provide strong indications that RT deposition of Sb does not produce a perfectly ordered overlayer at monolayer coverage, as was believed so far, but that thermal annealing is necessary to enhance the Sb surface mobility in order to reduce local disorder. We note that no changes in the (1×1) LEED pattern could be detected upon annealing and that *I-V* curves for the Sb (1 ML) covered surface were in good agreement with published data.[5] The effect is even more pronounced for Sb adsorption on InP(110) where no Sb-induced structure is observed in the spectra at monolayer deposition (unannealed and annealed), although the LEED *I-V* data indicate an ordered (1×1) Sb overlayer when compared to other LEED studies.[6] A RT-deposition of 2 ML Sb followed by thermal annealing at about 200–300 °C is necessary to produce the Sb surface state shown in Fig. 1. Still it is much weaker than that observed for GaAs, possibly indicating remaining local disorder.

The two-dimensional character of the Sb state can be probed by changing the electron momentum normal to the surface via the electron energy. Energy-dependent spectra at $k_\parallel=0$ (Fig. 2) show no energy shift of this state whereas the substrate related peaks disperse with changing $k_\perp$ due to their three-dimensional character. The intensity of the Sb peak, however, varies significantly.

Recent band structure calculations for Sb/GaAs (Refs. 10 and 11) and Sb/InP (Ref. 10) predict two empty Sb-induced states. Mailhiot *et al.*[10] point out that these

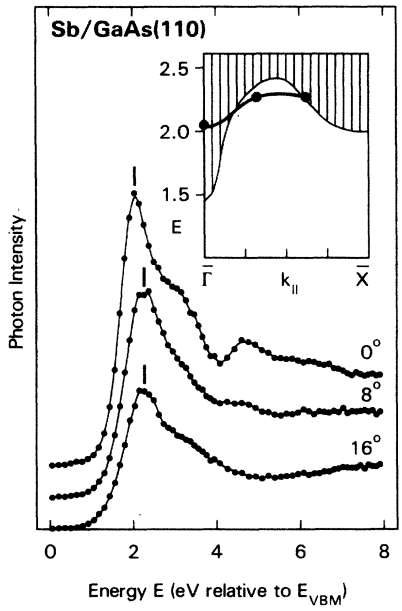

FIG. 3. E vs $k_\parallel$ band dispersion measured via angle-dependent inverse photoemission at an electron energy $E_i=15.6$ eV. The angle of incidence for the electrons is measured from the surface normal in the (001) plane. The inset shows a magnified section of the band structure in the $\bar{\Gamma}\bar{X}$ direction of the surface Brillouin zone. The shaded area indicates the bulk bands projected onto the surface.

states are mainly composed of antibonding π^* combinations of the p_z-like dangling bonds of the Sb chain. In their interpretation of a first-principles pseudopotential calculation for Sb/GaAs Bertoni *et al.*[11] assign these states to antibonding combinations of Sb p states with the sp^3 dangling orbitals of the Ga and As surface atoms, respectively. At $\bar{\Gamma}$, the Sb-Ga state disperses upwards into the bulk continuum and is quenched. Only the Sb-As state remains. Both interpretations are compatible in the sense that the dangling-bond Sb π^* and the backbond Sb-As σ^* states can mix since they both contain Sb p_z character. Angle-dependent data (Fig. 3) show a slight upward dispersion of 0.2 eV towards $\bar{X}$ (inset in Fig. 3) in qualitative agreement with a similar calculation for Sb/GaP(110).[12] For Sb/GaAs the measured energy at $\bar{\Gamma}$ is in good agreement with both first-principles and tight-binding calculations (Table I). For Sb/InP, however, our data disagree with the tight-binding calculation of Ref. 10 which predicts the lowest empty state in the bulk band gap whereas we locate it well above the conduction-band minimum as for Sb/GaAs. This discrepancy can probably be resolved by a self-consistent calculation.

It is interesting to focus on the Fermi-level position in the gap since the simple (1×1) overlayer structure is ideal for theoretical treatments of Schottky-barrier formation. The absence of unoccupied states in the band gap for a well-ordered Sb overlayer would prevent the formation of an n-type Schottky barrier at the (1×1)-Sb/InP interface. Indeed we observe the same Fermi-energy position for the (1×1) Sb overlayer as for the clean n-type sample where one has nearly flat band conditions. However, submonolayer Sb coverage without annealing results in a considerable Schottky barrier most likely induced by disorder [we find a 0.4 eV band bending relative to the clean InP(110) surface for a 0.5-ML Sb exposure at RT]. Local disorder may also account for the Schottky barrier at the unannealed Sb/InP(110) interface previously reported[9] in a photoemission experiment. For Sb/GaAs we used p-type samples and find a significant upward shift (0.2 eV) of the Fermi level for the Sb-covered surface (even after annealing). This indicates the presence of occupied pinning states near the valence-band maximum. Possible candidates for such states are the bonding π states of the Sb p_z orbitals.

TABLE I. Position of the lower unoccupied Sb-induced surface state (eV above VBM).

	This expt.	Theory Ref. 10	Theory Ref. 11
Sb/GaAs	2.1	1.9	2.0
Sb/InP	2.1	1.2	

In summary, adsorbate-induced states are observed by inverse photoemission for a well-ordered (1×1) Sb overlayer on GaAs(110) and InP(110). It is found that thermal annealing is necessary to obtain a highly ordered interface structure. The states lie above the conduction-band minimum suggesting the absence of an n-type Schottky barrier.

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