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Photoemission study of interfacial chemistry at metal-InP(110) interfaces with Sb interlayers

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Photoemission spectroscopy is used to investigate interfacial chemistry at Au/InP(110) and Ag/InP(110) interfaces with one monolayer Sb interlayers. As long as we look at only the spectra of the In 4*d* and P 2*p* core levels, it is very hard to see any evidence of chemical reactions between the InP and the overlayer. However, a comparison between attenuation patterns of the In 4*d* and P 2*p* emission intensities suggests that P atoms are apt to segregate into the overlayer as compared with In atoms. On the other hand, a large change in the line shape of the Sb 4*d* is observed, suggesting that reactions are taking place between the Sb and the overlayer. Curve fittings also suggest that there is some outdiffusion of Sb atoms into the overlayer. This study suggests that the epitaxial morphology of the Sb monolayer on InP(110) is modified largely by the deposition of Au and Ag. However, the presence of the Sb monolayer strongly prevents chemical reactions between the substrate and the overlayer, whereas, without Sb, clear reactions are seen. This clearly shows that Schottky-barrier heights can be controlled by controlling the chemistry at the interface.

I. INTRODUCTION

An Sb monolayer adsorbed on not only Si surfaces[1,2] but also III-V compound semiconductor surfaces[3–6] has been attracting much attention recently. This has been driven by some technological desires to improve the quality of interfacial perfection in heteroepitaxial interfaces (e.g., Si-Ge), metal-semiconductor (MES) interfaces, and metal-insulator-semiconductor (MIS) interfaces.

The motivation for starting to investigate effects of Sb interlayers, especially at metal/InP interfaces, was to examine if Schottky-barrier heights can be controlled by controlling the chemistry at the interface. As we designed, we fortunately found that a large modification of Schottky-barrier heights on InP(110) is obtained by introducing Sb interlayers onto [nonreactive metal (Au and Ag)]/InP(110) interfaces.[4,5] In that time, this was understood by thinking that the reactions taking place at the interface were strongly inhibited by the Sb, so that the creation of defects which are responsible for the Fermi-level pinning at a common level (usually ranging from 0.30 to 0.55 eV below the conduction-band minimum) was prevented, and also possibly the charge neutrality point due to the metal-induced gap states (MIGS) might be modified by the topmost Sb monolayer.[7,8] Actually as long as we look at only photoelectrons coming from the InP substrate (e.g., In 4*d* and P 2*p* core levels), we can hardly see any detectable chemical reaction between the InP and the overlayer. Therefore, the most interesting question next would be if the Sb interlayer remains at the interface keeping the initial epitaxial structure or not when Au or Ag is deposited on the Sb-passivated surfaces.

In this paper, in order to understand completely what kinds of reactions are taking place at the interface, a detailed study of the chemical reactions at the Au/InP(110) and Ag/InP(110) interfaces with Sb interlayers is reported. For this purpose, photoemission spectra of the Sb 4*d* core level are analyzed as well as the In 4*d* and P 2*p* core levels. Especially, the Sb 4*d* spectra are discussed in detail.

II. EXPERIMENT

Photoemission experiments were performed using a standard ultrahigh-vacuum chamber equipped with a cylindrical mirror analyzer. As an x-ray source, we used a tunable monochromatized synchrotron radiation at Beam Line III-1 of the Stanford Synchrotron Radiation Laboratory (SSRL). The base pressure of the chamber was in the high 10^{-11}-Torr scale. The total-energy resolution of this system, which is primarily limited by the instrumental design (i.e., grating, slits, and electron energy analyzer), was between 0.35 and 0.5 eV. In order to avoid any photovoltage effects, InP crystals doped at above 10^{18} cm^{-3} were used.[9] Atomically clean InP(110) surfaces were prepared by cleaving crystals in high vacuum. One monolayer (ML) was defined as the surface density of atoms on the InP(110) surface (8.2×10^{14} cm^{-2}). Passivated surfaces by one monolayer of Sb were prepared by depositing two monolayers of Sb removing the excess coverage of Sb, annealing at around 300 °C was definitely required.[3] Sb was evaporated from a heated tungsten coil and the thickness was monitored by a quartz crystal monitor assuming that the sticking coefficient is unity for all of them. Then metals (Au and Ag) were deposited from heated tungsten coils to make Schottky barriers on these Sb-passivated surfaces. In order to get surface-sensitive spectra, the photon energy was tuned to 80 eV for both In 4*d* and Sb 4*d* and 170 eV for P 2*p*.

The curve fitting requires inputs like spin-orbit splitting, branching ratio, Lorentzian width, and Gaussian width. The Lorentzian width is associated with the core-hole lifetime, and the Gaussian width is determined primarily by the instrumental energy resolution. These data are summarized in Table I. In order to estimate surface Fermi-level shifts, all spectra were decomposed into surface, bulk, and reacted components, and then surface Fermi-level shifts were estimated from changes in the binding energies of the bulk components. The measurement error is ±0.05 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows photoemission spectra of the In 4*d*, P 2*p*, and Sb 4*d* core levels as a function of Au coverage at the Au/Sb/[*n*-type InP(110)] interface. Figure 2 shows the same set of photoemission spectra obtained at the Ag/Sb/[*n*-type InP(110)] interface. As long as we look at only the photoelectrons coming from the InP substrate, detectable changes in the line shapes of the In 4*d* and P 2*p* are hardly observed at both cases. The In 4*d* and P 2*p* core-level spectra on clean cleaved surfaces are deconvoluted into two components, that is bulk and surface components shifted by 0.30±0.02 eV as reported by other researchers.[10] However, after the deposition of two monolayers of Sb, both the In 4*d* and P 2*p* spectra sharpen and are fitted by only the bulk component because of removal of the surface component. The shift in both the In 4*d* and P 2*p* peak positions to the low-kinetic-energy side with the annealing suggests that the interface returns to nearly flat-band conditions. Actually, even though the deposition of two monolayers of Sb gives the Fermi-level pinning at 0.35 eV below the conduction-band minimum (CBM) for *n*-type InP, the annealing of these interfaces moves the Fermi level back to the CBM (e.g., 0.18 eV below the CBM in Fig. 1 and 0.14 eV below the CBM in Fig. 2). The effect of the presence of Sb is striking in these nonreactive-metal–InP interfaces. Usually without Sb interlayers, we can see a reacted component due to In-Au alloying at the Au/InP interface[11] and also a reacted component which indicates segregation of In atoms into the Ag overlayer at the Ag/InP interface.[12] However, the only thing we observe here is the monotonic attenuation of the In 4*d* and P 2*p* emission intensities without any detectable change in the line shapes and the peak shifts of the In 4*d* and P 2*p* to the high-kinetic-energy side as would be expected from the band bending. The final Fermi-level pinning positions obtained at 10 ML coverages are at about 0.75 eV below the CBM for Au/Sb/(*n*-type InP) and about 0.62 eV below the CBM for Ag/Sb/(*n*-type InP) in these experiments. Incidentally, without the Sb, the Fermi-level positions lie at 0.45 eV (±0.05 eV) below the CBM for both cases. On the other hand, significant changes in the Sb 4*d* core-level spectra are observed for both cases. Especially of interest is that a significant difference in the Sb 4*d* is observed at the intermediate coverages (from 1 to 10 ML), while the final line shapes of the Sb 4*d* at 20 ML coverage look similar for both cases.

The curve-fitting results of the Sb 4*d* suggest that there is definitely a growing component on the high-kinetic-energy side with increasing coverage, and the chemical shift of the reacted component is different between Au and Ag cases. Let us discuss this point in detail. Figure 3 shows a series of curve fittings starting from one monolayer of Sb on the clean cleaved surface to Au deposition up to 20 ML on it. Figure 4 shows the same set of the data at the Ag/Sb/(*n*-type InP) interface. The deposition of Sb two monolayers followed by annealing at 300 °C gives a well-defined epitaxial structure. Actually, the Sb 4*d* core-level spectrum is deconvoluted into two components shifted by 0.5 eV with approximately the same emission intensity. These two components are interpreted in terms of two different chemical bonding sites, that is, Sb-In bonds and Sb-P bonds. We assigned Sb-P bonds to the low-kinetic-energy side and Sb-In bonds to the high-kinetic-energy side. This "so-called" epitaxially continued layer structure (ECLS) was enforced by the other structural investigation using x-ray standing-wave technique.[13] The deposition of Au and Ag creates one more component in addition to these two components on the high-kinetic-energy side. Although we tried to fit these Sb 4*d* core-level spectra by using three or four components, the three components fittings gave us much more realistic results than four components fittings. The successful curve fittings using three components suggest that chemical reactions are certainly taking place at the interface. That is, two components are assigned to Sb-In bonds and Sb-P bonds and one more component is assigned to reacted Sb atoms with the overlayer. On the contrary, even though it was not successful to fit spectra by using four components, if it was successful, such curve fittings would suggest that the one set consisting of two peaks lying on the low-kinetic-energy side is due to uncovered area and the other set consisting of the other two peaks lying on the high-kinetic-energy side is due to the periphery of the covered area, indicating that the Sb monolayer is still remaining at the interface keeping the initial epitaxial structure without any chemical reaction.

In the curve-fitting scheme using three components, the reacted component grows rapidly with increasing coverage, while the other two components due to Sb

TABLE I. Curve-fitting parameters.

	Spin-orbit splitting (eV)	Branching ratio	Gaussian width (eV)	Lorentzian width (eV)
In 4*d*	0.86	1.5	0.40±0.03	0.20±0.02
P 2*p*	0.87	2.0	0.48±0.03	0.10±0.02
Sb 4*d*	1.24	1.5	0.40±0.03	0.20±0.02

atoms bonded to the InP substrate decrease conversely. At 20 ML coverage, the reacted component almost dominates the Sb 4*d* spectra. The difference in the binding energies of the reacted Sb 4*d* components between Au and Ag overlayers is about 0.35 eV. We consider that this difference in the binding energies would be interpreted in terms of the difference in electronegativity between Au and Ag (Au, 2.4; Ag, 1.9). We consider that the reason why the Sb 4*d* line shapes at the intermediate coverages look different between Au and Ag is due to such different chemical shifts between the two cases in spite of the fact that similar chemical reactions are taking place at both interfaces.

The attenuation patterns of the core-level emission intensities suggest not only the morphology of the overlayer but also the degree of outdiffusion of the segregated atoms. Figure 5 shows the attenuation in the core-level emission intensities for the In 4*d*, P 2*p*, and Sb 4*d*, not

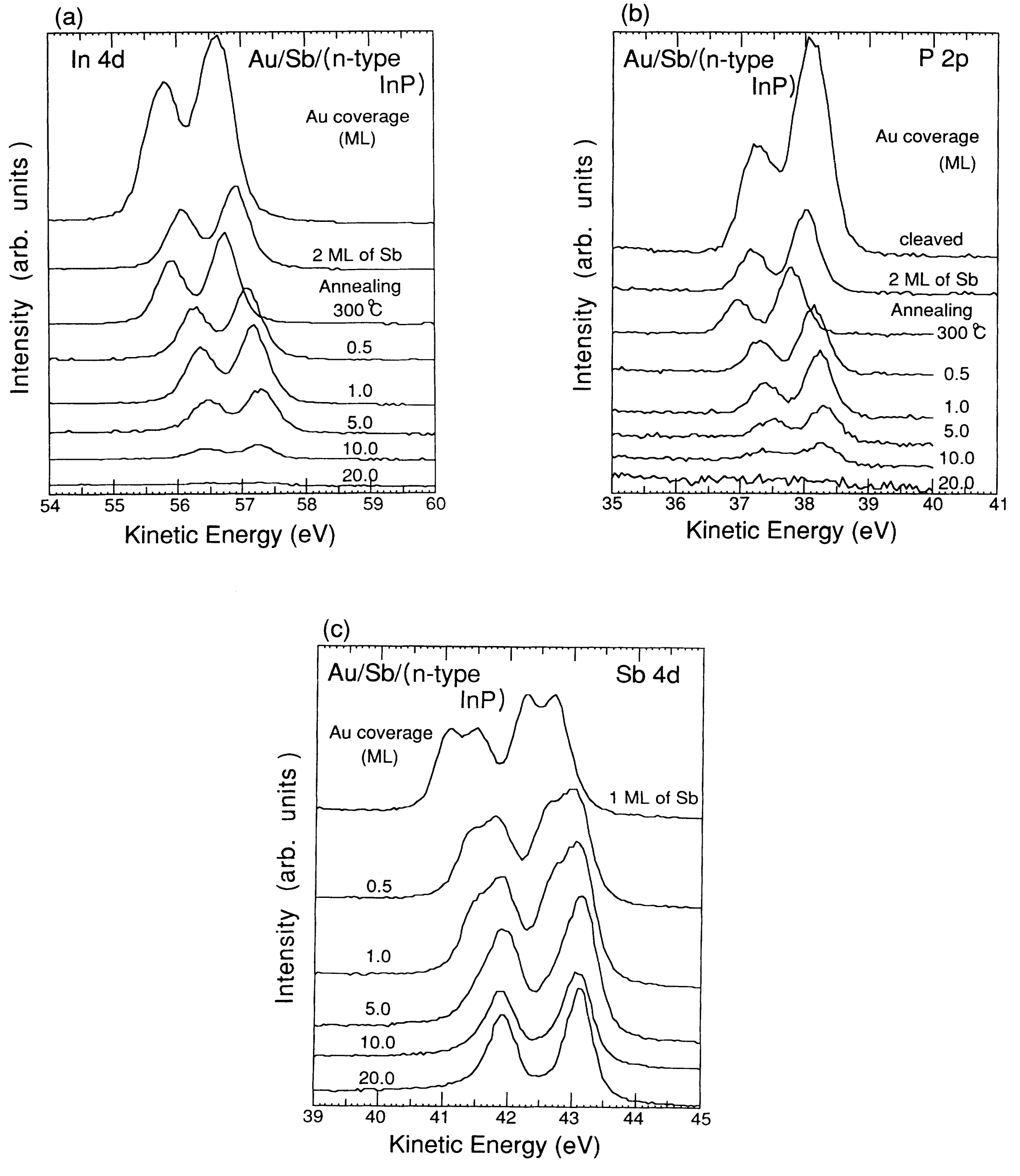

FIG. 1. Photoemission spectra at the Au/Sb/(*n*-type InP) interface: (a) In 4*d*, (b) P 2*p*, and (c) Sb 4*d*.

only the total intensities but also deconvoluted three components of the Sb 4*d* at the Au/Sb/(*n*-type InP) interface. Figure 6 shows the same set of the data obtained at the Ag/Sb/(*n*-type InP) interface. First of all, the low attenuation of the In 4*d* and P 2*p* emission intensities without any discernible change in the line shapes suggests that clustering of the overlayer is taking place on the Sb-passivated InP surface.[14] Usually, there are two possibilities in order to explain this slow attenuation of the intensity. One is the effect of clustering and the other is the segregation of substrate atoms (In and P atoms) into the overlayer. If Au and Ag grow uniformly in layer-by-layer fashion on these Sb-passivated surfaces, the intensity should decrease exponentially and drop to under 40% at 2–3 ML coverages, whereas such an exponential decrease is not observed here. Even though such an exponential decrease of the intensity might be expected at low submonolayer coverages, because we do not have enough data points at coverages below 1 ML, the deviation from the exponential decrease without any detectable change in the In 4*d* and P 2*p* line shapes would strongly suggest that the slow attenuation is due to clus-

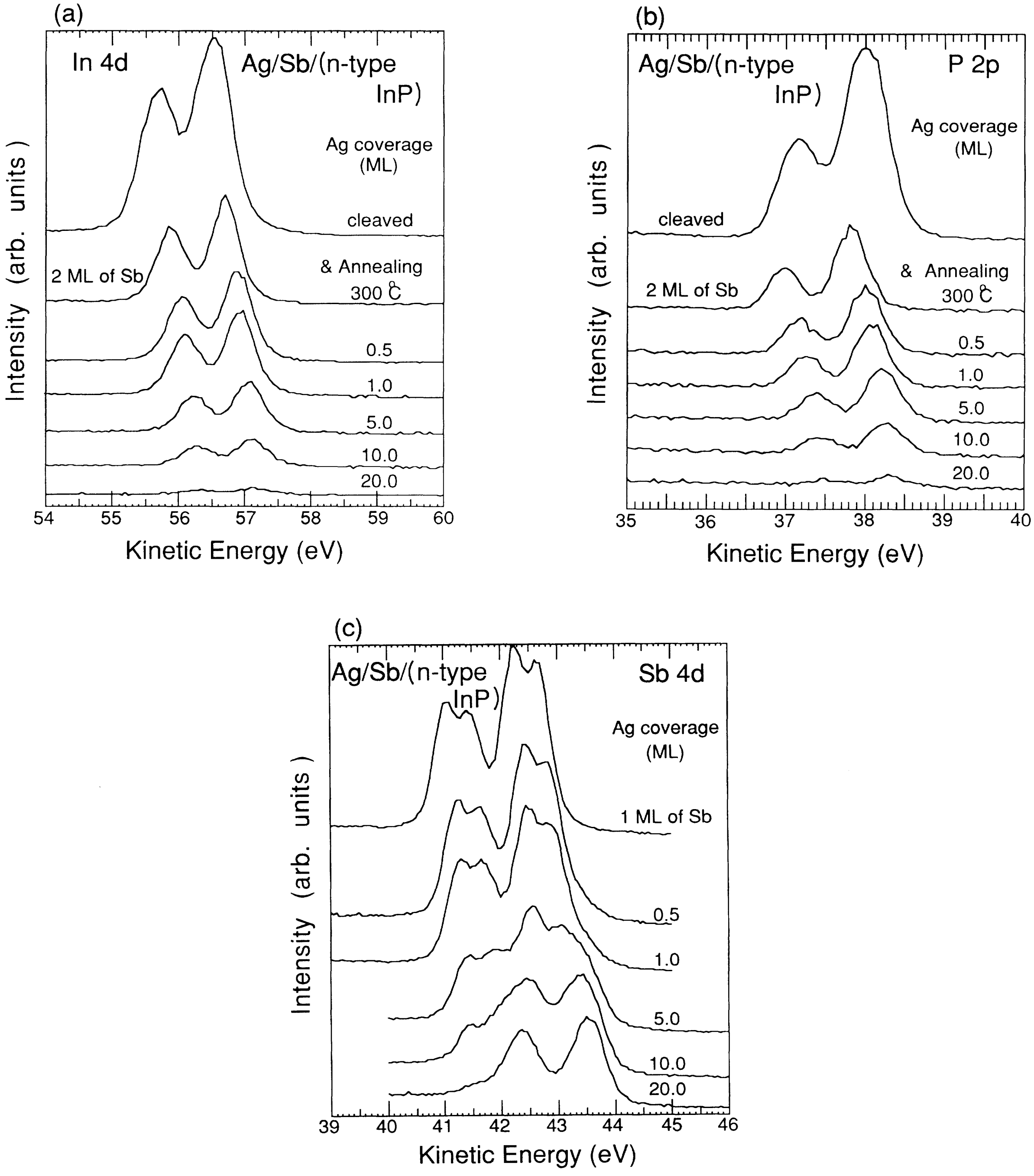

FIG 2. Photoemission spectra at the Ag/Sb/(*n*-type InP) interface: (a) In 4*d*, (b) P 2*p*, and (c) Sb 4*d*.

tering of the overlayer. Needless to say, the fact that no detectable change in those line shapes is observed suggests that there is little segregation of substrate atoms (In and P atoms) into the overlayer. Second, however, we cannot deny that P atoms have a tendency to segregate easily into the overlayer as compared with In atoms, because the attenuation of the P 2*p* emission intensity is a little bit slower than that of the In 4*d*. However, as long as we look at the P 2*p* emission, it is very hard to see the presence of elemental phosphorus on the low-kinetic-energy side of the bulk component as mentioned before. Therefore, even though there might be segregation of P atoms into the overlayer, the quantity would not be so large. Third, the slower attenuation of the total Sb 4*d* emission intensity than those of the In 4*d* and P 2*p* suggests that the epitaxial morphology of the Sb is modified

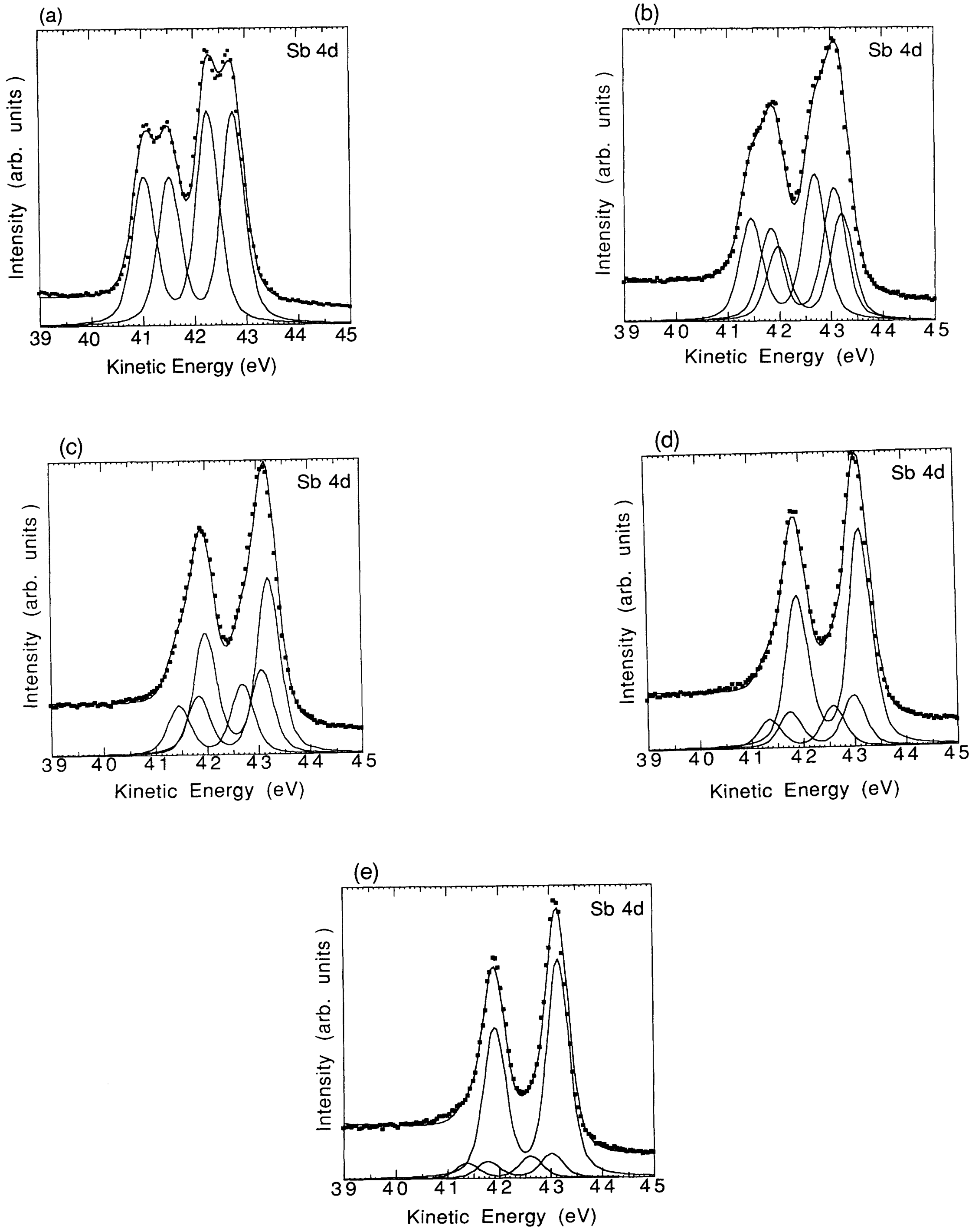

FIG. 3. Curve fittings using three components at the Au/Sb/(*n*-type InP) interface: (a) 1 ML Sb on InP, (b) 1.0 ML Au, (c) 5.0 ML Au, (d) 10 ML Au, and (e) 20 ML Au.

by the deposition of Au and Ag and simultaneously there is segregation of Sb atoms into the overlayer. Of particular interest is the rapid increase in the emission intensity due to the reacted Sb component at the Au/Sb/(*n*-type InP) interface as compared with that at the Ag/Sb/(*n*-type InP) interface. This certainly suggests that the segregation of Sb atoms into the Au overlayer is stronger than that into the Ag overlayer.

IV. CONCLUSIONS

Photoemission spectroscopy was used to investigate the interfacial chemistry at Au/InP(110) and Ag/InP(110) interfaces with Sb interlayers, especially to investigate if the Sb remains at the interface when Au and Ag are deposited. This study suggests that the epit-

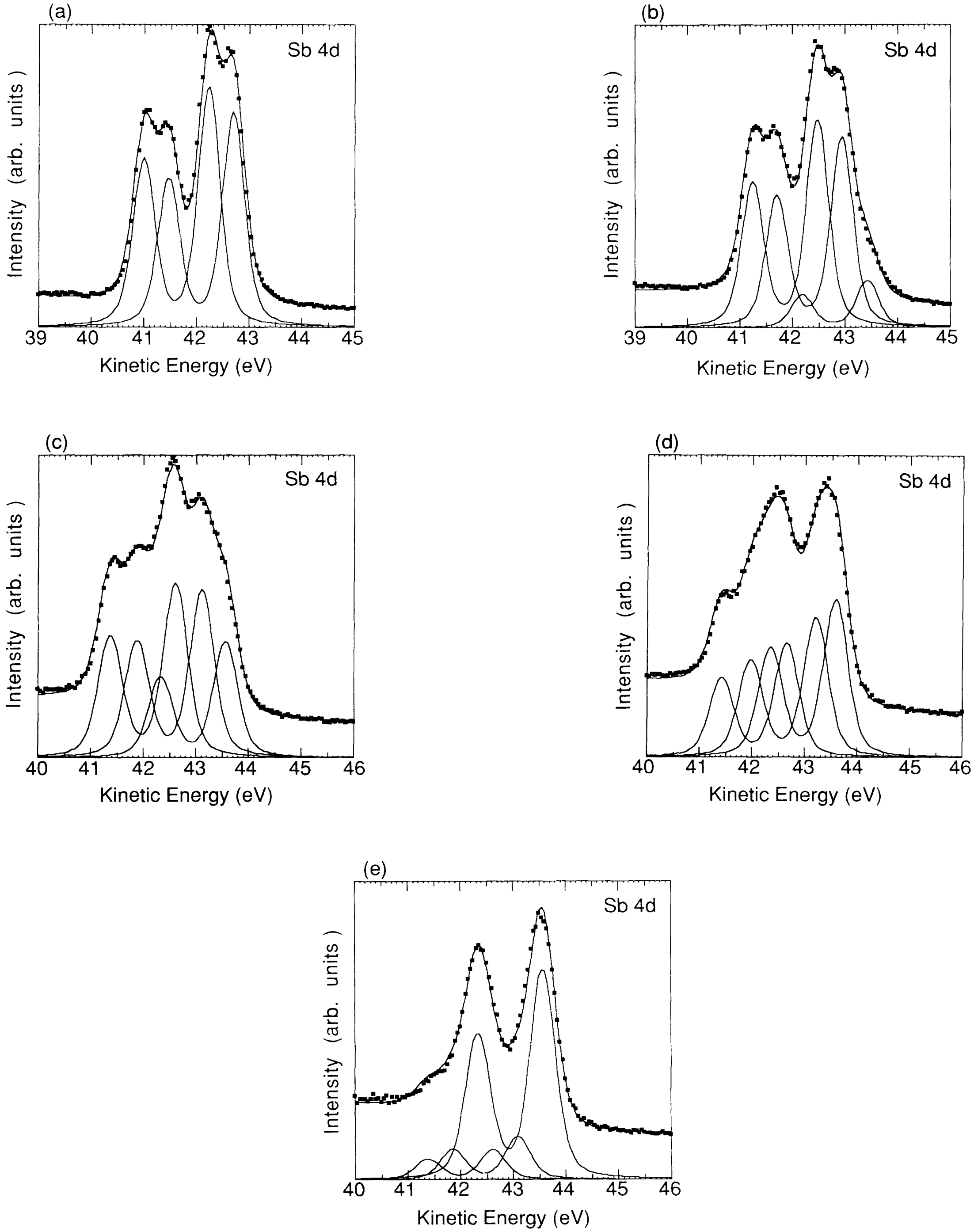

FIG. 4. Curve fittings using three components at the Ag/Sb/(*n*-type InP) interface: (a) 1 ML Sb on InP, (b) 1.0 ML Ag, (c) 5.0 ML Ag, (d) 10 ML Ag, and (e) 20 ML Ag.

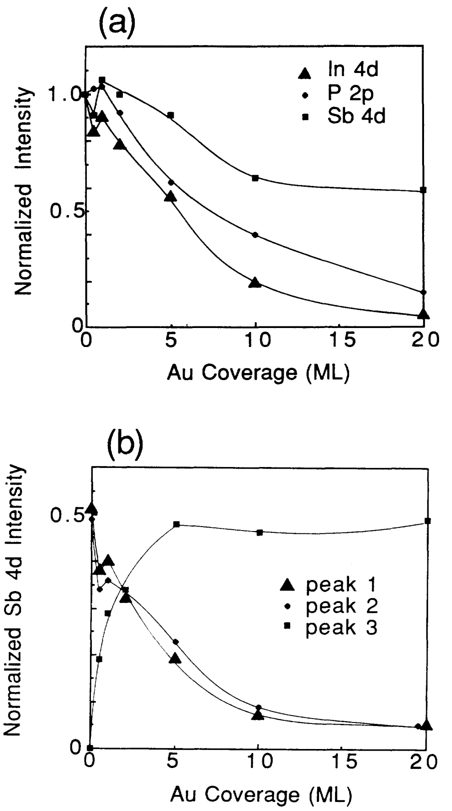

FIG. 5. Attenuation in the core-level intensities (In 4*d*, P 2*p*, and Sb 4*d*) at the Au/Sb/(*n*-type InP) interface: (a) total intensities and (b) deconvoluted three components of the Sb 4*d* (peak 1, peak 2, and peak 3 are assigned to Sb-P bonds, Sb-In bonds, and segregated Sb atoms, respectively).

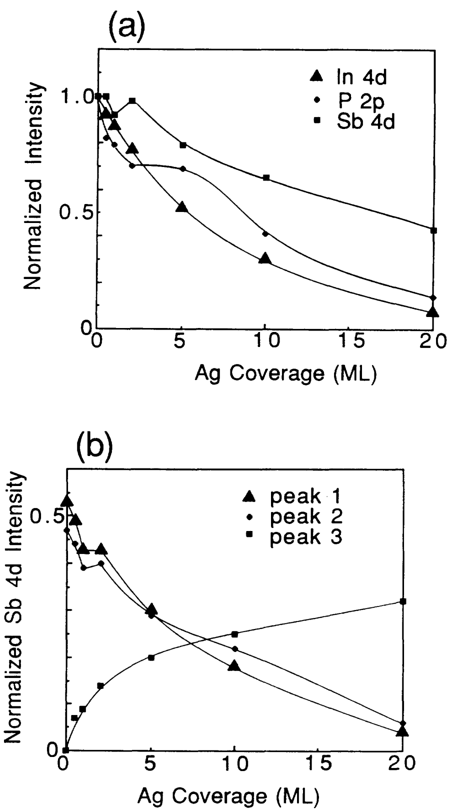

FIG. 6. Attenuation in the core-level intensities (In 4*d*, P 2*p*, and Sb 4*d*) at the Ag/Sb/(*n*-type InP) interface: (a) total intensities and (b) deconvoluted three components at the Sb 4*d* (peak 1, peak 2, and peak 3 are assigned to Sb-P bonds, Sb-In bonds, and segregated Sb atoms, respectively).

axial morphology of an Sb monolayer on InP(110) is modified largely by the deposition of Au and Ag. However, the presence of an Sb monolayer strongly prevents chemical reactions between the InP substrate and the Au and Ag overlayers, whereas, without Sb, clear reactions are seen. This clearly shows that Schottky-barrier heights can be controlled by controlling the chemistry at the interface.

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