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Photoemission study of Au Schottky-barrier formation on GaSb, GaAs, and InP using synchrotron radiation

P. W. Chye, I. Lindau, P. Pianetta, C. M. Garner, C. Y. Su, and W. E. Spicer
Stanford Electronics Laboratories and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

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Photoemission spectroscopy, constant-final-state spectroscopy, and ion-depth profiling techniques were applied to the study of the formation of Au Schottky barrier on cleaved GaSb, GaAs, and InP. It is found that the deposited Au interacts strongly with the semiconductors, causing decomposition of their surfaces. Further, the Fermi-level pinning is nearly complete at < 0.2-monolayer Au coverage, when the Au is still "atomiclike." It is suggested that defect states at the interface are responsible for the Schottky-barrier pinning, and a mechanism for their creation is proposed. It appears that many of the known phenomena on Schottky barriers can be explained using a "defect" model proposed here.

I. INTRODUCTION

In the fabrication of semiconductor devices, a metal overlayer is often used in making interconnections, Ohmic contacts, or Schottky contacts. Because of its importance, the Schottky barrier (SB) has been the subject of numerous theoretical and experimental investigations. Much of the earlier experimental work may be summarized in a set of empirical rules. For covalent semiconductors, Mead and Spitzer[1] showed that a "two-thirds" rule often applies, that is, the electron barrier height ϕ_B is approximately equal to two-thirds of the energy gap E_g. The exceptions are InAs, GaSb, and InP. The barrier energies of the covalent materials are relatively insensitive to the metal used in forming the barrier. In contrast, on the more ionic materials, Mead[2] and Kurtin *et al.*[3] observed a strong dependence on the metal used. They showed[3] that the separation between the covalent and ionic behavior (ionic-covalent transition) came at an electronegativity difference of 0.6. The index of interface behavior S is then defined by $S = d\phi_B/dX_M$, where X_M is the metal electronegativity. The covalent semiconductors then have $S \sim 0.1$, while insulators such as SiO_2 have $S \sim 1.0$; however, the latter has very recently been questioned by Schlüter,[4] who argued that $S > 1$ for the insulators. Recently, McCaldin *et al.*[5] pointed out that for III-V and II-VI compounds the SB height for holes is dependent only on the particular anion, and is roughly a linear function of the anion electronegativity. This "anion rule" applies also to materials that do not follow the two-thirds rule and to more ionic compounds such as ZnS, which has $S \approx 1.0$. The aluminum compounds are the exceptions.

Back in 1947, Bardeen[6] proposed that on (covalent) semiconductors intrinsic surface states of sufficiently high density in the band gap stabilize the Fermi level (E_F), and the barrier height is then largely independent of the metal. Many years later, Heine[7] suggested that metalliclike states with wave functions decaying into the semiconductor—the tails of the metal wave functions—are responsible for E_F pinning. Photoemission and constant-final-state (CFS) experiments on group III-V compounds[8,9] at first appeared to support the Bardeen model, but it was soon realized that E_F pinning due to imperfections and strong excitonic effects in the CFS spectra led to incorrect conclusions on GaSb. For example, Chye *et al.*[10] demonstrated directly SB pinning without the presence of intrinsic surface states in the band gap. It is now believed that there are no intrinsic surface states in the band gap of most group III-V semiconductors, and therefore the SB pinning cannot be due to intrinsic surface states.[11-13] Rowe *et al.*[14-18] did much work on group III metal overlayers on semiconductors, and reported metal-induced surface states. They also showed that the first metal overlayer is important in determining the interface behavior, and emphasized the need for a microscopic theory of chemical bonding. It was suggested that the metal forms covalent bonds with the semiconductor surface, giving rise to the observed metal-induced states that pin E_F.

Since the early stages of SB formation are so important, experiments were performed to study the effects of metal overlayers from submonolayer amounts to relatively thick coverages. In this paper, we report experimental results for Au overlayers on the III-V semiconductors GaAs, GaSb, and InP. The cleaved (110) surfaces were studied in ultrahigh vacuum in order to avoid complications arising from irreproducibility or nonstoichiometry of the initial surface. (e.g., on heat-cleaned or sputter-annealed surfaces) or from surface contamination by oxides or carbon. The experimental methods are outlined in Sec. II. Section III presents the experimental results that are further discussed in Sec. IV, where a "defect" model for SB pinning is presented.

II. EXPERIMENTAL

Several spectroscopic techniques were used in this study: uv and soft-x-ray photoemission spectroscopy (UPS and SXPS), CFS spectroscopy,[19] and Auger-electron spectroscopy (AES), used in conjunction with ion sputtering to yield composition profiles with depth. All the surfaces were prepared by cleaving in stainless-steel chambers with base pressures ~10^{-10} Torr, exposing the (110) surfaces that were usually 5×5 mm^2 in area. The UPS, SXPS, and CFS experiments were all performed at the 8° and 4° beam lines at the Stanford Synchrotron Radiation Laboratory (SSRL), where continuous radiation up to 600 eV is available. The photoelectrons were energy analyzed with a PH-I double-pass cylindrical mirror analyzer (CMA) set to 0.3-eV resolution, and the spectrum was recorded using a Tracor-Northern digital signal averager. Au deposition was made by one of two methods: (i) by rotating the sample through a stream of Au emerging from an evaporator consisting of a shield and a Au bead suspended on W wire; and (ii) by placing the sample in front of an evaporator and opening a shutter. To avoid heating of the sample surface in method (ii), the shutter was never left open for more than 20 sec (typically, 10-sec exposures were used). The evaporation rates were monitored in method (ii) by means of a quartz-crystal thickness monitor placed to the side of the evaporator in front of an opening cut in the side of the evaporator shield. This monitor was previously calibrated in a separate pump-down against another placed in front of the evaporator near the sample position. The coverage in monolayers (θ) is then determined from the Å's of Au evaporated, with one monolayer defined to be (one Au atom)/(surface atom). Evaporation rates were not monitored in method (i), but very rough estimates may be made from the current input to the evaporator, since the evaporation rate was subsequently calibrated with the quartz oscillator as a function of current input.

Pressure during evaporation was generally $<10^{-9}$ Torr. AES on a different portion of the surface from that studied in photoemission showed no contamination from oxygen or carbon. The ion-profiling experiments were performed in a system manufactured by Varian Associates, and used a single-pass CMA as the energy analyzer.

In photoemission spectroscopy, it is important to be able to establish a meaningful reference level to set the energy scale. In these experiments, reference spectra were taken from Au evaporated onto a stainless-steel substrate attached to the same sample carousel as the semiconductors. The sample carousel is grounded to the analyzer. The electron energy E_e measured is relative to the Fermi energy E_F of the analyzer. The binding energy (BE) relative to E_F, E_B^F, is then

$$E_B^F = h\nu - E_e - e\phi_A\,, \tag{1}$$

where $h\nu$ is the photon energy and ϕ_A is the analyzer work function. The location of E_F (and hence ϕ_A) may be found from the Fermi edge of the Au reference. However, in a semiconductor, E_F is not the best reference level, as it shifts around in the band gap at the surface due to changes in band bending and type (n or p) of semiconductor. Nor is the vacuum level a good reference, as electron affinities are not well known, and also change with the addition of adsorbates. The BE of a core level in a semiconductor does not change with band bending when measured relative to the valence-band maximum (VBM) at the surface, and we shall use this binding energy E_B^{VBM}. However, when the semiconductor dissociates and the individual components become metallic, the meaningful reference level becomes the metal E_F. Thus one needs to be careful in interpreting spectra from mixed metallic and semiconducting states, and in comparing BE's made on metals and semiconductors (e.g., Ga metal and Ga in GaAs). It is important to remember that E_B^F in a semiconductor may vary from sample to sample, whereas $E_B^{\text{VBM}}$is constant. Thus, the band bending of a semiconductor with small amounts of adsorbates may be followed using the movement of the core level since ϕ_A is very stable. That is, from Eq. (1), $\Delta E_B^F = \Delta E_e$. At higher coverages, other factors need to be considered, e.g., charge transfer, changes in screening, conversion into metallic form due to dissociation, and so on, which will give extra contributions to ΔE_B^F.

At the lower photon energies, E_F and its position relative to the VBM may be very accurately determined. Our procedure is to use photoelectron energy distribution curves (EDC's) at $h\nu = 10.2$ eV to study E_F movement and locate the VBM.[10] The electron-escape depth is a function of electron kinetic energy[20] and is relatively long (≈20 Å) near 10 eV, but is short compared to the depletion-layer width of several hundred angstroms at the doping levels used here. Thus, bulk band-structure features remain up to relatively thick coverages of adsorbates. By aligning the bulk peaks, the amount of E_F movement can be measured by locating E_F on the different spectra using the Au reference. The position of E_F relative to the VBM is obtained from the clean sample. The VBM on the more heavily Au covered surface, where VBM is masked by Au emission, can be obtained from knowledge of E_F movement obtained from the 10.2-eV EDC's.

III. EXPERIMENTAL RESULTS

A. SXPS spectra

Figures 1–3 show SXPS spectra (taken on the 4° beam line) of the outer core levels of Au and the III-V semiconductor substrates as the Au coverage is gradually increased. Evaporation method (i) was used. Parts of Figs. 1 and 3 have been published in a previous paper[20] in somewhat less detail. These samples are all *n*-type. The photon energies used were 165 eV for GaAs, 120 eV for GaSb, and 120 eV for the In-4*d* and 165 eV for P-2*p*. At 165 eV, the cross section for Au-4*f* is much larger than at 120 eV, and the escape depth for the photoelectrons[21, 22] is also shorter (4 vs 10 Å at 120 eV). However, the 4*d* cross section is very small at 165 eV—the Cooper minimum[23]—thus it was necessary to use the lower photon energy for studying GaSb. The escape depths of the core levels presented here are all estimated to be between 5 and 10 Å, based on escape depth curves published by Pianetta *et al.*[22] and Lindau and Spicer.[21] Thus SXPS is extremely surface sensitive [the escape depths here may be compared to those for x-ray photoemission spectroscopy (XPS) which are generally ≳ 20 Å]. It is immediately obvious from Figs. 1–3 that, while for GaAs and InP both anion and cation core level emissions decrease at roughly the same rate until a residual level is reached, for GaSb the Ga emission is attenuated as Au is deposited and decreases rapidly, while the Sb emission remains strong. This increase in the SB-to-Ga ratio is already

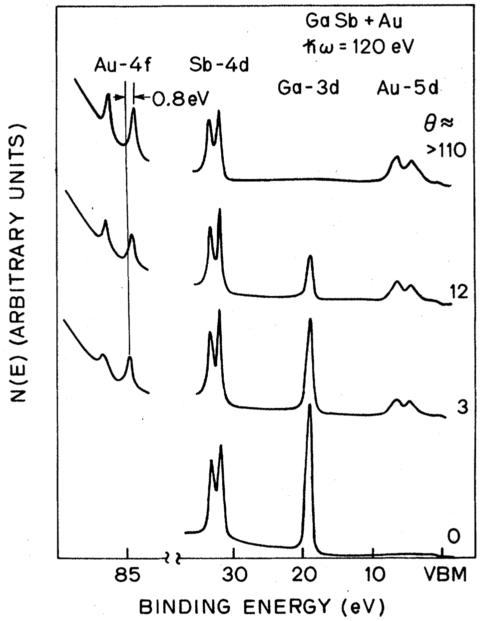

FIG. 1. Photoemission spectra taken at a photon energy of 120 eV for GaSb with different Au coverages.

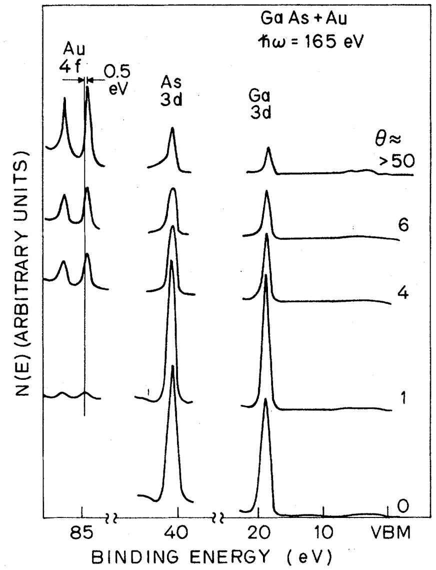

FIG. 2. Photoemission spectra taken at a photon energy of 165 eV for GaAs with different Au coverages.

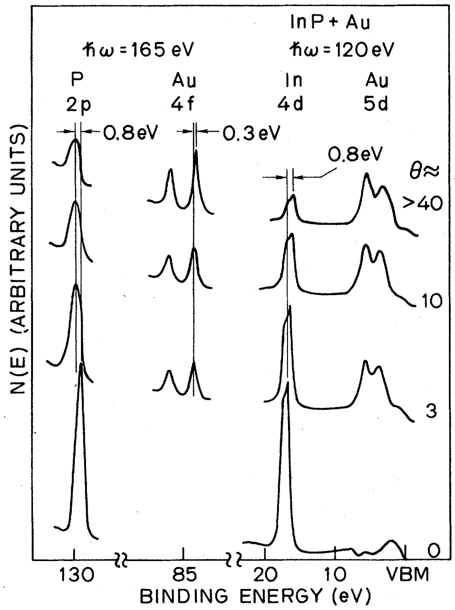

FIG. 3. Photoemission spectra taken at the photon energies 120 eV (In 4*d*, Au 5*d*) and 165 eV (P 2*p*, Au 4*f*) for InP with different Au coverages.

quite pronounced at a few monolayers coverage.

Chye *et al.*[20] interpreted the Au-GaSb spectra as showing selective removal of Sb from the interface such that a layer of Sb "floats" to the surface of the Au. One can give an explanation of this based on known bulk properties. In bulk GaSb, it is well known[24-27] that crystals tend to grow nonstoichiometric with an excess of Ga. Thus, GaSb may favor removal of the Sb at the surface. It is also well known from alloy studies[28] that the surface composition is different from the bulk composition in an alloy and that the component with the smallest surface free energy is normally enhanced at the surface. Thus the Sb the GaSb gave up upon Au deposition moves to the surface since it has the smallest surface free energy. Some caution must be exercised, since the system studied here is a very thin film and equilibrium probably has not been attained. Therefore, bulk phase diagrams and properties can only serve as rough guides. Semiconductor components are also present on the surface of Au-GaAs and Au-InP, and may be there for the same reason of minimizing the surface free energy.

At thick Au coverage, there is an apparent enhancement of the As-to-Ga ratio. This may be due to a preferential removal of As from the semiconductor, or may be due to several factors that become important as the Au thickness becomes appreciable. One factor is the relative solubility of the semiconductor elements in the Au layer. Another factor is the relative tendency to form compounds or alloys with the Au. A third factor is the relative diffusion rate. This last factor is quite unlikely here, as Ga diffuses rather rapidly in Au.[29] It seems more likely that Ga forms compounds or alloys, thus remaining in the Au layer. One may conclude from the increase in the As-to-Ga ratio that at least partial dissociation of Ga from As has occurred. It is also important to realize that on GaSb the Sb-to-Ga enhancement is apparent at low coverages when the complicating factors mentioned above are not yet significant. Thus, while it is clear that on Au-GaSb, Sb is removed preferentially, it is more difficult to tell on GaAs whether preferential removal of the As has taken place. The present data favor near-stoichiometric removal. In order to study the composition versus depth, ion depth profiling studies were made and the results shown in Figs. 4 and 5.

Evaporation method (ii) was used without a thickness monitor. The amount of Au evaporated in Fig. 4 is known to be ~50–70 Å based on a calibration run using the same evaporator after this depth profile was taken. The ion beam is incident on the surface at a grazing angle near 80° (normal incidence of 0°). The Ar^+ current density is measured using a Faraday cup at an angle of 53.5° to the beam. A simple geometrical correction was applied. The sputtering rate, calculated from sputtering yields for Au in the literature for 1-keV ions,[30] was 13.4 Å/min. The profile was measured after the Au-covered sample was allowed to sit in vacuum (2×10^{-10} Torr) for 20 h.

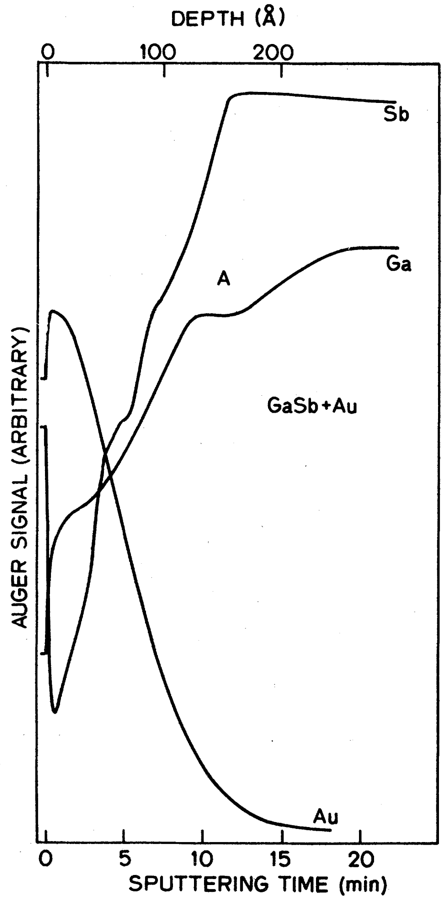

FIG. 4. Compositional depth profile of Au-covered GaSb obtained using AES in combination with argon-ion etching.

The profile unambiguously shows a layer of Sb forming the top few monolayers. This layer may be in the form of Sb metal, $AuSb_2$, a mixture of the two, or an Sb-Au alloy. Since the increase in Au signal is slight as the top layer is sputtered away, it is likely that Au is present in this top layer. The apparent interface width (90%–10% Au) is 110 Å, neglecting broadening factors. Broadening due to finite escape depth is small (<10 Å) and, at the glancing ion incidence used here, knock-on mixing effects should be less important. In any event, even allowing for a 30-Å broadening due to knock-on, the interface is still quite wide. It is

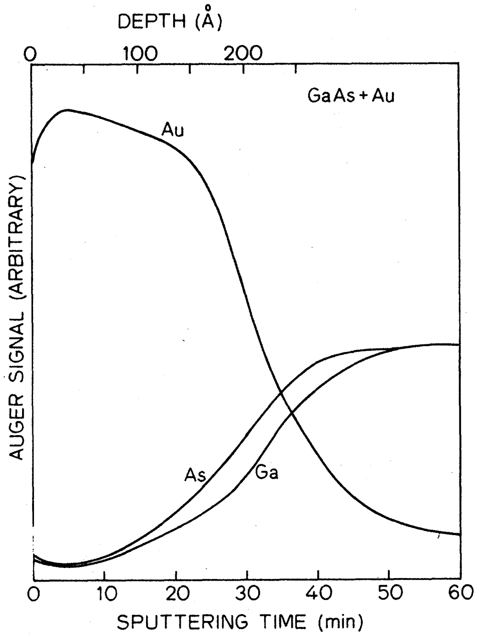

FIG. 5. Compositional depth profile of Au-covered GaAs obtained with AES in combination with argon ion etching.

possible that substantial intermixing of semiconductor and Au has occurred at room temperature. One other broadening factor that may be important here is the well-known tendency of Au to form islands or to "clump." If the Au film were nonuniform in thickness, then the interface would appear broadened. This clumping may not be very pronounced at room temperature. The existence of region *A* in Fig. 4 also argues against significant clumping. In this region the Ga signal stays constant, while the Sb signal increases steadily. This region also was observed on a second Au-GaSb sample with thicker Au coverage. If there was clumping, then one should just observe a steady increase in both the Ga and Sb signal. (If such a steady increase were observed as in Fig. 5, one would not be able to distinguish between broadening by intermixing or by clumping.) In this region, too, nonstoichiometry is likely, since one semiconductor component is steadily increasing while the other is constant. This region is roughly 30 Å wide. For comparison, the depth profile for Au-GaAs is shown in Fig. 5. The sputtering rate is 6.7 Å/min. Here, nothing similar to region *A* is seen. Other workers[31-33] have also studied Au-GaAs depth profiles with various techniques, and observed interdiffusion, particularly at high temperatures. In general, more Ga than As was found to be on the surface. For example, Hiraki *et al.*[33] studied Au overlayers on semiconductors and insulators, and found that at room temperature the surface is Ga rich, with an "alloyed" interface, while for Au-insulator systems the interface is sharp. Figure 3 shows the presence of both Ga and As on the surface, with somewhat more As at the higher coverages. The discrepancy may be explained by difference in initial surface preparation (Hiraki *et al.*[33] used ion-sputter and anneal methods rather than cleaving), by a probable difference in crystal face [which they did not specify but was not likely to be (110)], and possibly by differences in Au evaporation techniques. The most significant thing in their findings is the absence of an alloyed interface on insulators. Further discussion will be postponed until Sec. IV.

A close examination of Figs. 1–3 shows that some levels are shifted and some are broadened. The Au-$4f_{7/2}$ level has a BE of 84 eV relative to E_F at thick coverages, in agreement with measurements on bulk Au. However, at low coverages, the $4f$'s have a higher BE. This increase is as large as 0.8 eV on GaSb, possibly larger at still lower coverages. The shift is 0.6 eV on GaAs (partially masked by band bending, these spectra are plotted with the VBM aligned) and 0.3 eV on InP. As will be shown below, at low coverages, the Au is in a dispersed, or "atomiclike" state. Thus it appears that the Au $4f$'s are higher in BE relative to E_F by >0.8 eV in the dispersed or atomiclike state, and move continuously toward lower BE as more Au is deposited. The shift of a core level may be due to chemical effects such as charge transfer, or due to configuration changes or differences in screening and relaxation. Since Au is quite electronegative,[34] shifts due to chemical effects should be towards higher BE as bulk Au is formed, so the observed shift is probably due to changes in screening and relaxation.

On the GaSb cleave of Fig. 1, E_F appears to be pinned near midgap after cleaving. While E_F is usually unpinned on *n*-GaSb, occasionally, extrinsic states cause pinning either over the whole crystal surface or over parts of it, as in Fig. 9. As Au coverage is increased, there is little change in the position of the core peaks relative to VBM. There may be a small shift (~0.2 eV) of the Sb-$4d$ towards higher BE, but it is difficult to be certain with the present experimental resolution. The full width at half maximum (FWHM) of these levels also shows negligible change. The Sb $4d_{5/2}$ in metallic Sb has a BE of 32.1 eV (relative to E_F) according to XPS measurements.[35] Here, the surface Sb-$4d_{5/2}$ has a B of 31.9 eV (relative to E_F) and, for clean GaSb, a BE of 31.6 eV (relative to VBM). The difference in BE between XPS and the present measurements is within experimental uncertainties, so it is not possible to tell whether Sb, $AuSb_2$, or an alloy is at the surface. However, the relatively strong intensity of the Au emission and the absence of bulk Au structure favor $AuSb_2$ or an alloy, with perhaps some metallic Sb mixed in. Although the *bulk* phase diagram[36] for Au-Sb indicates that only $Sb+AuSb_2$ is possible at high concentration of Sb at room temperature, the surface phase diagram is likely to be different. In addition, the present system may not have reached equilibrium.

In GaAs, the Ga-3*d* and As-3*d* levels are broadened by ~0.5 eV (FWHM) for this particular cleave immediately after cleaving, although most GaAs cleaves do not show this. This is a good example of inhomogeneous band bending over the surface. Further examples will follow in Sec. III B. This pinning due to extrinsic states from the cleaving process has caused considerable confusion in the past, leading to erroneous conclusions that intrinsic surface states are responsible for the SB pinning.[8-13] The inhomogeneity in band bending disappears with the addition of Au, since Au causes pinning at the same energy position over the entire surface. Thus the core levels narrow with Au deposition. There is no observable change in the peak position of either core level (relative to VBM), although at thick Au coverage a tail toward higher BE in the As 3*d* can be clearly seen. This tail falls at the right energy for bulk As 3*d*, which has slightly higher BE. Once again, since valence-band spectra (Figs. 13 and 16) show that bulk Au is not present at the surface, the surface layer is likely to be As, Ga-Au alloys, or compounds such as $AuGa_2$ or AuGa, and perhaps some free Ga. The surface composition is probably such that the surface free energy is minimized. Our preliminary data on Ga + GaAs indicate that the BE of Ga 3*d* in Ga metal (relative to E_F) is close to that for Ga 3*d* in GaAs (relative to VBM), so any Ga metal here would be difficult to distinguish.

For InP, the behavior of the P level with Au deposition indicates the possible presence of free P. The P 2*p* level broadens by ~0.4 eV (FWHM) with the addition of several monolayers of Au, and at thick coverage the peak position has shifted by 0.8 eV towards higher BE. No such broadening is observed in the In 4*d* level, although a shift by 0.8 eV towards lower BE is observed. Once again, valence-band spectra indicate formation of compounds or alloys of Au. These are probably Au-In alloys or compounds such as $AuIn_2$ or AuIn, and the lack of broadening indicates that there is one dominant compound or alloy. However, the broadening of the P 2*p* indicates the presence of (at least) two different species of P—possibly free P and a Au-P alloy. There is a suggestion of excess P, since even though the P amplitude decreases at roughly the same rate as In, it is broadened. This may be due to a true excess of P removed from the semiconductor, since this excess is already observed at several monolayers coverage.

The important conclusions to be drawn from this subsection is (i) Au interacts strongly even at room temperature with the semiconductor when deposited, causing large amounts of intermixing with some surface enhancements; (ii) the semiconductor material removed from the crystal may be partially or totally dissociated, and may remain in the free state or form compounds or alloys with Au; and (iii) the semiconductor components may be removed nonstoichiometrically, and the excess elements appear to be Sb and (to a lesser extent) P in GaSb and InP, respectively. Ga and As appear to be removed in nearly stoichiometric amounts in GaAs.

B. UPS and CFS spectra

From previous work,[10,37] one knows that a small fraction of a monolayer of Cs can cause E_F pinning on GaSb. The experiments of Rowe *et al.*[16,17] for group-III metals on Si(111) (7×7) indicate that 70% of E_F stabilization takes place for the first monolayer of metal coverage. It is therefore extremely important to follow the pinning change and the surface electronic structure for the first monolayer of metal coverage. With the photon energies available on the 8° line at SSRL (5–35 eV), one can carry out such studies easily. In this subsection, unless otherwise noted, Au deposition method (ii) was used.

In Figs. 6–8, the position of E_F in the band gap as a function of Au coverage is plotted for the three semiconductors studied. The most striking thing is the extreme sensitivity of E_F to Au. It is apparent that for coverages of <0.2 monolayer, E_F has already stabilized near the positions for bulk Au on cleaved surfaces reported by Mead and Spitzer.[1] This sensitivity is high both for GaSb and InP, which are unpinned here after cleaving, and for GaAs, which has E_F pinned

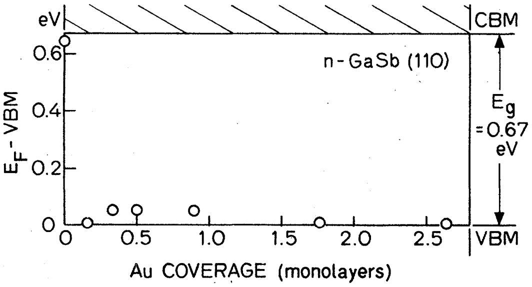

FIG. 6. Positions of the surface Fermi level relative to the VBM on GaSb, plotted as a function of Au coverage. Note the stabilization of E_F at < 0.2 monolayer.

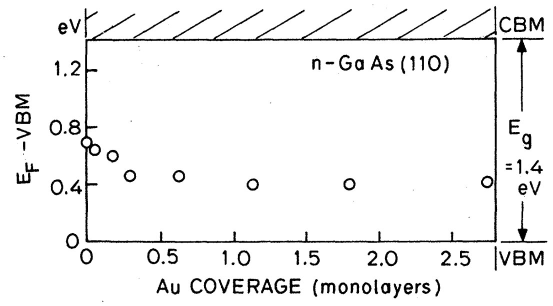

FIG. 7. Positions of the surface Fermi level relative to the VBM on GaAs, plotted as a function of Au coverage.

at midgap. (Occasionally, on "good" cleaves, E_F on GaAs is unpinned.[13]) It is perhaps more accurate to refer to GaSb as mostly unpinned after cleaving, since band bending varies over the surface with most areas being unpinned. This will be discussed below. The behavior of E_F on GaSb with adsorbate is similar to that observed for Cs on GaSb,[37] where ~0.1 monolayer is sufficient to pin E_F at the VBM. The barrier height is similar to that of Au-GaSb, even though these metals have very different electronegativities. The barrier heights on the other two semiconductors are slightly lower for Cs than for Au; the difference is $\lesssim 0.2$ eV, however.

We have established here that <0.2 monolayer of Au at room temperature is sufficient to stabilize E_F near the bulk metal overlayer position, so that a microscopic or "atomic-scale" model involving a very small number of states is needed to explain the experimental observations. This is important since practical devices are made with bulk metal overlayers, but the relevant layer is the first 0.2 monolayer or less, so that one needs to concentrate on understanding the first few monolayers to solve the problem of E_F pinning and the SB height. The SB height is, of course, only part of the difficult problem in the study of SB's. The electrical behavior (e.g., departure from ideality, $n \neq 1$), reverse current characteristics, and degradation of the barrier may all be related to the complex phenomena at thick layers such as widening of the interface, enhanced intermixing, compound formation in the metal layer, and so on.

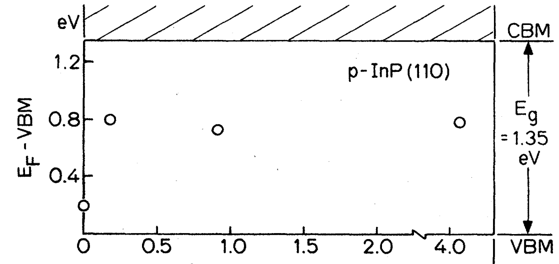

FIG. 8. Positions of the surface Fermi level relative to the VBM on InP, plotted as a function of Au coverage.

At $\hbar\omega > 25$ eV, the semiconductor valence-band matrix elements and the photoelectron-escape depth decrease. On the other hand, the Au 5*d* matrix elements increase. These factors enable small amounts of Au to be easily observed. It is usually important to know whether the Au is well dispersed on the surface. By following the development of the Au 5*d* bands, one can gather such information. From photoemission work on Au alloys,[38] it is known that when Au atoms are well dispersed as in a dilute Au alloy, the splitting of the Au 5*d* peaks is reduced from the bulk value of 2.3 eV until it approaches the value for atomic Au (1.5 eV). In addition, there is a shift towards higher BE of these bands. Therefore, the Au distribution may be probed by following the details of the 5*d* bands. If Au islands of appreciable size form, then one would expect to see bulk Au valence bands, which include a shoulder to the lower-binding side of the supper *d* band and larger splittings (>2 eV) of the 5*d* peaks. Because of band-structure effects at these photon energies, the splitting of the peaks in the 5*d* bands is a function of photon energy.[39] The splitting at $\hbar\omega = 21$ eV is small (2.0 eV, Fig. 16), but a very strong shoulder is present on the low-binding side of the upper 5*d*

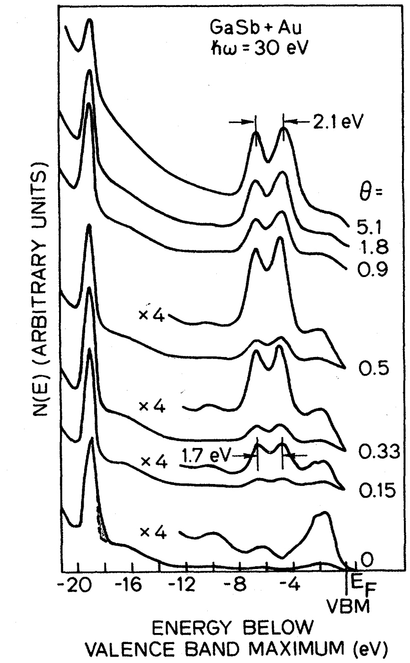

FIG. 9. EDC's of GaSb at a photon energy of 30 eV as a function of Au coverage.

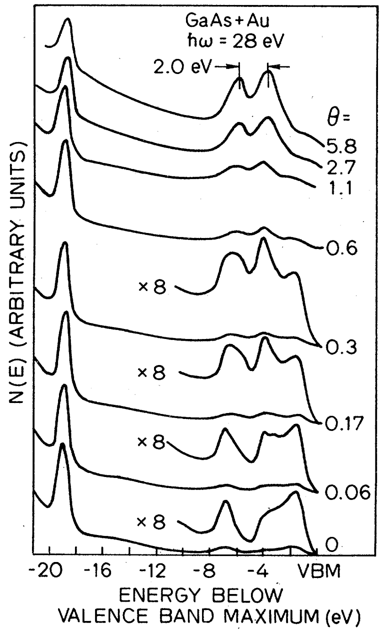

FIG. 10. EDC's of GaAs at a photon energy of 28 eV as a function of Au coverage.

peak. The splitting at 28 eV is larger—2.3 eV—but the shoulder is less pronounced. This shoulder is characteristic of pure bulk Au at these photon energies. In Figs. 9 and 11, one can see that the splitting for <0.2 monolayer is 1.7 and 1.6 eV for GaSb and InP, respectively. The splitting for 0.17 monolayer of Au on GaAs (Fig. 10) is larger—1.9 eV—but still is less than the bulk value. The shoulder mentioned above is also absent. Thus we may conclude that, *when E_F has stabilized, the* Au *on the surface is still well dispersed and has not formed large clumps, so that it remains rather atomiclike.*

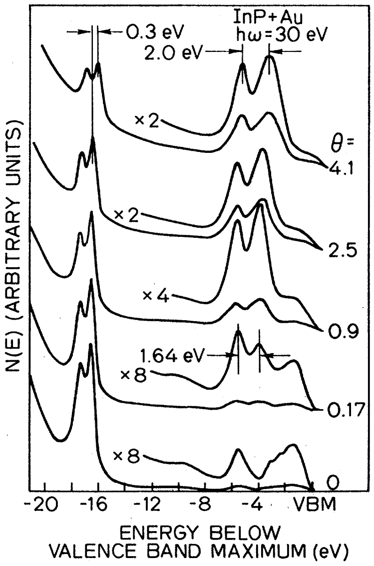

FIG. 11. EDC's of InP at a photon energy of 30 eV as a function of Au coverage.

This observation makes all "jellium" theories of SB's respect. Obviously, there can be no *bulk* metal wave-function tails that penetrate into the semiconductor; rather, any theories would have to depend on a much more "atomic" model of the metal atom. At higher coverages, the splitting increases, but the valence bands still do not resemble bulk Au, with the shoulder still absent. This is especially clear in the 21 eV EDC's shown later in this section. This is due to the formation of compounds or alloys with the semiconductor components, so the Au atoms do not assume the lattice structure of metallic Au.

Another way to determine the dispersion of the Au atoms is to look for nonuniform band bending, i.e., "patch" effects, from the broadening of the Ga or In levels. If Au clumps, then pinning will be nonuniform over the surface and the core levels will be broadened. This method works extremely well when E_F changes in energy position by large values with deposition of Au. A striking example of the effects of nonuniform band bending is the clean GaSb surface studied here. In Fig. 9, there is a tail on the low-BE side of the Ga 3*d* level (shaded area), due to emission from portions of the surface where E_F is pinned. The depostion of 0.15 monolayer of Au caused the tails to disappear, suggesting that the pinning has become uniform over the surface, once again indicating that the Au is well dispersed over the surface. The CFS spectra (Fig. 17) also show this.

Observation of the core levels show that the In-4*d* level moves upward towards lower BE as Au is added and, at 4.1 monolayers, has shifted up by 0.3 eV, less than the 0.8 eV observed in SXPS at much higher coverage. This possibly is because a more dilute In-Au alloy shows a larger In 4*d* shift, and may indicate formation of a Au-In alloy. The Ga 3*d* levels on the other two semiconductors appear to have no resolvable shift.

Figures 12–14 show the EDC's of GaAs, GaSb, and InP at 21 eV at various Au coverages. At 21 eV, the matrix elements of the semiconductor valence band are much larger than at 30 eV, while the Au-5*d* matrix elements decrease. There is the question of whether submonolayers (or even several monolayers) of metal atoms can be considered as metallic. One common feature in these spectra is the absence of a Au Fermi edge near E_F up to about two monolayers. To show this more clearly, the top 3 eV of Fig. 14 is reproduced in Fig. 15. Note, in particular, the lack of emission near E_F below 1.1 monolayers

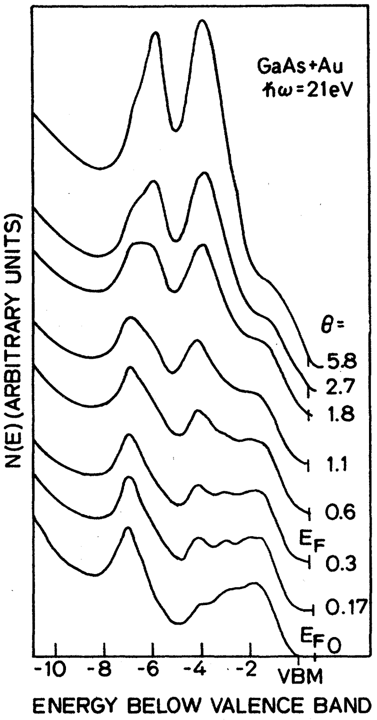

FIG. 12. EDC's at GaAs at a photon energy of 21 eV as a function of Au coverage.

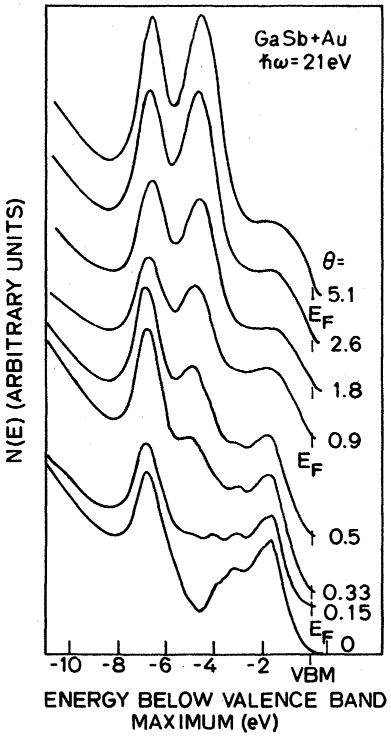

FIG. 13. EDC's of GaSb at a photon energy of 21 eV as a function of Au coverage.

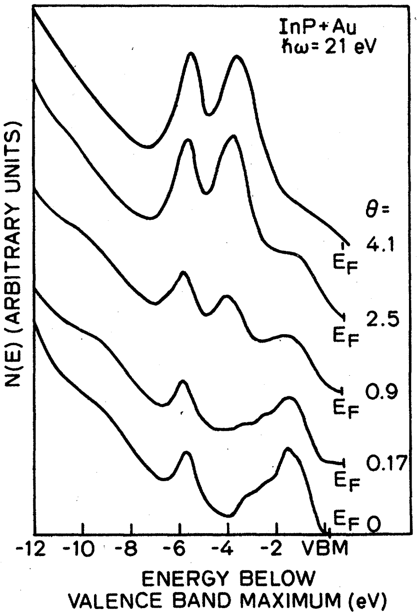

FIG. 14. EDC's of InP at a photon energy of 21 eV as a function of Au coverage.

when the barrier is already formed. Since the escape depth near E_F for $\hbar\omega = 21$ eV is ~10 Å, there should be sufficient surface sensitivity to detect any emission. This further argues against a jellium-type model of the SB. The evidence is that the adlayer does not become metallic till coverages of four to five monolayers, quite possi-

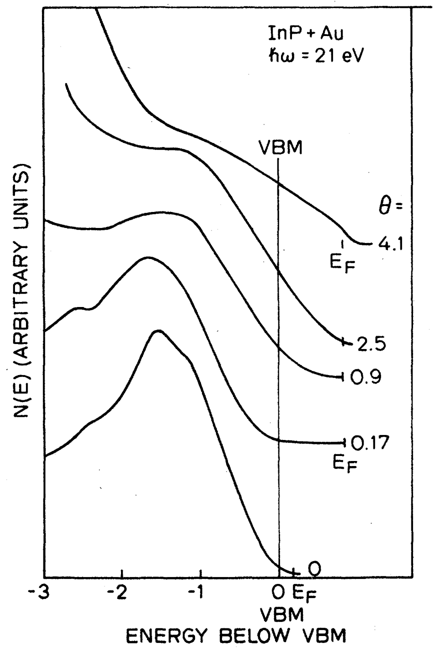

FIG. 15. Top 3 eV of the InP valence band at a photon energy of 21 eV as a function of Au coverage.

bly because of intermixing or diffusion. Emission in the band gap is gradually appearing at 0.6 monolayer, and is probably from the Au 6*s* electrons. At coverages near half a monolayer, the structure in the semiconductor valence bands have disappeared, indicating that the surface layers have become severely disordered and possibly amorphous. Note that the Au emission at 0.6 monolayer is not sufficiently strong to mask the semiconductor valence-band emission; note, too, that at several monolayers, the emission from the top 3 eV in the EDC is from both Au and the semiconductor components, as the emission is much higher than is observed for Au. The EDC's at $\hbar\omega = 21$ eV for thicker coverages deposited using method (i) for these semiconductors are shown together with one for Au in Fig. 16. The striking thing is that even for fairly thick layers the Au 5*d* bands from the overlayers still do not closely resemble that from Au—note the absence of the shoulder mentioned previously. The metal Fermi edge is well established in these EDC's.

We have supplemented our photoemission measurements with CFS spectroscopy.[8,9] In CFS, one monitors the secondary electron yield at a CFS energy (constant retarding voltage) while varying the photon energy incident on the sample. At photon energies that cause transitions from the Ga- or In-*d* levels, *d* core holes are created. Recombination of electrons with these holes gives rise to secondary Auger electrons whose final-state energy does not change with photon energy. The final-state energy chosen here is 4 eV.

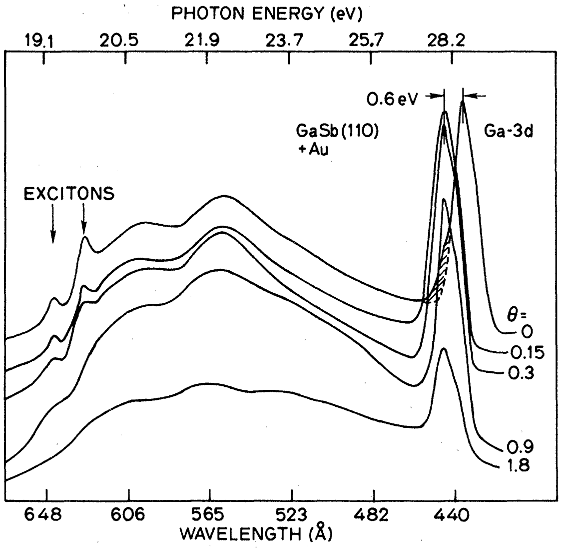

FIG. 17. CFS spectra of GaSb as a function of Au coverage.

In Figs. 17–19, CFS spectra for GaSb, GaAs, and InP are shown. The double-peak structure near 19 eV is believed to be excitonic levels involving transitions from the spin-orbit-split anion *d* core level (Ga 3*d* and In 4*d*) and empty states—possibly surface states—above the conduction-band minimum.[40] The energy necessary to cause a transition into them is lowered by the exciton BE (~0.5–1.0 eV). The transition strength is matrix-element dependent.[41] The broad peaks at higher photon energies are due to transitions into the bulk conduction band, reflecting the density of states. At still higher photon energies in Figs. 17 and 19, the sharp peaks are due to sweeping of the core *d* level (primary) photoelectrons through the final-state energy of 4 eV.

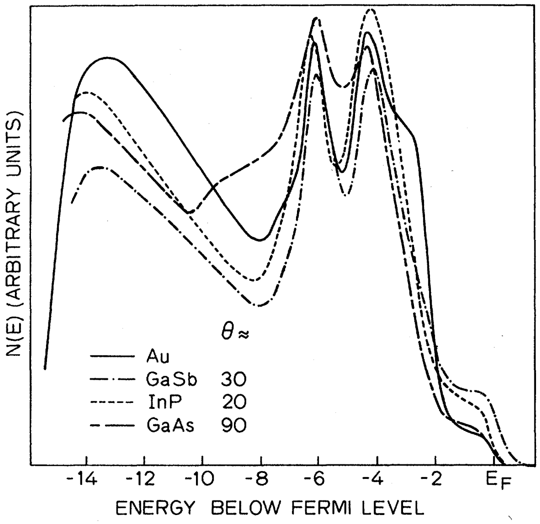

FIG. 16. EDC's of Au and of thicker Au layers on GaAs, GaSb, and InP at a photon energy of 21 eV.

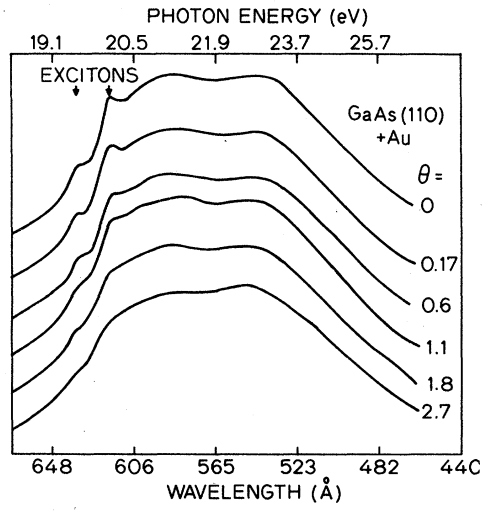

FIG. 18. CFS spectra of GaAs as a function of Au coverage.

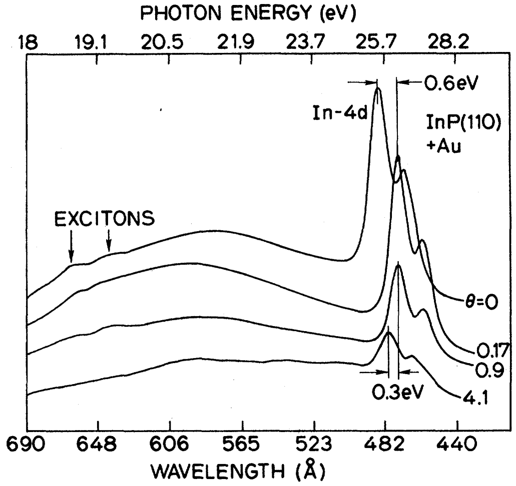

FIG. 19. CFS spectra of InP as a function of Au coverage.

In Fig. 17, the Ga $3d$ peak near 28 eV shows the tail (shaded) mentioned earlier (Fig. 9). After 0.15 monolayer of Au, the peak shifts by 0.6 eV due to movement of E_F by that amount, and the tail disappears since pinning is now uniform over the surface (see earlier discussion on Fig. 9). Further deposition of Au fails to cause any extra E_F movement, once again demonstrating that pinning is complete at 0.15 monolayer. Note, however, that even though pinning is complete at 0.15 monolayer, the surface excitons are little affected and, in particular, remain at the same energy, showing that the final states are not shifted by the presence of Au. By 0.9 monolayer, however, much of the excitonic structure has disappeared. The coverage for exciton extinction appears slightly higher for the other two semiconductors, but, when pinning is complete, the excitons are little affected. Note that, in Fig. 19, the shift in the In $4d$ is due initially to E_F movement, but the shift (0.3 eV) at 4.1 monolayer is due not to E_F movement but to compound or alloy formation.

Our results here are in contrast to those of Eastman and Freeouf[8,9] for Pd overlayers on GaAs(110) and In overlayers on GaAs(110), GaSb(110), and InAs(110), where the surface excitons were little affected by two to three metal layers. Our results are similar to those of Rowe *et al.* for group III metal overlayers on Ge, Si, and GaAs(110) and (100) surfaces.[14-18] Rowe *et al.* had proposed that the (110) surface is anomalous; our results here indicate that it is not. Possibly, the discrepancy is due to some peculiarity of Pd and In overlayers; further experiments are needed to resolve this discrepancy.

One question that might be asked is whether the Au creates any new empty levels. The data here show no clear evidence of new levels arising from the depostion of Au. One explanation is that the density of new empty states created (metal-induced states) is low since $<10^{12}$ states/cm^2 are sufficient to pin E_F. However, if Au forms covalent bonds with the surface atoms, as proposed for group III metals on Si(111),[16] then one would expect creation of $\sim10^{15}$ states/cm^2 and introduce new levels into the CFS spectra. The absence of these levels near one monolayer suggests that covalent bonding may not be the correct description for the materials studied here.

IV. DISCUSSION

It is appropriate at this point to summarize what is now known about SB's, both from other work and from the present study.

(i) SB heights in covalent semiconductors are nearly independent of the metal work function φ_M, and, with a few exceptions, are equal to two-thirds of the band gap (the two-thirds rule); however, for ionic materials, strong φ_M dependence is observed.[2,3]

(ii) The anion rule proposed by McCaldin *et al.*,[5] which states that the SB height for holes is dependent only on the anion, applies to both covalent and more ionic materials such as CdSe, ZnSe, CdS, and ZnS. Materials that are the exceptions to the two-thirds rule, such as InP and GaSb, obey the anion rule.

(iii) Observations (i) and (ii) are made on atomically clean surfaces. However, barrier heights on "real" surfaces with native oxides and other contaminants appear to be very similar, and are not strongly affected by moderate heat treatment. For example, Kim *et al.*[32] found that, for Au-GaAs, heating up to 400°C for 7 min only changed the barrier height by 0.02 eV. The measurements were made at room temperature. At 500°C, the barrier height drops by ~0.26 eV compared to room temperature, and there is a large increase in the ideality factor n defined in the thermionic emission current equation for emission over the barrier:

$$J = A^* T^2 \exp(-q\phi_B/kT)[\exp(qV/nkT) - 1] ,$$

where J is the diode current density, A^* is the effective Richardson constant, ϕ_B is the barrier height, and V the applied voltage. For an ideal barrier, $n = 1$; departures of n from unity are always to higher values.

(iv) ϕ_B does not change very much going from submonolayer or monolayer coverage to hundreds of monolayers, and, as this work shows, E_F is stabilized by the first 0.15 monolayer (or less) of metal on the III-V semiconductors, i.e., before a clearly metallic layer forms; thus, a microscopic, or atomic-scale model based more on the interaction of Au atoms with the semiconductor than with a well-formed Au metallic layer is necessary to explain the data.

(v) Since it is now believed that for most III-V semiconductors there exist no intrinsic surface states in the band gap, metal-induced states must be responsible for E_F stabilization. Our observations lead us to the conclusion that they are extrinsic states. Here, it is wise to define what one means by extrinsic. We define extrinsic states to be those states not present on a clean, perfect, defect-free surface. The surface may have a reproducible reconstruction, e.g., Si(111) 2×1. Extrinsic states may be induced by surface strain or defects introduced by surface preparation or by the presence of foreign atoms on the surface.

(vi) From CFS data, the excitonic transition involving final states above the conduction-band maximum (CBM) are barely affected when E_F has stabilized at <0.2 monolayer coverage, and approximately one monolayer of metal is required to remove this transition. At one monolayer coverage, no new transitions into final states in the band gap can be seen.

(vii) There apparently is a large amount of intermixing of metal and semiconductor, although for insulators Hiraki *et al.*[33] observed no alloyed junction. There is thus a (possibly nonstoichiometric) removal of semiconductor material at the interface. For example, Sb is removed to the surface of the Au layer on Au-GaSb to leave an excess of Ga at the interface.

A successful model for SB formation must be able to explain or, at the very least, not be inconsistent with the above observations. While it is not possible at this time to present a definitive model that accounts for all the known phenomena, many of the observations can be explained by a "defect" model. Confirmation of this model will require much further experimentation; one should hope that presentation of the model here will stimulate interest in performing work to test it.

This model is motivated largely by observation (vii) above. Removal of semiconductor materials from the interface is likely to give rise to large numbers of defects that can pin E_F. Although a departure from stoichiometry is unnecessary for E_F pinning (see below), it is almost certain that there is a nonstoichiometric interface in Au-GaSb and probably in some others, although small departures from stoichiometry (e.g., 1%) will be nearly impossible to detect with the techniques used in this paper although they are sufficient to produce pinning.

The bulk growth properties of GaSb support an interpretation of nonstoichiometry. It has long been known[24-27] that high-purity undoped GaSb is *p* type due to nonstoichiometry. The acceptors in that semiconductor are related to a Ga excess or an Sb definciency, are related to vacancies, and are fairly immobile. van der Meulen[26] ruled out the possibility of a simple defect, and suggested that the complex center $\mathrm{Ga}_{\mathrm{Sb}}V_{\mathrm{Ga}}$, that is, a Ga vacancy associated with an antisite defect of Ga on an Sb site, gives rise to these acceptors. These same acceptors may be responsible for pinning E_F at the VBM at the surface. It appears that GaSb surface is highly *p* type, and the deposited Au provides the energy to create the acceptors. One point to note is that the semiconductors are dissociated by the Au, causing considerable intermixing; this indicates that a substantial amount of energy is deposited by the Au. Now, what is the source of this energy?

When Au is evaporated, it is in a higher-energy state, with an energy equal to the heat of sublimation (89 kcal/mole = 3.87 eV/atom) above the metallic state at room temperature. Upon arrival at the semiconductor surface, the Au atoms go into a lower-energy state, releasing large amounts of energy. The amount of energy each condensed Au atom gives up will depend on the strength of binding to the substrate, that is, whether it forms a compound with the semiconductor, chemisorbs, sits interstitially, goes substitutionally into the semiconductor lattice, or bonds weakly to the semiconductor surface or to other Au atoms. This energy will—especially for the first monolayer of Au—be different from the heat of sublimation of Au, since in Sec. III we have seen that bulk Au structure is not obtained until tens of monolayers have been deposited. For example, the initial heat of adsorption of Cs on GaAs(110) is ~60 kcal/mole, while the heat of sublimation of bulk Cs is ~19 kcal/mole.[42] The excess energy carried by the deposited Au is released in a localized volume, thus causing a "thermal spike" that can create defects. Van Vechten[43] has calculated the enthalpies in forming various *bulk* defects, and for vacancies the values are typically 2–3 eV for III-V semiconductors. At the surface, these values will be reduced because of reduced area in his macroscopic "cavity", thus lowering the surface energy. Another way of looking at this is that at the surface fewer bonds need to be broken to form a defect. Brillson[44] and Lindau *et al.*[45] have presented plots of the index of interface behavior S versus the heat of formation (HF) of numerous covalent and ionic compounds, and there is a striking relation. The more ionic compounds have high HF and $S=1$, while the covalent compounds have low HF and small S (indicating weak dependence on φ_M). From this, one might argue that the defects formed with metal deposition are more numerous when HF is small and that these defects are more important than the particular metal used in determining the pinning, consistent with observations (i) and (iii), although the metal used still affects the pinning position slightly. (This may be due to interactions between the metal and defects.) For more ionic compounds with higher HF, fewer defects are formed, so the dependence on φ_M is stronger.

Although the defects that pin E_F are probably complex (see below), one may consider as a reasonable approximation that simple vacancies are first formed that later interact with other lattice atoms or impurities to form complexes. Van Vechten's calculations[43] show that, in general, the enthalpies for anion and cation vacancies are different. Therefore, it is likely that more vacancies of one component will be formed. In his simple model, the larger the covalent radius, the greater the enthalpy for vacancy formation. For the semiconductors studied here, GaSb, InP, and GaAs, respectively, $\Delta H(V_{\mathrm{Sb}})=2.56$ eV, $\Delta H(V_{\mathrm{Ga}})=2.03$ eV, $\Delta H(V_{\mathrm{P}})=2.17$ eV, $\Delta H(V_{\mathrm{In}})=3.04$ eV, and $\Delta H(V_{\mathrm{As}})=\Delta H(V_{\mathrm{Ga}})$ 2.59 eV. These estimates predict that V_{Ga} should be more numerous that V_{Sb}, but, as mentioned previously, the Sb goes to the surface of the Au. Estimates for antisite defects[46] predict that the enthalpy to put a larger atom at the site of a smaller atom is greater, and vice versa. Thus it is more likely for $\mathrm{Ga}_{\mathrm{Sb}}$ (Ga atom in an Sb site) than $\mathrm{Sb}_{\mathrm{Ga}}$ to form. Some of the Ga atoms then move into vacant Sb sites to form $V_{\mathrm{Ga}}\,\mathrm{Ga}_{\mathrm{Sb}}$. Now, an anion vacancy is believed to be a donor, while a cation vacancy is believed to be an acceptor; a cation or an anion site is an acceptor, whereas an anion on a cation site is a donor. Thus, the $V_{\mathrm{Ga}}\,\mathrm{Ga}_{\mathrm{Sb}}$ complex in GaSb would give rise to acceptor levels.

Assuming that the defects formed introduce acceptor and donor levels into the band gap, we can gain some insight into the behavior of E_F by considering two simple situations discussed in Blakemore[47] (and references therein). Consider first the case of an n-type semiconductor. When N_A acceptors are introduced at the energy E_C-E_A into the band gap (E_C is the energy of CBM) by making the interface nonstoichiometric, then compensation occurs until N_A exceeds N_d, the concentration of dopants. (Note that compensation may reduce the energy needed to create a defect.) At that point, E_F drops very rapidly and locks onto the acceptor level. This probably the case for GaSb.

A second case is when N donors and an equal number of acceptor levels are introduced (for example, through creation of As and Ga vacancies) at energies E_D and E_A measured relative to the CBM. For an n-type semiconductor, E_F would drop very rapidly when N approaches the dopant concentration of the crystal, and when N is much larger than the dopant concentration, E_F would come to rest at an energy intermediate between E_D and E_A. Thus it is not necessary for nonstoichiometry to exist before pinning occurs.

What are the kind of defects found at or near the surface or interface after metal deposition? Many types of defects can occur in the compound AB. The simplest ones are vacancies ($V_{A,B}$) and antisite defects (A_B, B_A). These can interact with each other or with the metal (e.g., Au) to form complexes. All these defects may form as Au is deposited, but one or two types of defects are likely to dominate E_F pinning and particularly the more immobile ones as more mobile defects can diffuse away from the interface. Thus, as mentioned above, the $V_{\mathrm{Ga}}\,\mathrm{Ga}_{\mathrm{Sb}}$ complex is likely to be responsible for pinning E_F in GaSb. On GaAs, Lang *et al.*[48] measured eight different levels in the band gap, two (located near midgap and a few tenths eV below midgap) of which are present before irradiation of the semiconductor with 1-MeV electrons. It is generally accepted[48] that in isochronal annealing experiments the lowest-temperature stages are associated with simple defects that have high mobility, while the highest-temperature stages are associated with defect clusters or impurity complexes that have low mobility. In addition, it is known that simple defects in GaSb and InSb are unstable above 200° K. Although simple defects may exist in GaAs and InP, judging from isochronal annealing data that show that materials which have higher Debye temperatures have defects with lower mobility,[48] the evidence argues against their playing an important role in SB pinning. Lang *et al.*[48] identified one level as being a simple Ga vacancy level. This level, however, lies in the top part of the band gap, away from the SB pinning position. A level H1, which they believe is related to impurities, may be responsible for SB pinning, since it lies at approximately the right energy position. Also, as mentioned earlier, the more mobile simple defects are likely to diffuse away from the interface with time, so it is more probable that the nonmobile complexes or clusters that remain near the interface are responsible for SB pinning. Measurement of defect level positions in other semiconductors such as InP should prove very useful.

The "defect" model presented above will explain many of the observations summarized at the beginning of this section. It explains observation (i) from a consideration of HF and explains observation (iii), since adsorbates with sufficient heats of condensation or adsorption will create defect levels that are characteristic of the semiconductor and depend only weakly on the particular metal deposited. Observation (ii) is more difficult to explain, but, if for GaSb and GaAs we assume the presence of V_{Ga} or a complex depending strongly on V_{Ga}, then the dangling bonds in the vacancy are anion bonds; since the VBM is anionlike, it is quite reasonable for the energy separating between the defect level (due to anion dangling bonds) to be dependent only on the particular anion. The defect model is also a microscopic or atomic-scale model, and it is not unreasonable for sufficient defect states to have formed with <0.2 monolayer of metal to pin E_F [observations (iv) and (v)]. Observation (vi) may provide evidence for rejecting a model based on formation of covalent bonds between the metal and the semiconductor surface in the III-V semiconductors (other semiconductors, e.g., group IV semiconducotrs, may behave differently). Since covalent bonding is expected to provide $\sim 10^{15}$ surface states/cm^2, one might expect to see new transitions due to these states in the CFS spectra. None was observed. The absence of pinning in Ga-GaAs (described below) also argues against covalent bonding, since Ga should also form covalent bonds with GaAs and thus pin E_F whereas if Ga created Ga defects, it might heal these defects and remove the pinning. Note that since only a very small fraction of the Au atoms create a defect state, new structure in CFS spectra is not expected. Finally, observation (vii) is related to observation (i), and is explained quite readily by the present model since HF is much higher for the insulators and the metal is unable to create defects and remove material.

Experimentally, much work will have to be done to test the defect model. One possible experiment would be to use the appropriate column III or V metal as overlayer in the hope of eliminating pinning due to the deficit of one of the components. Bachrach[49] has studied Ga on p GaAs, and observed no pinning. Woodall *et al.*[50] also reported a suppression of pinning on n GaAs. These experiments suggest that the pinning is Ga related, possibly due to Ga vacancies, as Ga metal should readily heal V_{Ga}, and thus support the model. In has also been reported[51] to form Ohmic contacts to InP. If antisite defects were involved, it is no longer clear what might happen. Other work might be done using very pure undoped material to eliminate the donor-vacancy complex. Theoretically, a good calculation of the enthalpies for surface defect formation would be very helpful. Estimates of the defect level energy positions would be invaluable.

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