Electronic structure and Schottky-barrier formation on GaAs (100) surfaces prepared by thermal desorption of a protective arsenic coating

C. J. Spindt, M. Yamada, P. L. Meissner, K. E. Miyano, T. Kendelewicz, A. Herrera-Gomez, and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305-4055

A. J. Arko
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 19 February 1991; revised manuscript received 22 October 1991)

Soft-x-ray photoemission spectroscopy has been used to characterize GaAs(100) surfaces and interfaces grown by molecular-beam epitaxy and prepared by the thermal desorption of a protective As coating. The samples studied were grown and arsenic capped identically to those used in a previous study [Brillson *et al.*, J. Vac. Sci. Technol. B **6**, 1263 (1988)]. In this previous work, "unpinned" Schottky-barrier formation was reported, with barrier heights over a wide (0.75-eV) range. This is a striking result, as it was previously believed that all metals will pin GaAs surfaces in a narrow energy range near the middle of the band gap. This large range of barrier heights later led to the suggestion that the (100) surface could become an insulating layer that could screen out the effects of metal-induced gap states. Motivated by this work, we have studied Al and Au Schottky barriers since the deposition of these two metals gave the extreme low and high barriers in the 0.75-eV range. We have also characterized the clean surfaces prepared by desorbing the As caps at different temperatures. The As $3d$ and Ga $3d$ core levels showed that the surface stoichiometry could be varied significantly with the desorption temperature. The As $3d$ line shape was found to be the best indication of the surface stoichiometry after the anneal. The valence-band spectra did not show any strong features which could be used to determine when the sample was completely decapped. The electronic structure of the surface layer was investigated experimentally, and no evidence of an insulating reconstruction was found. In our study of band bending, we found that the low-doped samples used here and in the earlier study showed significant photovoltages resulting in incorrect band-bending measurements. We also found that the Au measurements are made difficult by the presence of core-level shifts due to Au-Ga alloying. After solving the problems with the photovoltages and alloying, we found that the barriers heights for Au and Al differ by only 0.25 eV.

INTRODUCTION

It has recently been reported that a wide range (0.75 eV) of Schottky-barrier heights could be obtained on the GaAs (100) surface prepared by molecular-beam epitaxy (MBE).[1] These measurements indicate that the barrier heights correlate with the work function of the metal, approaching the Schottky limit. This is an extremely interesting result, which could be of great practical importance. However, these measurements have yet to be reproduced by any other group. Because of this, we have undertaken an independent study of identical GaAs samples, in the hope of confirming and understanding the previous work.

In order to carefully analyze the formation of the metal-semiconductor interface using core-level photoemission spectroscopy, it is important to first gain an understanding of the spectra from the clean surface. We present Ga $3d$ and As $3d$ core-level spectra, and deconvolve them into their surface atom and bulk GaAs components. This is important since it is the shift in the component of a spectrum arising from the bulk GaAs which gives the Fermi-level movement. This information can then be used to separate the bulk component from the surface shifts and shifts due to chemical reaction with the overlayer during metallization, making an accurate band-bending determination possible.

We performed experiments on both $n=5\times10^{16}$ cm^{-3} (as was used in Ref. 1) and on $n=5\times10^{18}$ cm^{-3} doped material. When we studied the $n=5\times10^{16}$ cm^{-3} samples, we found that there was a significant photovoltaic band flattening[2,3] *even at room temperature*. This photovoltage occurs because of the large n-type barrier height (0.85 eV) and low doping (5×10^{16} cm^{-3}) of the samples examined in this experiment and in the n-type work of Ref. 1. As will be discussed, these photovoltaic shifts can lead to errors in the band-bending measurements for which it is difficult to correct.

We have studied samples which are annealed at 580 °C, the temperature typically used by the Brillson group.[4] In addition, we have studied the decapping process at the lower temperatures of 300 °C and 450 °C, as well as at a temperature slightly above the decomposition temperature of the GaAs. The surface stoichiometry and electronic structure of the resulting surfaces have been examined.

 ©1992 The American Physical Society

Prior to the work of Ref. 1, it had generally been found that the surface Fermi-level position at GaAs Schottky barriers fell in a narrow energy range near the midgap. The striking result of the wide range of barrier heights has been explained as being due to several different factors. First, the high quality of the non-arsenic-rich MBE material used resulted in a reduction of the density of electrically active near-surface defects, such as the As antisite.[5,6] In order to explain the inability of metal-induced gap states[7–11] (MIGS) to pin the surface Fermi level at the midgap, it was proposed that the (100) surface was terminated in an insulating reconstruction which would screen out these pinning states.[12] However, we find no evidence for an insulating reconstruction in our experiments. We present data which suggest that the surface may be *less* insulating (have a higher dielectric constant) than the (110) surface. Another explanation for the Schottky-like behavior, which says that the MIGS should be weak, is that of Duke and Mailhot.[13]

We also have studied the deposition of Al and Au on these surfaces and have found that there are several complications to the measurement and analysis of the data. We do not find a large range of barrier heights, but instead a difference between the two metals of only 0.25 eV, which is quite similar to the values commonly reported in the literature (Ref. 14). We only see large shifts in the surface Fermi level during the metallization of the low-doped samples which show the surface photovoltaic effect. In addition, alloying with the overlayer can cause problems in the extraction of band bending from the Au photoemission data.

EXPERIMENTAL

The photoemission experiments were performed on the grasshopper monochromator beamline III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL), beamline U3C at the National Synchrotron Light Source (NSLS), and the monochromatized He discharge lamp at Stanford Electronics Laboratories (SEL). A cylindrical mirror electron analyzer was used at the SSRL and SEL, while an angle-resolved analyzer with a relatively large aperture ($\pm 4°$) was used at the NSLS. The clean surface data, valence bands, and constant final state (CFS) data were taken at the SSRL and SEL, while the high-doped metallization experiments were performed at the NSLS. The GaAs was epitaxially grown on degenerately doped substrates, and was doped *n* type with 5×10^{16} cm^{-3} or 5×10^{18} cm^{-3} Si, and then given a protective coating of arsenic. These samples were prepared in the same laboratory as those of Ref. 1 by the same technique and were believed to be as identical as possible. The wafers were shipped from IBM to Stanford under vacuum where they were stored in vacuum at approximately 2×10^{-7} Torr. The samples were briefly (<5 min) exposed to air only long enough to be indium bonded to a molybdenum sample holder and loaded into the analysis chamber. Photoemission spectra taken before annealing show a single As 3*d* peak, and no Ga 3*d* emission, indicating that the arsenic cap was intact.

In order to remove the As coat, the samples were annealed by a resistively heated Ta filament mounted behind the Mo sample holder, and the temperature was monitored by a chromel-alumel thermocouple. In addition to the In bonding, the samples were held in front by four small Pt clips. The heating cycles were typically a 15-min ramp to the maximum temperature, which was held constant for 8 min. In all cases, the sample temperature dropped to less than 100 °C in ≈ 10 min. The maximum chamber pressure during the decapping anneal was about 1×10^{-9} Torr and dropped to between 1 and 3×10^{-10} Torr during the last few minutes of the anneal. Au and Al depositions were made using resistively heated tungsten baskets, and the thicknesses were measured using a quartz-oscillator thickness monitor. Au depositions were done at pressures in the low 10^{-10} Torr range, and the Al depositions were done in the high 10^{-10} Torr range.

PHOTOEMISSION FROM THE CLEAN SURFACE; CURVE FITTING OF THE CORE LEVELS

In order to carefully study the initial stages of Schottky-barrier formation using photoemission spectroscopy, it is necessary to take into account any surface-shifted components in the core-level spectra. This is particularly important when looking at metals which react with the semiconductor (such as Al, Au, and Cu) or metals which have core levels overlapping with the substrate peaks (as in the case of the In 4*d* and Ga 3*d* core levels in the In on GaAs system.) If the surface-shifted components of the clean surface and the reacted components caused by the overlayer are carefully accounted for, then an accurate determination of the band bending is possible.

The situation for the stoichiometric (110) surface of GaAs prepared by cleaving in UHV has been well characterized, originally in Ref. 15. The (100) case is considerably more complicated, since different surface stoichiometries result in a large number of different surface reconstructions,[16,17] and resulting different core-level surface shifts.[18] These earlier studies (Refs. 16–18) of the (100) surface were all performed on samples grown *in situ* by MBE. In the present work, and in the experiments reporting the wide range of barrier heights (Ref. 1) the samples were grown in a separate MBE chamber, and given a protective arsenic cap for transfer through air.

In Fig. 1, curve fitting of the Ga 3*d* and As 3*d* core levels are shown for the surface which is annealed at 580 °C. Each component shown is a spin-orbit-split Lorentzian line shape convolved with a Gaussian. The Lorentzian shape is the natural broadening mostly due to the lifetime of the core hole. The Gaussian broadening accounts for the instrumental resolution, and any broadening due to disorder or potential variation on the surface. The Gaussian line shape is to our knowledge the best representation for the instrumental and random atomic scale disorder. Surface potential variation is not necessarily Gaussian, but we use that approximation here.

The fits were obtained in the following manner: The Lorentzian widths were taken as a rough average from earlier reports, such as Refs. 15 and 18, and they were

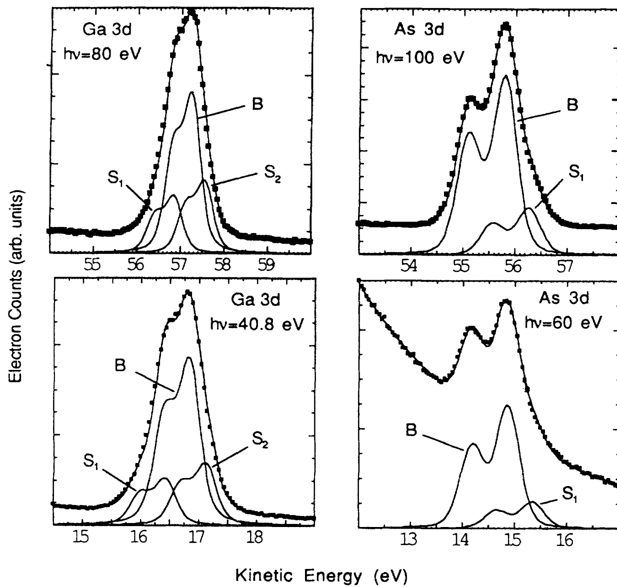

FIG. 1. Ga 3*d* and As 3*d* core-level spectra from the 580 °C annealed surface along with their decomposition into surface and bulk components. The spectra taken with the 80- and 100-eV light are slightly more surface sensitive than those taken at 40 and 60 eV. The method used to obtain the fits is described in the text, and the parameters obtained are summarized in Table I.

fixed during the fitting process. χ^2 was then minimized as a function of the Gaussian width and the energy position of the various peaks. Two constraints were imposed on the fitting. First, we required that the energy positions of the bulk peak give the same band-bending value for both Ga 3*d* and As 3*d*. This was done by fitting the Ga 3*d* and As 3*d* peaks from the (110) vacuum-cleaved surface which was in the flat-band condition, so that the band bending of the (100) surface could be obtained from the difference in binding energy between the (110) and (100) bulk components. As a second constraint, the Gaussian widths for all components in a given spectrum were assumed to be the same.

The assumption of the same Gaussian width for all components within a spectrum is not ideal. As stated above, the Gaussian width represents the experimental resolution, disorder on the surface, and any potential variation across the surface. The assumption that the Gaussian width should be the same for all components within a single spectrum is correct for the instrumental broadening. For the case of broadening due to *random* disorder (in the absence of a macroscopic surface potential variation), the Gaussian will be a good function but will apply only to the surface components, since the bulk component should remain unbroadened. The case of a varying surface potential is even more complicated. There is no reason to expect such a distribution to be Gaussian. Also, regions of the surface having a particular surface-shifted component may have correspondingly different types or densities of surface electronic gap states and therefore different band bending. In any case, attempts to allow the Gaussian widths to vary independently resulted in nonphysical fits for the minimum χ^2, and probably represent an attempt to extract more information from the curve fitting than is actually contained in the spectrum.

The parameters which resulted from this procedure are summarized in Table I. In both the case of the Ga 3*d* and As 3*d*, the Gaussian width is significantly broader than the experimental resolution, indicating that there is indeed significant disorder and/or surface potential variation. The Gaussians for the (110) Ga 3*d* (80-eV photons) and As 3*d* (100-eV photons) for the same experimental apparatus were 0.28 and 0.39 eV, respectively, which means that the corresponding (100) peaks have an additional Gaussian broadening of 0.22 and 0.26 eV (see Ref. 19). In light of this, it is interesting to note that scanning tunneling microscope (STM) experiments on As-rich terminations prepared from As-capped samples[20] show significantly more disorder than those which were grown *in situ*.[17] Also, Ludeke, Chiang, and Eastman[18] did not seem to observe such broadening in their photoemission spectra from *in situ* prepared (100) surfaces. The similarity of the Ga 3*d* and As 3*d* broadening would seem to favor the explanation of surface potential variation, but it may simply be a coincidence.

Fits using different numbers of components were explored, in particular, the addition of a third component and narrower Gaussian widths for the As 3*d*. Although this method gave good fits to the data, it was rejected because of poor band-bending agreement and poor behavior as the surface sensitivity was varied. While this paper was being reviewed, a paper that discusses the fitting of the clean surface in detail was published.[21] For our purposes, it is only necessary to know that the surface com-

TABLE I. Parameters used in the fitting of the Ga 3*d* and As 3*d* core levels in Fig. 1. The procedure used in the fitting process is described in the text.

	Ga 3*d* (80-eV photons)	Ga 3*d* (40-eV photons)	As 3*d* (100-eV photons)	As 3*d* (60-eV photons)
Lorentzian FWHM (eV)	0.18	0.18	0.14	0.14
Gaussian FWHM (eV)	0.35	0.32	0.47	0.47
% area bulk (B)	55	61	79	85
% area surface (S_1)	20	17	21	15
% area surface (S_2)	25	22		
Energy shift (eV) (S_1)	−0.41	−0.40	+0.46	+0.47
Energy shift (eV) (S_2)	+0.29	+0.28		

ponents are there so that we can account for them while analyzing the band bending and chemistry at the surface and metal interfaces.

THERMAL DESORPTION OF THE As COATING

We now turn to the desorption of the protective As coat. Wafers which have been given a protective arsenic "cap" have a diffuse white appearance. When the samples are heated to remove this cap, the thick layer can be seen by eye to disappear at about 300 °C. We found that if the sample was in good thermal contact with the Mo sample holder that the cap would simply "fade" away, but that if the thermal contact were poor, or nonuniform, that it would appear to slowly "peel" from one corner. Nonuniformity will certainly be worse at the higher annealing temperatures, and must be avoided. We were able to ensure that our thermal contact was good by uniformly indium bonding the backs of all of the samples to their molybdenum holders. Between the temperature at which the thick As cap desorbs and the decomposition temperature of about 650 °C, the surface goes through a wide range of stoichiometries and several surface reconstructions.[16–18]

The Ga 3*d* and As 3*d* spectra taken for different annealing temperatures are shown in Fig. 2. The As 3*d* undergoes the most dramatic changes, since the effect of increasing the annealing temperature is to desorb As from the surface. In Fig. 3(a) the As 3*d* taken after the 300 °C and 450 °C anneal are shown along with their difference. The 450 °C anneal removes a peak which most likely arises from two components: (1) excess As atoms which are bonded primarily to other As atoms and (2) As from the As dimers which terminate the As-rich reconstructions.[17,20] In Fig. 3(b) the 450 °C spectrum is deconvolved into its bulk and surface components, with the higher-binding-energy (lower-kinetic-energy) component consisting of the dimers only. Annealing to 580 °C completely removes the higher-binding-energy surface As component, but leaves the surface-shifted peak at lower binding energy unchanged.

The bottom curves in Figs. 2(a) and 2(b) show the core-level spectra taken after annealing above the GaAs decomposition temperature. In the Ga 3*d* spectrum, a

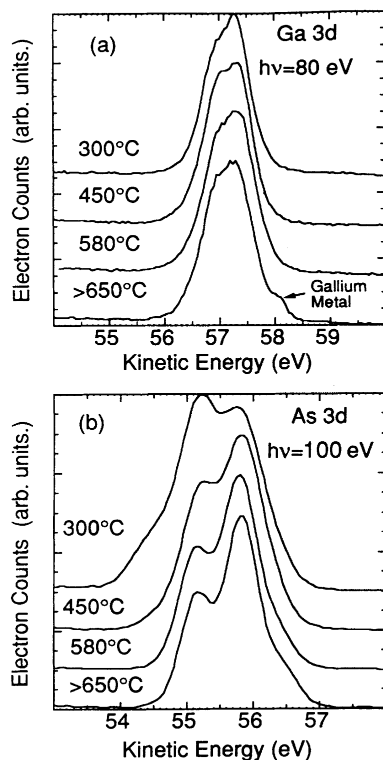

FIG. 2. Surface-sensitive Ga 3*d* and As 3*d* spectra taken for different As desorption temperatures. Above 650 °C, the surface begins to decompose, releasing volatile As species and forming Ga clusters on the surface. The Ga clusters result in the small component seen on the low-binding-energy side of the Ga 3*d* spectra. The 300 °C anneal is the temperature at which the thick protective layer is visibly seen to disappear. This spectra is shown in more detail in Fig. 3(a). The spectra are all normalized to each other.

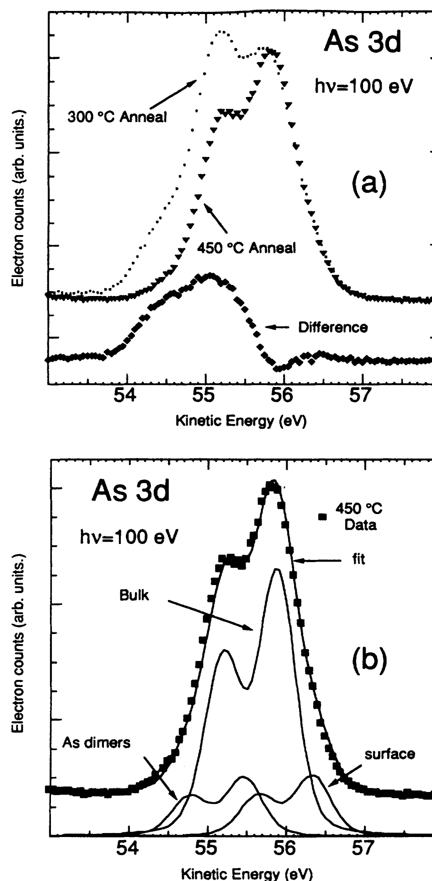

FIG. 3. A more detailed look at the 300 °C and 450 °C As 3*d* specta. In (a), the 300 °C and 450 °C anneals are shown along with their difference. The difference is attributed to both As atoms left on the surface which are bonded primarily to other As atoms, as well as dimers from the As-terminated reconstructions. In (b), the 450 °C spectra is separated into its surface and bulk components. The higher-binding-energy surface component is in this case due only to the dimers.

component due to metallic Ga clusters appears. We interpret this data as being the result of the surface decomposing into volatile As species and the metallic Ga clusters. Despite the fact that As is being removed, the low-binding (high-kinetic) -energy surface component in the As 3*d* remains at full strength. This seems to indicate that a maximum Ga to As ratio for the (100) GaAs (as opposed to decomposed) surface is already achieved after the 580 °C anneal.

In Fig. 4, valence-band spectra taken at a photon energy of 47 eV are shown for the 300 °C and the 580 °C anneals. These spectra are very surface sensitive, with the signal coming from the last two or three atomic layers of the crystal. It is somewhat surprising that there is no significant difference between the two spectra, since we can see from the corresponding As 3*d* spectrum in Fig. 2 that the stoichiometry of the two surfaces is very different. This means that (1) the valence bands are not particularly useful as a test of how completely the As cap has been removed, and (2) the electronic density of states of the As-terminated surface is not dramatically different from the predominantly Ga-terminated surface.

Although the valence bands are not sensitive to arsenic, they are extremely sensitive to contamination due to oxygen. As an example, we show the effect of oxygen on a different GaAs kind of (100) surface. Valence-band spectra taken from GaAs (100) prepared by etching and heat cleaning are shown in Fig. 5 with no oxygen, and with a fraction of a monolayer of oxygen. The oxidized surface was prepared as follows: After heat cleaning it was exposed to roughly 10^6 langmuirs (1 L $=10^{-6}$ Torr s) (Ref. 23) of oxygen and then annealed at 400 °C, which is hot enough to remove the As oxides but not the Ga oxides.[24] A very strong feature due to the gallium oxides appears at about 6 eV below the valence-band maximum (VBM). The presence of As oxides would broaden the peak on the lower-kinetic-energy side. This feature is much more sensitive than the core levels and can be used as a test of the integrity of the As cap. If the capped samples are left in the atmosphere, they will be degraded and allow the GaAs to oxidize. This will occur in a few days or even hours in a sufficiently humid environment. Small amounts of oxygen contamination can be thermally desorbed from the GaAs surface in the 550 to 600 °C temperature range. Since we stored our samples at $\approx 10^{-7}$ Torr, we never observed any features due to oxygen on the surfaces used in these experiments.

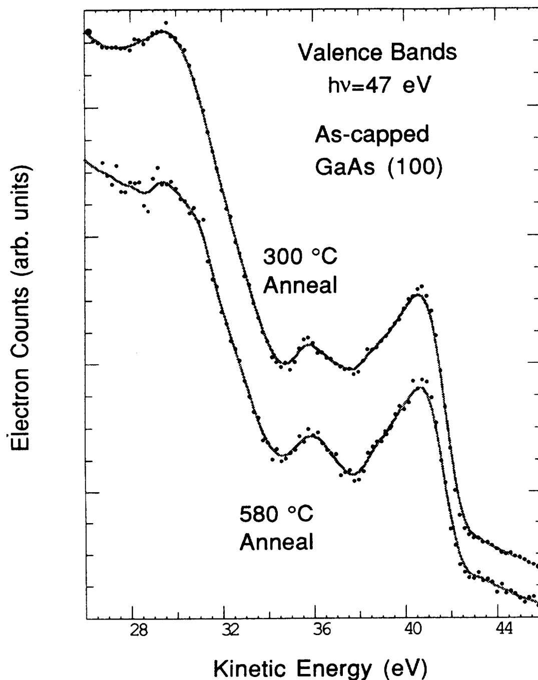

FIG. 4. Comparison of the valence-band spectra taken after the 300 °C anneal and 580 °C anneal. Despite the large amount of excess As on the 300 °C surface, there is no significant difference in the two spectra.

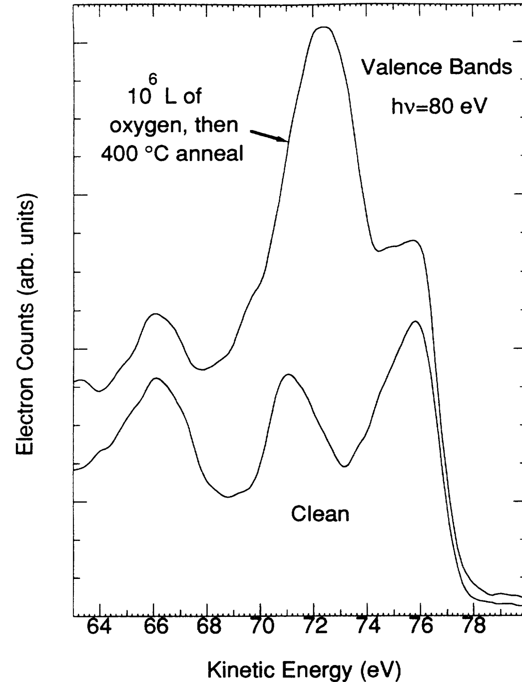

FIG. 5. Example of the presence of oxygen in the valence-band spectra. These spectra are not from As capped samples, but rather from a sample which was etched and heat cleaned to remove all oxygen. The lower spectra is the heat-cleaned surface which has no oxygen. The upper spectra is the same surface after exposure to 10^6 L (Ref. 22) of oxygen and heating to 400 °C to remove the As oxides, but not the Ga oxides. The peak roughly 6 eV below the VBM is due to the Ga oxide. Without the 400 °C anneal, the As oxides would broaden this feature to the lower kinetic-energy side.

ELECTRONIC STRUCTURE OF THE 580 °C ANNEALED SURFACE

The result of barrier heights which vary strongly with the overlayer work function is inconsistent with the metal-induced gap states (MIGS) model of interface states for ideal metal-semiconductor interfaces as calculated for jellium or aluminum.[7–11] Because of this, it was

suggested that the surface reconstruction served as an insulating layer,[12] which could prevent the MIGS from "pinning" the GaAs at midgap. This interface was described as a metal-insulator-semiconductor (MIS) structure. However, there is no direct experimental evidence to support this claim. Here we address what we feel are problems with this model, and then present data which suggest that the surface is not insulating.

The data which led to the suggestion of an insulating reconstruction was taken from the formation of Au, Cu, Al, and In Schottky barriers. If we start with the assumption that the clean surface has an insulating reconstructed layer, we must further assume that this insulating layer remains intact after metal deposition. It is clear that Al, Au, and Cu all react with and disrupt the GaAs surface. Because of this, it is difficult to understand how an insulating reconstruction could survive in all of these cases. Furthermore, it is difficult to understand why indium, the one metal used which does *not* react strongly with the GaAs, shows the highest interface state density (see Fig. 4 of Ref. 1), and the least Schottky-like behavior (see Fig. 3 of Ref. 1).

It is interesting to compare the electronic structure of the (100) surface directly to a (110) cleave, which is known to *not* have an insulating reconstruction. The valence states of the two surfaces are compared in Fig. 6. The spectra have been shifted to remove the difference in band bending at the two surfaces. As in the comparison of different annealing temperatures, there is no dramatic difference, despite the fact that the signal is dominated by the first two or three atomic layers of the material. However, to remove the MIGS pinning effect by providing an "insulating" gap as suggested in Ref. 12, the effective

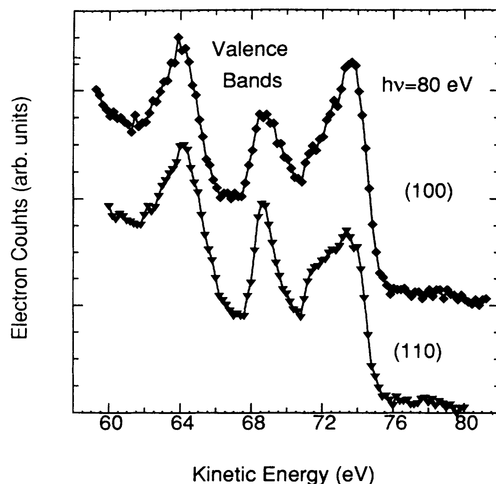

FIG. 6. Comparison of surface-sensitive valence bands for the 580 °C annealed (100) surface and the cleaved (110) surface. The spectra have been aligned to remove the difference in band bending. The signal comes almost entirely from the last two or three atomic layers of the material. If the (100) were to have an insulating surface reconstruction, a shift in the density of states away from the band gap should be expected. In this case a small shift *toward* the gap is observed, which would tend to increase the susceptibility to MIGS.

band gap would have to increase by *several eV*. Thus, one would expect a dramatic effect, which could be easily seen in the surface-sensitive density of states. This is clearly not seen in Fig. 6. One can argue, even though the valence-band (VB) shows no evidence of becoming insulating, that an insulating surface layer could result from the conduction-band minimum (CBM) raising strongly. This seems unlikely since the high density-of-states region associated with the X and L points lie only a few tenths of an eV above the CBM at Γ. Although the low density of states at Γ can be moved in energy (by applying pressure, for example), the high density of states near X and L, which are more important for MIGS (Ref. 25), have proven very resistant to movement in energy.

SCHOTTKY-BARRIER MEASUREMENT USING PHOTOEMISSION

Photoemission has been used extensively by many workers to measure band bending in semiconductors as a function of the deposition of various materials. This is typically done by monitoring the movement of electronic core levels, such as the As $3d$ and Ga $3d$. The binding energy of these core levels will shift with the bending valence and conduction bands, while the Fermi level remains fixed with the system ground.

During our studies of the Schottky-barrier formation, several difficulties became apparent. Since our samples were identical to those in Ref. 1, these difficulties must have also been present in that prior work.

As we stated above in the experimental section, we set out to study samples which were as identical as possible to those used in Ref. 1. The first wafer we looked at was made to the specifications of the earlier investigators, and was an n-type epilayer doped with 5×10^{16} cm^{-3} Si. We studied the deposition of several different metals on samples taken from this wafer and found that the photoemission peaks moved around significantly, suggesting that there was a great deal of movement in the surface Fermi level with metal deposition. Eventually we realized that the large shifts in the photoemission peaks were not due to movement of the dark Fermi level, but rather to photovoltaic band flattening[2,3] caused by electron-hole pair formation. This was at first surprising, since the calculations[2] indicated that for our photon flux[26] ($\approx 10^{11}-10^{12}$ photons $\mathrm{S}^{-1}\,\mathrm{cm}^{-2}$ corresponding to a J_{cp0} of $10^{-7}-10^{-6}$ $\mathrm{A\,cm}^{-2}$ in Ref. 2) there should be no photovoltaic effect at room temperature, even for doping as low as 1×10^{16} cm^{-3}. The calculations of Ref. 2 were made for a typical barrier height of 0.65 eV, and showed that there will be a photovoltaic shift in the spectra for temperatures at or below 250 K. Above this temperature, thermionic emission of electrons from the bulk to the surface will prevent the development of a large photovoltage, and the measurements will give the true, dark band bending. The difference is that the n-type barrier height in our case is closer to 0.85 eV. This is important because the barrier height appears exponentially in the equations of Ref. 2 along with the temperature. The effect of this barrier-height difference will be roughly to shift the temperature

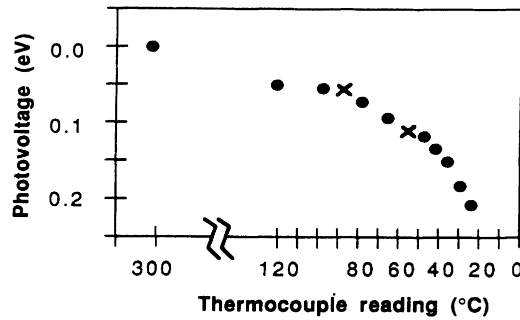

FIG. 7. The photovoltage as a function of temperature for the clean surface as monitored by the As $3d$ shift. The circles are taken while the temperature is decreasing. The ×'s are taken upon reheating to show the reversibility of the effect. This is a simple method of checking for photovoltages at room temperature (note the break in the temperature axis).

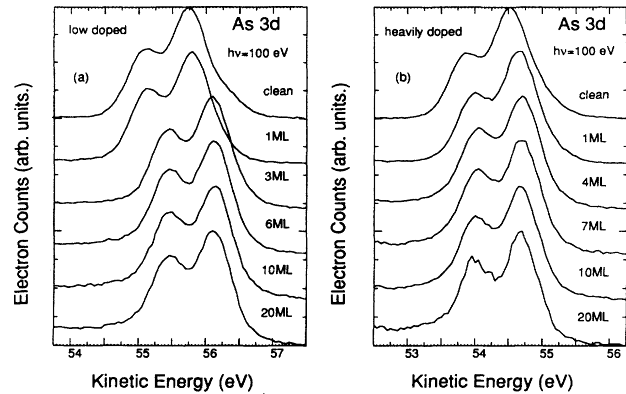

FIG. 8. As $3d$ vs Au coverage for (a) lightly and (b) heavily doped n-type GaAs. Note that the shifts are completed at coverages below 3 ML. The larger shifts in the lightly doped case are due to the shorting out of the photovoltage by the Au overlayer. The spectra are all normalized to each other.

dependence by a factor of 0.85/0.65, meaning that the onset of the photovoltaic effect will occur at closer to 327 K, or 54 °C. A simple way to check for photovoltages at room temperature is to take spectra as a function of increasing temperature and look for shifts. A plot of the change in the As $3d$ peak position with temperature (whose shift represents the apparent change in barrier height due to the photovoltaic band flattening) is given in Fig. 7. This reversible shift during cooling and warming conclusively shows the surface photovoltage at 25 °C.

This effect could result in an increased range of initial positions for the measured Fermi level, such as is reported in Ref. 1. In UHV, the sample will tend to equilibrate to room temperature slowly through the last 50 °C or so. Depending on how long the sample was allowed to cool, the measured surface Fermi-level position can vary over a range of a few tenths of an electron volt.

By way of summarizing this section, photoemission spectra from low-doped samples are unreliable unless extreme care is taken to measure the photovoltage accurately and account for it. It makes far more sense, however, to simply do the experiments on more heavily doped material.

ALUMINUM AND GOLD SHOTTKY BARRIERS

Of the barrier heights reported in Ref. 1, Au is the most different from previous reports of metal contacts on GaAs. We have studied Au deposition on both $n = 5\times10^{16}$ cm^{-3} and $n = 5\times10^{18}$ cm^{-3} doped layers. The raw As $3d$ data is shown for the low-doped sample in Fig. 8(a), and the heavily doped sample in Fig. 8(b). The most striking difference is of course the large shifts seen in the early coverages for the lower-doped samples. The band bending is plotted as a function of coverage in Fig. 9. We find that the final band-bending value is reached by the 2 ML coverage for the low-doped case, and by the 1 ML coverage in the heavily doped case. The total change in barrier height for the heavily doped case is only 0.15 eV, while in the lightly doped case, the change is a more substantial 0.35 eV. Note that this difference in energy is just what we measured for the photovoltaic band flattening in Fig. 7. In the case where the photovoltage is important, the larger shifts occur when the deposition "shorts out" the photovoltage by providing an alternate electrical path from the surface to ground. This shorting out process will depend on the exact details of sample mounting and overlayer morphology and could vary from experiment to experiment.

The measurements of Ref. 1 indicated that additional Fermi-level movement occurs at higher Au coverages, even above 10 Å. Although this is not the case in our experiments, it is true that the centroid of the Ga $3d$ peak continues to shift to higher kinetic energy, the direction which indicates increased band bending on n type. This can be seen for the heavily doped Ga $3d$ spectra in Fig. 10. This shift led to reports of anomalously high barrier heights in earlier work on cleaved GaAs(110).[27] These reports of high barrier heights were subsequently proven incorrect as is documented extensively in Ref. 28. The reason for this shift is not band bending, but rather the formation of Au-Ga alloys when the Au reacts with the

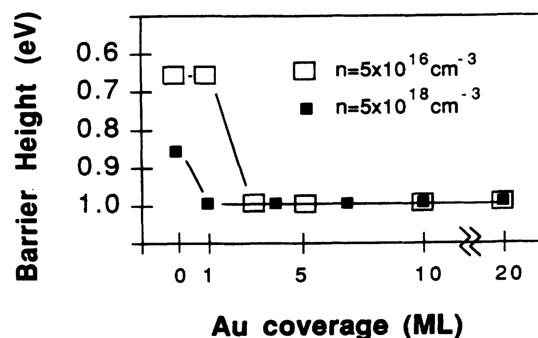

FIG. 9. Plot of the Schottky-barrier height vs Au coverage for the light and heavily doped case. The large shifts and different starting position of the low-doped case is due to the photovoltaic shift, and its subsequent removal by Au deposition.

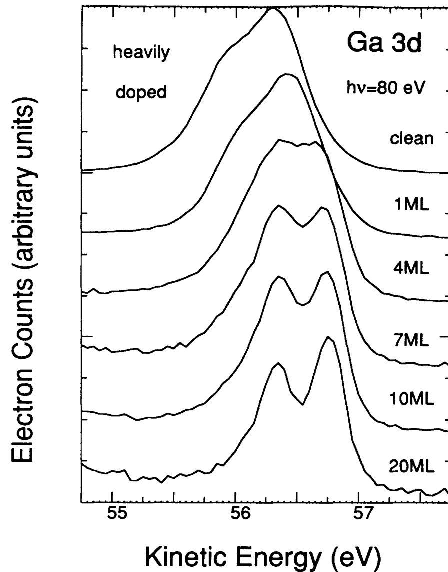

FIG. 10. The Ga 3*d* spectra corresponding to the As 3*d* in Fig. 8. Note that the centroids of the spectra continue to shift at coverages which are higher than the band-bending saturation coverage. This is due to the formation of clusters of a Au-Ga alloy.

GaAs. In Fig. 11, the true band bending is compared to the band bending obtained by simply following the centroid of the Ga 3*d*. This shift is the reason for the incorrect high barrier heights reported in Ref. 27, and also strongly resembles the barrier height versus Au coverage curves of Ref. 1. Such shifts do not occur in the As 3*d*'s as can be seen from Fig. 8(b) (see also Ref. 28). The position of the As 3*d* gives the correct band bending despite the fact that at high coverages the signal is from As which has segregated to the surface of the Au rather than As in the underlying GaAs. It is by coincidence that the binding energy of this reacted As is the same as that of the As in the GaAs.[29]

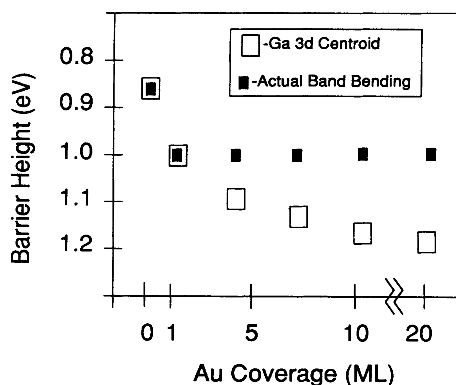

FIG. 11. Band bending vs Au coverage as determined correctly (solid squares) or by following the Ga 3*d* centroid (open squares). The additional "band bending" determined by the Ga 3*d* centroid is due to the changing chemical environment of Ga in the Au-Ga alloy.

There are other indications that the Au-Ga may have been misinterpreted in Ref. 1. In the caption for Fig. 1, it says that the spectra which are taken with a final kinetic energy of ≈ 15 eV are "bulk sensitive" and "exhibit rigid shifts due to band bending." However, it is known that electrons at this kinetic energy are still very surface sensitive, with an escape depth of ≈ 6 Å, compared to the "surface-sensitive" electrons in the 50–60-eV range which have an escape depth of ≈ 4.5 Å.[30] Because of this, the 15-eV kinetic-energy spectra will be dominated by the Au-Ga alloying, nearly to the extent that the 50–60-eV spectra are.

The Ga 3*d* spectra in Fig. 10 were taken at $h\nu = 80$ eV and have a kinetic energy of ≈ 55 eV and therefore a very short escape depth of ≈ 4.5 Å. Because of this, the signal comes almost entirely from Ga atoms in the Au-Ga alloy on the surface. By going to very low kinetic energies, we can increase the escape depth to roughly 30 Å and get significantly more signal from the bulk GaAs.[31] The Ga 3*d* spectrum taken at a constant-final-state (CFS) kinetic energy of 3 eV are shown in Fig. 12. Whereas the photoemission spectra are taken by fixing the photon energy and counting electrons as a function of the electron kinetic energy, the CFS spectra are taken by fixing the kinetic energy and counting electrons as a function of photon energy. The spectra are interpreted similarly, with the higher kinetic-energy features corresponding to the low photon energies in the CFS spectrum. At the kinetic energy of 3 eV, the increased escape depth of the electrons means that the measurement samples a greater depth into the material. This increased bulk sensitivity results in a spectrum which can clearly be separated into a component from the Ga atoms in the GaAs (which give the band bending), and a component which is from Ga atoms which are incorporated in the Au-Ga alloy and dominate the surface-sensitive photoemission spectra at high coverages. This spectrum shows clearly that the continued shift of the Ga 3*d* centroid is due to an alloying effect rather than true band bending.

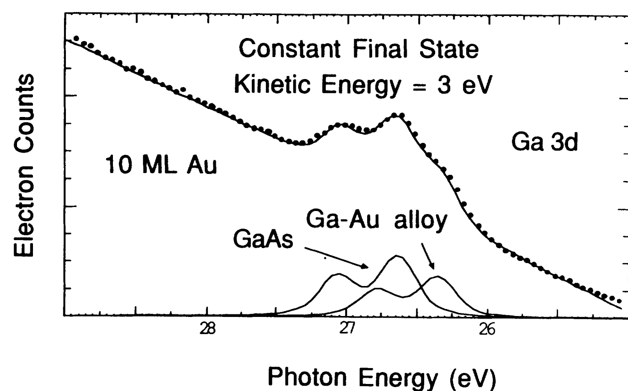

FIG. 12. Constant final state (CFS) Ga 3*d* spectrum for 10 ML of Au. In this spectrum the kinetic energy is set at 3 eV, and the photon energy is varied. The spectrum is far more bulk sensitive due to the reduced inelastic scattering at low kinetic energies. With this greater bulk sensitivity, the Ga 3*d* signal from Ga atoms can be clearly separated from the shifted Ga 3*d* in the Au-Ga alloy (Ref. 31).

The deconvolution of the Ga 3d and As 3d spectra into their various components are shown in Fig. 13. The band bending is most easily obtained from the As 3d, shown in Fig. 13(a), which shows spectra from the clean surface, and after depositions of 4 and 10 ML of Au. After 4 ML, the surface component is almost completely removed, and a segregated As signal begins to appear at the same energy as the bulk As.[29] At 10 ML, the surface component is completely removed, and the spectrum is entirely due to bulk and segregated As, which gives the band bending.

The Ga 3d, shown in Fig. 13(b), is much less straightforward to analyze. The 4 ML deposition removes the surface components, and a large reacted component is seen due to the Au-Ga alloying. After 10 ML, the spectrum is dominated by the reacted component. Although the two components are difficult to separate because they are so close in energy, we can use the bulk-sensitive spectrum in Fig. 12 and the band-bending information from the As 3d to easily get a consistent deconvolution.

The deposition of Al results in the usual Ga replacement reaction, but is easier to analyze than the Au. The deconvolution of the As 3d and Ga 3d spectra are shown in Figs. 14(a) and 14(b), respectively. We find a final barrier height of 0.75 eV, which is the value typically found in the literature for either (100) or (110). There is some clustering of the Al, as is shown by the persistence of the As 3d surface shift (S) and the S_2 Ga 3d surface shift. This behavior would seem to indicate a growth mode where the Al clusters over areas of the surface with Ga atoms giving the S_1 surface shift, leaving bare GaAs in areas with surface-shifted As and S_2 Ga. This is only

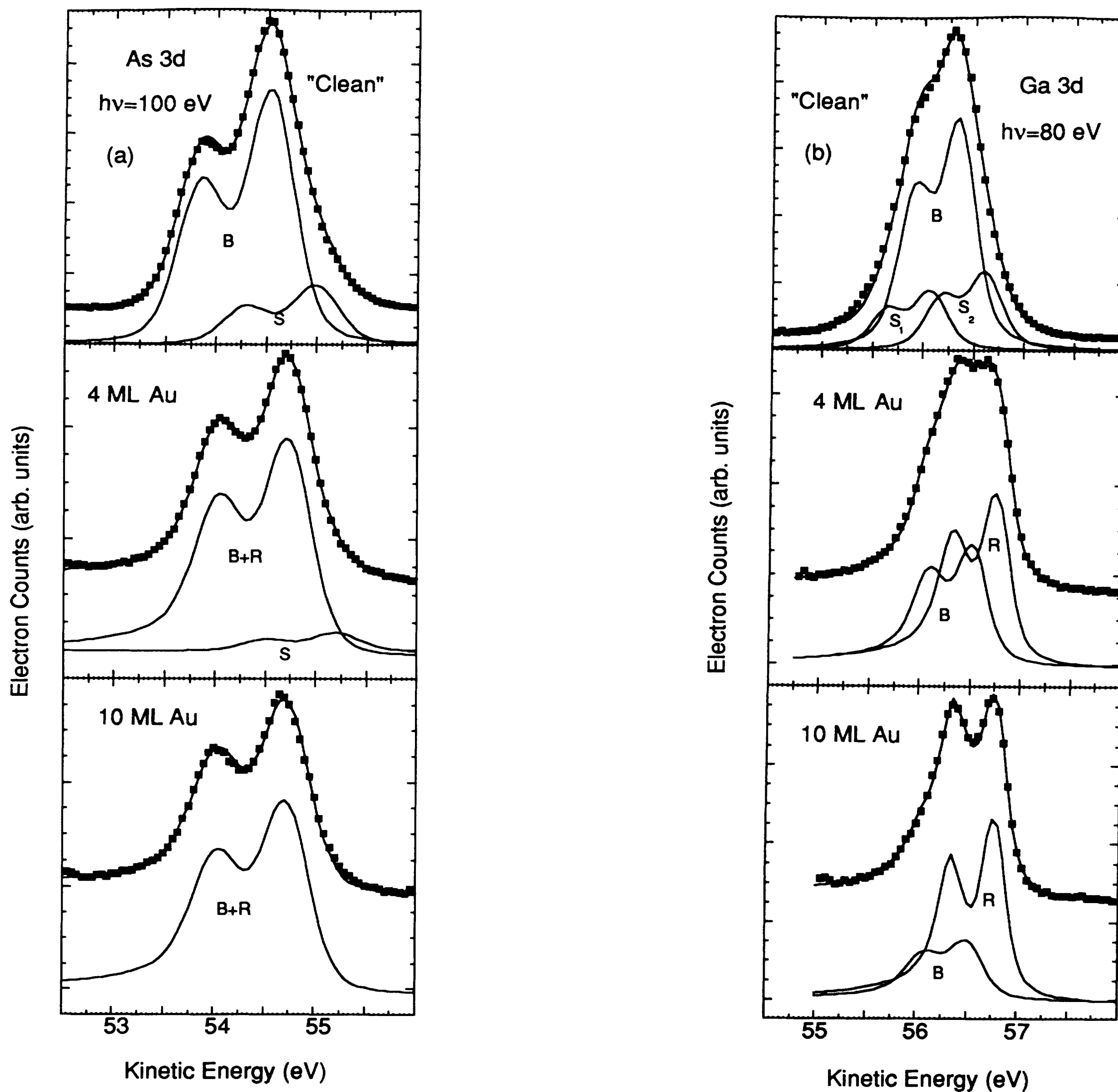

FIG. 13. (a) Curve fits of the As 3d as a function of Au deposition. Shown are the bulk (B) GaAs signal, surface As (S), and reacted As (R) signals. The bulk and reacted signals have the same binding energies and are shown as a single peak. (b) Curve fits of the Ga 3d as a function of Au deposition. The bulk GaAs (B) component and surface-shifted (S_1 and S_2) components are shown in the clean spectra, and the reacted (R) Au-Ga alloy is shown along with the bulk after Au deposition. By 10 ML, the spectrum is dominated by the Au-Ga alloy component (Ref. 31).

speculation, and knowledge of the exact origin of these peaks is not necessary for the determination of the band bending.

In Fig. 15 we show the band bending versus coverage curves which result from experiments which do not have photovoltaic shifts, and for which chemistry and alloying are carefully accounted for. As indicated, we find only a 0.25-eV difference in barrier height between Al and Au, which is in sharp contrast to the 0.75 eV reported earlier. While we have discussed possible reasons for the difference in the Au barriers, we have yet to address the 0.25-eV difference in the Al case. The most likely candidate is the presence of the photovoltaic band flattening. While Au is known to form leaky diodes, even at very low temperatures,[22] Al seems to remain unshorted even at high coverages. In fact, it has been shown that at low temperature the bands can remain flat due to photovoltages even at the highest Al coverages.[22] Although this result was not interpreted in Ref. 22 as being due to a surface photovoltage, it seems in retrospect to be the best explanation. In the present room-temperature case, a smaller effect could explain the difference. In any case, the photovoltaic effect casts serious doubt on any claim of unusually low barrier heights measured by photoemission on low-doped samples.

The clean spectra for the Au and Al experiments bring us back to the question of the large range of initial barrier heights for the starting surfaces reported in Ref. 1. Although some of this 0.35-eV range is probably due to the presence of photovoltages (PV), the range is slightly too

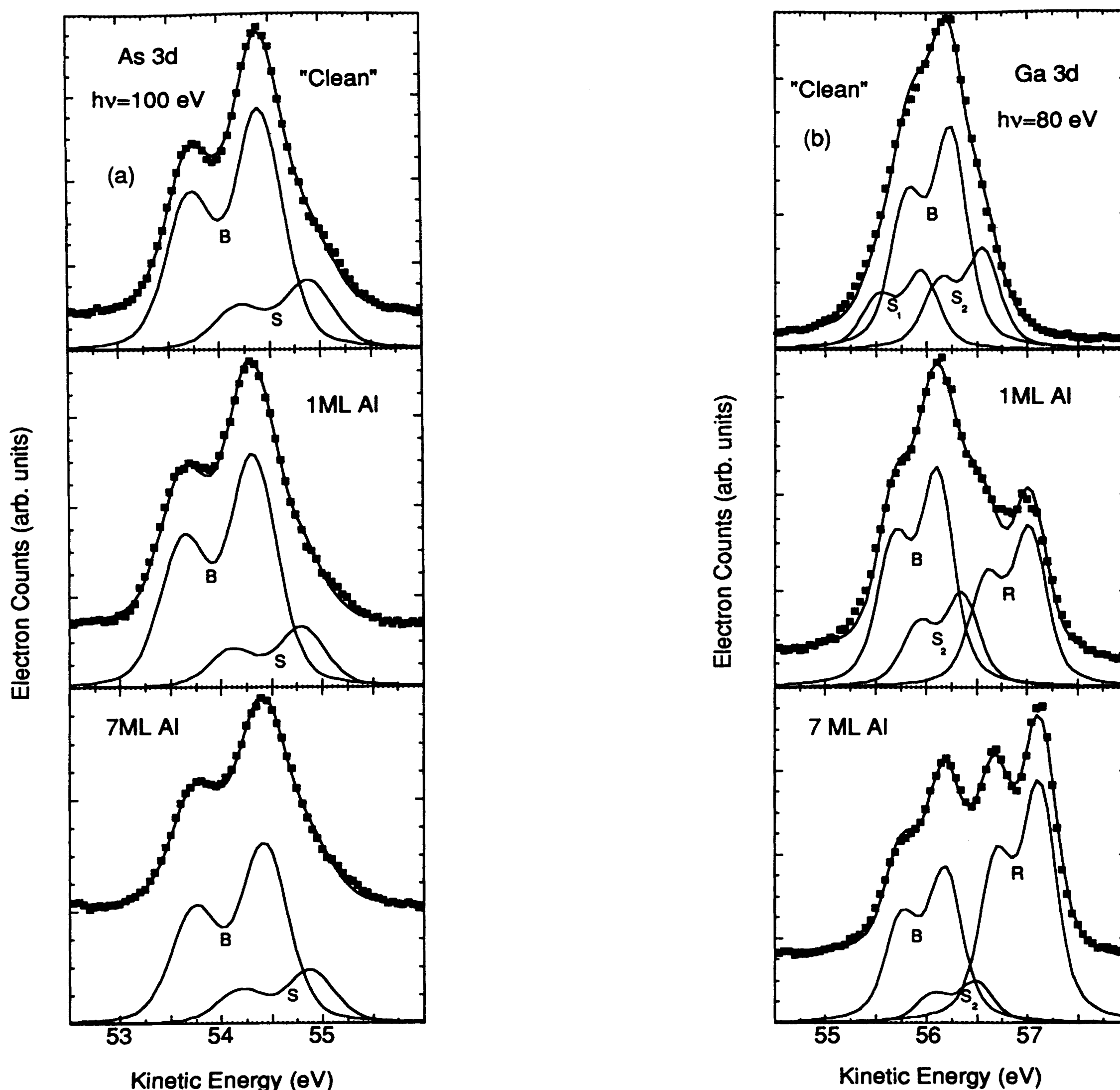

FIG. 14. (a) Curve fits of the As 3*d* as a function Al deposition. The two components are from the bulk (*B*) of the GaAs, and the surface As (*S*). The surface signal persists at the higher coverages, showing that there is some clustering of the Al. (b) Curve fits of the Ga 3*d* as a function of Al deposition. The bulk GaAs (*B*) component and surface-shifted (S_1 and S_2) components are shown in the clean spectra, and the reacted (*R*) Ga due to the replacement of Ga atoms by Al is shown along with the bulk after Al deposition. The S_2 component persists at higher coverage, as does the As surface component (Ref. 31).

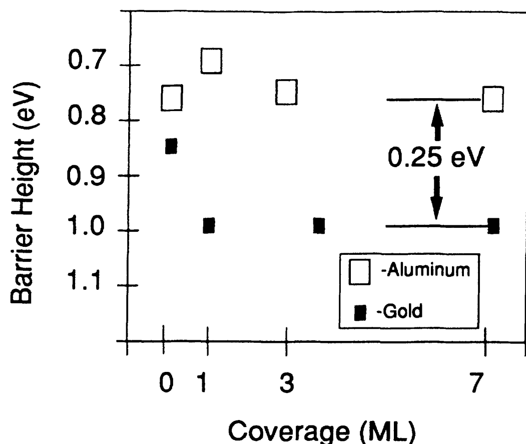

FIG. 15. Band bending vs Al and Au coverage determined for the heavily doped samples. In the absence of photovoltaic effects there are no large shifts with coverage and the difference between the two metals is only 0.25 eV.

large to be due completely to the PV. In Fig. 15 the initial starting point for Al is nearly 0.1 eV closer to the VBM than the Au case. This starting difference would seem to increase the possibility of obtaining a large difference in the final barrier heights, but despite this we see only the 0.25-eV difference between the final Au and Al barriers.

SUMMARY AND CONCLUSIONS

We have studied both the clean surface and Schottky-barrier formation on GaAs (100) surfaces which have been prepared by the thermal desorption of a protective As "cap." These samples have been grown and capped identically to those which were reported to show a wide range of Schottky-barrier heights.

We have studied the temperature dependence of the decapping process, and have found that a wide range of surface stoichiometries can be obtained in the 300–600 °C temperature range. The best measure of the surface stoichiometry is found to be the low-kinetic-energy shoulder of the As 3*d*. The valence bands are found to be relatively insensitive to the annealing temperature and surface stoichiometry, but are an excellent test for oxygen contamination. The 580 °C annealed (100) surface is compared to the (110) cleaved surface, and it is found that there is no evidence for an increase in the band gap or decrease in the high-frequency dielectric constant due to an insulating reconstructed layer.

Although prior workers (Ref. 1) reported a range in barrier heights of as much as 0.75 eV for Al and Au, we find a difference of only 0.25 eV for the two metals. Our study of *n*-type samples which were doped with the same density as was used in Ref. 1 showed that there is a significant photovoltage due to the photoemission measurement. The low-doped samples which show the photovoltaic effect were also the only samples which showed large shifts in the apparent Fermi-level position. We point out that the Au experiments have the additional complication that the Ga 3*d* continues to shift beyond the coverage at which the Fermi level stabilizes, giving the false impression of increased band bending on *n* type. From this we must conclude that the differences between the results reported here and those reported in Ref. 1 are due to differences in interpreting core-level shifts caused by photovoltaic effects and chemistry.

ACKNOWLEDGMENTS

We would like to thank Ron Morris, Ann Waldhauer, Rick Gaylord, and Dave Shuh for their help in performing the experiments. C. J. Spindt was supported by IBM, as was K. E. Miyano. This work was supported by the joint DARPA and ONR Contract No. N00014-83-K-0073. Experiments were performed at SSRL which is supported by the U.S. Department of Energy, and at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Material Sciences and Division of Chemical Sciences under Contract DE-AC02-76CH00016.

APPENDIX

It is well known that the (100) surface can be terminated in many different reconstructions, depending on the surface stoichiometry and surface treatments. The authors of Refs. 1 and 22 report that they have a very special surface-preparation technique based on the thermal desorption of an As cap. It is claimed that "unpinned" Schottky barriers can be grown on the resulting surface. Such a capability would represent a major advance in surface engineering. Although these special surfaces have not been extensively characterized, we have tried to look carefully at the data which has been published.

As we have shown earlier in the text, the As 3*d* is the key feature in photoemission for determining the

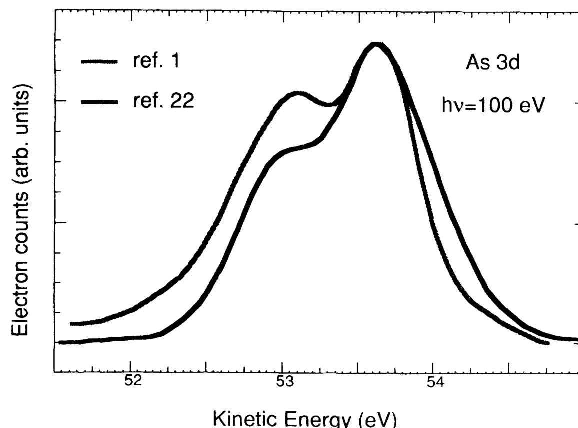

FIG. 16. Comparison of As 3*d* spectra reproduced from Refs. 1 and 22. The spectra have been shifted and normalized to align their maxima. Comparison with Figs. 2 and 3 make it clear that the annealing temperatures and resulting amount of excess As are very different.

stoichiometry of the surface. In Figs. 2 and 3 we show how the line shape changes as the annealing temperature is increased and excess As is removed (see also Ref. 21). The only clean As 3*d* published by Brillson's group are presented in Refs. 1 and 22. We have digitized these spectra and overlayed them for comparison in Fig. 16. It is clear from this figure that the two surfaces are quite dissimilar. The spectrum from Ref. 22 is similar to our 580 °C spectrum. However, comparison of the spectra from Ref. 1 with Fig. 2(b) of this paper shows that their surface appears to have been annealed at a temperature between 300 and 450 °C, leaving a significant amount of excess As. This excess As can clearly be seen on the low-kinetic-energy side of the spectrum. It is our opinion that this large difference in the two representative spectra that have been published casts serious doubt on any claim of a special surface treatment. At the very least, it would appear that whatever is done to obtain the wide range of Schottky-like barrier heights is independent of the surface stoichiometry and reconstruction. Since the surface stoichiometry does not seem to be crucial for obtaining the wide range of barrier heights on As cap-produced surfaces, it should be an easy result to reproduce. However, we find after removing the extraneous effects of alloying and SPV that the metals span only a narrow 0.25-eV range.

---

[1]L. J. Brillson, R. E. Vituorro, C. Mailhiot, J. L. Shaw, N. Tache, J. McKinley, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. L. Wright, J. Vac. Sci. Technol. B **6**, 1263 (1988).

[2]M. H. Hecht, Phys. Rev. B **41**, 7918 (1990).

[3]M. Alonso, R. Cimino, Ch. Maierhofer, Th. Chasse, W. Braun, and K. Horn, J. Vac. Sci. Technol. B **8**, 995 (1990).

[4]S. Chang and L. J. Brillson (private communication).

[5]W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. **16**, 1422 (1979).

[6]W. E. Spicer, Z. Lilliental-Weber, E. Weber, N. Newman, T. Kendelewicz, R. Cao, C. McCants, P. Mahowald, K. Miyano, and I. Lindau, J. Vac. Sci. Technol. B **6**, 1245 (1988).

[7]Volker Heine, Phys. Rev. A **138**, 1689 (1965).

[8]Steven G. Louie and Marvin L. Cohen, Phys. Rev. B **13**, 2461 (1976).

[9]C. Tejedor, F. Flores, and E. Louis, J. Phys. C **10**, 2163 (1987).

[10]J. Tersoff, Phys. Rev. Lett. **32**, 465 (1984).

[11]J. Tersoff and Walter A. Harrison, J. Vac. Sci. Technol. B **5**, 1221 (1987).

[12]J. L. Freeouf, J. M. Woddall, L. J. Brillson, and R. E. Viturro, Appl. Phys. Lett. **56**, 69 (1990).

[13]C. B. Duke and C. Mailhot, J. Vac. Sci. Technol. B **3**, 1970 (1985).

[14]J. R. Waldrop, J. Vac. Sci. Technol. **2**, 445 (1984); Appl. Phys. Lett. **44**, 1004 (1984).

[15]D. E. Eastman, T. C. Chiang, P. Heimann, and F. J. Himpsel, Phys. Rev. Lett. **45**, 656 (1980).

[16]R. Z. Bachrach, R. S. Bauer, P. Chiaradia, and G. V. Hansson, J. Vac. Sci. Technol. **19**, 335 (1981).

[17]D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1990).

[18]R. Ludeke, T.-C. Chiang, and D. E. Eastman, Phys. Scr. **117b&118b**, 819 (1983).

[19]This assumes $\Gamma^2_{\text{total}} = \Gamma^2_{\text{instrumental}} + \Gamma^2_{\text{additional}}$, where the Γ's are the Gaussian widths from the instrumental resolution or the "additional" disorder or surface potential broadening.

[20]M. D. Pashley, K. W. Haberern, W. Friday, J. M. Woodall, and P. D. Kirchner, Phys. Rev. Lett. **60**, 2176 (1988).

[21]G. Le Lay, D. Mao, A. Kahn, Y. Hwu, and G. Margaritondo, Phys. Rev. B **43**, 14 301 (1991).

[22]R. E. Viturro, S. Chang, J. L. Shaw, C. Mailhot, L. J. Brillson, A. Terassi, Y. Hwu, G. Margaritondo, P. D. Kirchner, and J. M. Woodall, J. Vac. Sci. Technol B **7**, 1009 (1989).

[23]1 langmuir is equal to an exposure which would give 1 ML if every molecule of the gas were to stick. The sticking coefficient for oxygen on GaAs is quite low.

[24]C. J. Spindt, R. Cao, K. E. Miyano, and W. E. Spicer (unpublished).

[25]J. Tersoff, Phys. Rev. B **32**, 6968 (1985).

[26]B. B. Pate, Ph.D. thesis, Stanford University, 1984.

[27]W. G. Petro, I. A. Babalola, P. Skeath, C. Y. Su, I. Hino, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **21**, 585 (1982).

[28]W. G. Petro, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B **34**, 7089 (1986).

[29]M. Grioni, J. J. Joyce, and J. H. Weaver, J. Vac. Sci. Technol. A **4**, 965 (1986).

[30]K. Bertness, J.-J. Yeh, D. J. Friedman, P. H. Mahowald, A. K. Wahi, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B **38**, 5406 (1988).

[31]There are small differences in the surface sensitivity of different spectra due to the experimental setup. This is because the analyzer used at NSLS was angle resolved accepting a solid cone with a half angle of 4° of electrons, and the data at SSRL and SEL were taken using a cylindrical mirror analyzer (CMA), which accepts a hollow cone with a half angle of 43°. This means that the CMA data will be more surface sensitive (with an escape angle of $\approx 43°$ off normal) than the angle-resolved data taken at normal emission. The Al spectra are slightly more surface sensitive than the Au spectra due to an off-normal escape angle. The spectra shown in Fig. 1 are even more surface sensitive, as they were taken using the CMA. The CFS data was taken with the CMA.