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Chemisorption and oxidation studies of the (110) surfaces of GaAs, GaSb, and InP

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The surface chemistry of cleaved GaAs(110) (and, to a lesser extent, InP and GaSb) is studied as a function of oxygen exposure (both unexcited and excited) with soft-x-ray photoemission spectroscopy. When the cleaved GaAs (110) surface is exposed to molecular oxygen in the ground state, *chemisorption* to only the arsenics takes place. No back bonds are broken even for large exposures. Room-temperature *oxidation* of the surface can be induced by exciting the oxygen, e.g., by an ionization gauge. The adsorption of excited oxygen is initially the same as for the unexcited, except 500 times faster. However, after $> 20\%$ of a monolayer has been adsorbed, further exposure to excited oxygen causes back bonds to be broken and As_2O_5 and Ga_2O_3 are formed. Larger doses of excited oxygen result in the formation of thicker oxides composed primarily of Ga_2O_3 with small amounts of elemental As (or As bound to only one Ga) and As_2O_3, most of which has sublimed from the surface. No As_2O_5 is seen in the thicker oxide because there is a deficiency of oxygen, and any partially oxidized Ga present will reduce the arsenic oxides. The escape depth for GaAs(110) was measured for electron kinetic energies between 20 and 200 eV. This range includes the minimum in the escape depth which is about 6 Å at 60 eV. No chemical shift in the core levels between the atoms on the surface and in the bulk was observed. GaSb (110) and InP (110) surfaces were also studied. InP behaves like GaAs, whereas the GaSb is oxidized immediately even when exposed to only unexcited oxygen. The oxygen uptake curves for GaSb and GaAs were compared and found to be quite different with a sticking coefficient, at zero coverage, of 2×10^{-4} for GaSb and 8×10^{-10} for GaAs.

I. INTRODUCTION

The surface physics and chemistry of III-V compound semiconductors have attracted considerable interest, both experimental and theoretical. One of the things that makes III-V compounds such as GaAs so interesting from a fundamental point of view is the effect of the polar nature of the fundamentally covalent Ga-As bond on the surface properties of the crystal. III-V compounds have important practical applications such as infrared detectors, high-frequency metal-oxide-semiconductor (MOS) devices, and light-emitting diodes. One of the major obstacles in fabricating GaAs MOS devices, as well as in many other applications, is that it is very difficult to passivate the surface. Much work has been done in this area, but no oxides with the favorable properties characteristic of silicon-based devices have yet been developed. Thus, it is very important to gain more insight into the chemistry of the oxide-semiconductor interface.[1]

Crystals of the III-V compounds have the zincblende structure, and we should note that, in terminating the lattice to create the ideal surfaces, one covalent bond per surface site has been broken, leaving three intact.[3] On the (110) surface, which is the cleavage face of the III-V semiconductors, a rearrangement of charge takes place and it becomes energetically favorable for the surface atoms to seek a bonding configuration more characteristic of their covalent bonding in small molecules. To be more precise, a simplified version of the currently accepted model is that the surface Ga now has only three electrons (in an sp^2 configuration), all involved in back conding, while the As has five electrons (in a p^3s^2 configuration), three of these electrons take part in the back bonds (p^3) and the remaining two (s^2) are the "dangling-bond orbitals."[2-4] This charge rearrangement has two important consequences. First, the change in the bonding configuration of the surface atoms results in a distortion of the lattice at the surface consistent with the planar-sp^2-Ga back bonds and the prismatic-p^3-As back bonds, Fig. 1 (we should note this relaxation is not total).[3,5,6] Secondly, since all of the electrons on the surface Ga are used in forming the back bonds, the Ga has no filled surface-state orbitals. The surface As atoms, on the other hand, have two available electrons to contribute to the filled surface-state band which lies well below the valence-band maximum.[1,2] The position of the filled and empty surface states on an energy-level diagram is also shown in Fig. 1 after Gregory *et al.*[2,3,7-10]

The basic aspects of this model can also be applied to the polar faces in order to explain the greater chemical activity of the As-terminated $(\bar{1}\bar{1}\bar{1})$ face with respect to the Ga-terminated (111) face. However, the experimental situation for the polar faces is not as well defined as for the cleaved (110) surface since the surface atoms on the polar surfaces probably have some unsaturated bonds. This situation could be caused by deficiencies in

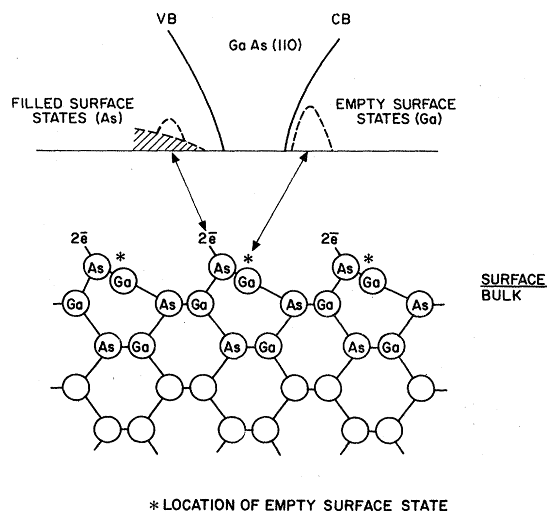

FIG. 1. Reconstructed (110) surface with an energy-level diagram showing the location of the filled (As-derived) and empty (Ga-derived) surface states.

the available surface preparation techniques or fundamental problems arising from the polar nature of these surfaces.[3,4,11,12]

One of the major predictions of the model of Fig. 1 is that, for the (110) surface, oxygen is absorbed preferentially on the arsenic atoms by interacting with the filled surface states. Furthermore, since all the bonding electrons associated with the surface gallium atoms are involved in the back bonds, the oxygen will bond to the gallium only after one or more of the back bonds are broken.[2,7,13] The oxidation of GaAs has been studied extensively by ultraviolet photoemission spectroscopy (UPS),[2,14] ellipsometry,[15] electron-energy-loss spectroscopy (EELS),[16,17] Auger-electron spectroscopy (AES),[12,14,15,18] and low-energy-electron diffraction (LEED).[5,15] The early experimental work on the cleaved (110) surface gave results that were consistent with the predictions outlined above,[2,15,16] whereas recent results on the polar surfaces have been interpreted to mean that the oxygen sticks preferentially to the surface Ga atoms.[12,17] However, the conclusions from one of the studies[17] on the polar surfaces are based on indirect evidence whose interpretation is open to question.[19] The interpretation given in the second set of studies[12] is probably correct, but the polar faces used had unsaturated Ga bonds so that absorption on the Ga sites does not necessarily disagree with the model of Fig.1 (this point will be discussed at the end of Sec. III. B).

In our recent work[7,13] on the GaAs (110) surface, we showed definitively that there is a charge transfer from surface As atoms to chemisorbed oxygen. We interpreted this to mean that the oxygen is bound preferentially to surface As atoms, in agreement with the earlier work cited above. We have also shown that InP behaves in the same way as GaAs, whereas the oxidation of GaSb proceeds in an entirely different manner. In GaSb, the oxygen bonds both species breaking the Ga-Sb back bonds.[7] This latter effect can then be compared to the situation when the GaAs (110) surface is exposed to excited oxygen.[20]

In this paper, we will present a detailed analysis of our previously reported results and new data on the very heavily oxidized surface of GaAs(110), which gives us greater insight into the oxidation of GaAs.

All the results presented here were obtained with soft-x-ray photoemission spectroscopy (SXPS) using synchrotron radiation from the "4° line" at the Stanford Synchrotron Radiation Project in the photon energy range $32 \leq h\nu \leq 350$ eV.[21] This photon energy range is interesting because it allows us to observe both the valence band and several core levels from both the Ga and As at high resolution (0.25 eV). By tuning through the available photon energies, we are able to adjust the kinetic energies of the various levels to be roughly between 20 and 200 eV. This is possibly the most significant aspect of our experiments because the escape length of electrons in a material is strongly dependent on the electron kinetic energy, and this escape depth goes through a minimum of $\lesssim 10$ Å for kinetic energies between 50 and 150 eV for most materials.[22]

The experimental methods, such as LEED, AES, and UPS, that were used in the earlier oxidation studies all have high surface sensitivity. However, they lack the chemical information which can be obtained from x-ray photoemission (XPS) studies of core-level shifts.[23] Auger-electron spectroscopy can be used to look at chemical shifts, but the use of an e beam as the excitation source can desorb the oxygen or destroy the integrity of the surface.[18,20,24] This damage is minimized when using uv light or x-rays. However, conventional XPS ($h\nu = 1486.7$ or 1253.6 eV) lacks the necessary surface sensitivity.[22] With SXPS, not only can we study the chemical shift of core levels upon forming a chemical bond, but we can also perform these studies at submonolayer coverages due to the inherent surface sensitivity of the technique.[7,13] In our experiment, we adsorb oxygen on GaAs, GaSb or InP and observe any core-level shifts that take place upon adsorption. We then measure the magnitude of the core-level shifts and correlate these shifts with chemical-shift measurements made on bulk oxides using conventional XPS. This correlation allows us to determine the type of oxides forming at the surface in

a relatively straightforward way.[23] The ratio of the area of the shifted to unshifted peaks can be used to determine converges versus exposure as well as escape depth information.

In Sec. II, we will discuss the experimental apparatus, procedure, and results. Section III will contain the discussion. In this section, we will correlate the chemical shifts obtained from the surface oxidation of GaAs(110) to the shifts obtained from XPS measurements of bulk oxides. These correlations will then be used to give a model for the oxidation of GaAs(110), starting from surface chemisorption and ending with the formation of actual bulk oxides. We will also determine the escape depth for GaAs as a function of photon energy as well as show a difference in adsorption kinetics between GaAs(110) and GaSb (110).

II. EXPERIMENTAL

A. Apparatus

The experimental chamber consists of a stainless-steel ultrahigh-vacuum bell jar and base pressure $< 1\times10^{-10}$ Torr. The pumping system is a 240-liter/sec ion pump plus titanium cryopump with a poppet valve for sealing the pump from the main chamber. The chamber contains a double pass cylindrical mirror analyzer (Physical Electronics), a cleaver, and a sample manipulator capable of holding four samples for cleaving, one sample for heat cleaning ($T_{max} \approx 2000$°C) and a substrate upon which Au or Cu may be evaporated for Fermi-level (and thus binding energy) determinations.[25] An evaporator which contains copper and gold beads is also housed in the chamber.

Research grade oxygen was admitted into the vacuum system through a bakeable leak valve. For large exposures (pressures up to 750-mm O_2), an auxiliary pumping system was used to return the main chamber to pressures below $\sim 10^{-8}$ Torr. This system consisted of vacsorb pumps, an ion pump, and all the necessary gauging to measure pressures for the gas exposures.

Pressures between 10^{-11} and 10^{-5} Torr were measured by a Redhead cold-cathode ionization gauge located in the main vacuum system. This pressure range was used for exposures up to 10^4 L (1 L $=10^{-6}$ Torr/sec) where the exposure time was no longer than 10^3 sec. A hot-filament ionization gauge with thoria-coated iridium filaments (Varian) was also located in the main vacuum system. This gauge was used initially to check the cold-cathode gauge and, more importantly, as a source of excited oxygen when used during a gas exposure. The effect of the ion gauge on the oxidation will be treated in a later section.

Pressures between 10^{-5} and 0.6 Torr were measured by a millitorr gauge (Varian) located in the auxiliary pumping system. This pressure range gives exposures between 10^4 and $\approx 10^9$ L. A thermocouple gauge (Hasting DV-4) again in the auxiliary pumping system, was used for pressures between 1 and 20 Torr, giving exposures between 10^9 L and 2×10^{10} L. For larger exposures of up to 10^{12} L, a mechanical-vacuum gauge (Wallace and Tiernen) was used, measuring pressures up to 800 Torr.

The synchrotron radiation is monochromatized by a grazing incidence monochromator (resolution 0.2 Å) with a refocusing mirror located after the exit slit.[26] The radiation enters the chamber through a bakeable straight-through valve. The energy of the photoemitted electrons is then determined by the double-pass cylindrical mirror analyzer operated in the retarding mode. This mode ensures a constant resolution which is equal to 0.6% of the electron pass energy through the analyzer. In these experiments, we used a pass energy of 25 eV, giving an electron energy resolution of 0.15 eV. At $h\nu = 100$ eV, typical counting rates on the Ga 3d levels are about 5×10^3 counts per second for a circulating electron current in SPEAR of 20 mA.

The signals from the electron energy analyzer are amplified and fed into a 2048 channel signal averager (Tracor Northern) used as a multichannel scaler. The energy of the detected electrons was controlled by the signal averager through a voltage ramp synchronized with the memory sweep.

The samples that were studied in these experiments are Te-doped n-type GaAs ($n = 3.5\times10^{17}$ cm^{-3} and $n = 0.5\times10^{18}$ cm^{-3})[27] and Zn-doped p-type GaAs ($p = 6\times10^{18}$ cm^{-3}) from Laser Diode (LD) Corporation; Te-doped n-type GaSb ($n = 1.1\times10^{18}$ cm^{-3}) from Asarco[28]; and Zn-doped p-type InP ($p = 2\times10^{18}$ cm^{-3}) from Varian Associates. The GaAs and GaSb samples were rectangular prisms $5\times5\times10$ mm^3, and the InP was $2\times5\times10$ mm^3. In all the samples, the [110] axis was along the long dimension.

B. Procedure

First, the samples were cleaved along the (110) planes by slowly squeezing the sample between the annealed copper anvil and tungsten-carbide knife of the cleaver. The cleaved sample is then inspected visually to ensure the cleave has a mirrorlike finish. A set of spectra is taken for $32 \leq h\nu \leq 300$. Now the sample is ready to be exposed to oxygen. The pump is valved off from the main chamber with the poppet valve, partially for exposures be-

low 10^4 L completely for larger exposures. The gas is admitted and the pressure monitored. After the desired exposure is reached, the majority of the gas is removed with the auxiliary pumping system. When the chamber reaches a pressure below $\sim 10^{-8}$, the poppet valve is opened and the main pump takes the chamber to pressures below $5 \sim 10^{-10}$ Torr for all gas exposures that are performed. During these exposures, the straight-through valve into the grazing incidence monochromator has been closed and is not opened until the pressure in the chamber $< 1\times10^{-9}$ Torr. With this scheme for making the gas exposures, the chamber is returned to its base pressure very quickly. Using the technique described above, the majority of the gas is pumped out in the first 15 sec and working pressure is achieved within 10–15 min, giving a minimum of down time between spectra.

The exposures with excited oxygen are performed with the ion gauge in the main chamber turned on.[29] This gauge is out of line of sight of the sample so that the gas molecules must strike at least two surfaces before hitting the sample. However, for the larger exposures, it is also possible that the oxygen is deflected to the sample through collisions with other gas molecules since the mean-free path of the molecules is between 1 and 10 cm for the pressures used in the ion-gauge exposures (10^{-2} -10^{-3} Torr). Two different ion-gauge emission currents were used in the exposures. One emission current setting was 4.0 mA (for pressures below 10^{-4} Torr), and the other was 0.4 mA (for pressures between 10^{-2} and 10^{-3} Torr). We did not directly determine if there was a tenfold increase in the amount of excited oxygen in going from the 0.4–to 4.0 mA emission currents, but the results of the oxidation indicate that this should be the case.[30]

The binding energies in these studies are measured relative to the valence-band maximum of the clean surface. Binding energies with respect to the Fermi level can be determined by referring the unknown binding energies to either the $4f$ levels of Au (binding energy of 84.0 eV) or the Fermi level of a gold film evaporated *in situ* on a substrate in electrical contact with the sample.[25]

In all the figures that follow, in which we show spectra for clean and oxidized samples on the same graph, the horizontal binding energy scale refers to the clean spectrum. The spectrum of the oxidized samples are adjusted so that the various unshifted peaks line up consistently. This must be done because the Fermi-level pinning for these samples changes as a function of oxygen exposure so that binding energies referenced to the Fermi level vary.[7,31] Furthermore, the structure in the valence band also changes considerably with oxidation so that the unshifted core levels must again be used as standards. Beyond 10^7-LO_2, the position of the Fermi level has stopped moving so that we may use the measured energy positions of the peaks as a consistency check.

C. Results

In Fig. 2, we show spectra for the clean and oxidized GaAs (110) surface at $h\nu = 100$ eV. As we expose the surface to oxygen, we see a single peak ($E_B = 43.7$ eV) growing 2.9 eV below the As $3d$ peak ($E_N = 40.8$ eV) with a proportionate decrease in the As $3d$ intensity. This is a chemically shifted peak indicating a transfer of charge from the surface As atoms to the adsorbed oxygen. Concurrent with the appearance of the shifted arsenic peak, we see the O $2p$ resonance level at a binding energy of about 5 eV. As we go to higher exposures, the shifted As $3d$ peak and O $2p$ level grow simultaneously until saturation is reached between 10^9 and 10^{12}-L O_2. We interpret the filling in of the valley between the shifted and unshifted peaks as due to the overlap between these two peaks since all the observed structure can be accounted for by this overlap without introducing any intermedi-

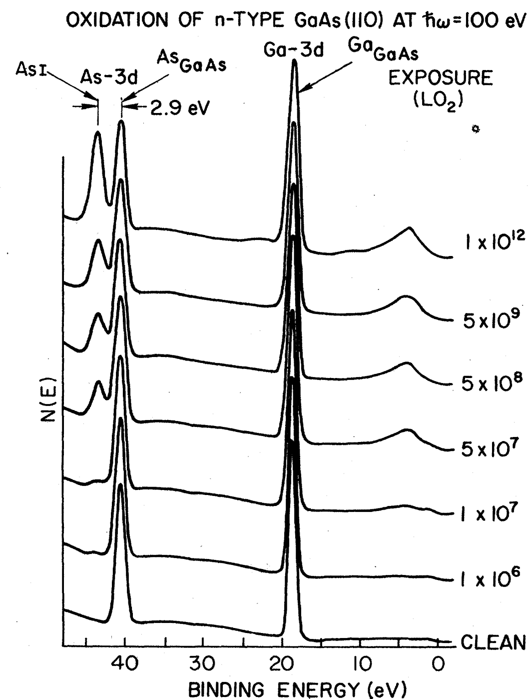

FIG. 2. Energy distribution curves of clean and oxygen-exposed n-type GaAs (110) at $h\nu = 100$ eV. The exposure of 1×10^{12}-L O_2 (1 L = 10^{-6} Torr sec) was made on sample LD1, while the smaller exposure were all on sample LD3.

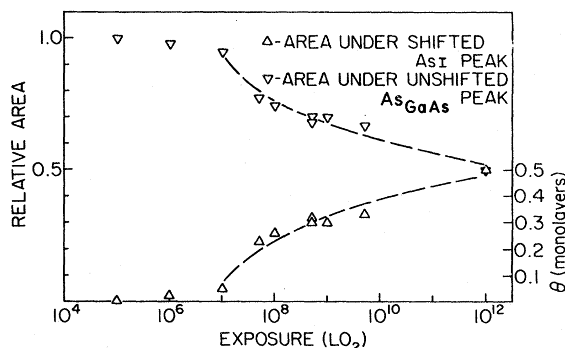

FIG. 3. Relative oxygen uptake of the GaAs (110) surface as a function of exposure determined from the area under the shifted As $3d$ levels (△). The area of the unshifted As $3d$ levels (▽) is also plotted. The scale on the right assumes saturation is reached at 10^{12} -L O_2.

ate states. The elimination of any such intermediate states has important implications when it comes to understanding the type of ligand which gives rise to the As I peak.

An estimate of the relative amount of oxidized As atoms on the surface can be obtained by comparing the areas under the shifted and unshifted peaks. This is done in Fig. 3, where we plot the area in relative units under the shifted and unshifted peaks as a function of exposure. Here, the sum of the areas under the shifted and unshifted peaks were normalized to unity. As expected, the amount of oxidized arsenic increases while the unoxidized decreases for increasing exposure. At 10^6-L O_2, where we first start to see the effect of oxygen in the valence band as well as seeing a chemically shifted As $3d$ level, the coverage is only about 2% of saturation.

If we consider only the points up to an exposure of 5×10^9-L O_2 in Fig. 3, saturation seems to have been reached at about 10^9-L O_2. If, however, we include the point at 10^{12}-L O_2, which gives a 1.7 times increase in coverage over that at 10^9-L O_2, the apparent saturation exposure is increased by three orders of magnitude. At present, we will not place too much emphasis on this one point because the spectrum for 10^{12}-L O_2 was obtained by exposing a freshly cleaved surface (sample LD1) to 10^{12}-L O_2 *in one step*, whereas all the other spectra were obtained by exposing sample LD3 *gradually* to increasing amounts of oxygen.

The relative oxygen coverages can also be obtained by measuring the area under the O $2p$ resonance in the valence band. The major drawback to this technique is that the valence band and the O-$2p$ signal overlap so that it is difficult to get reliable coverage information below exposures of about 5×10^7-L O_2. Even above this exposure, the GaAs valence band is still a significant fraction of

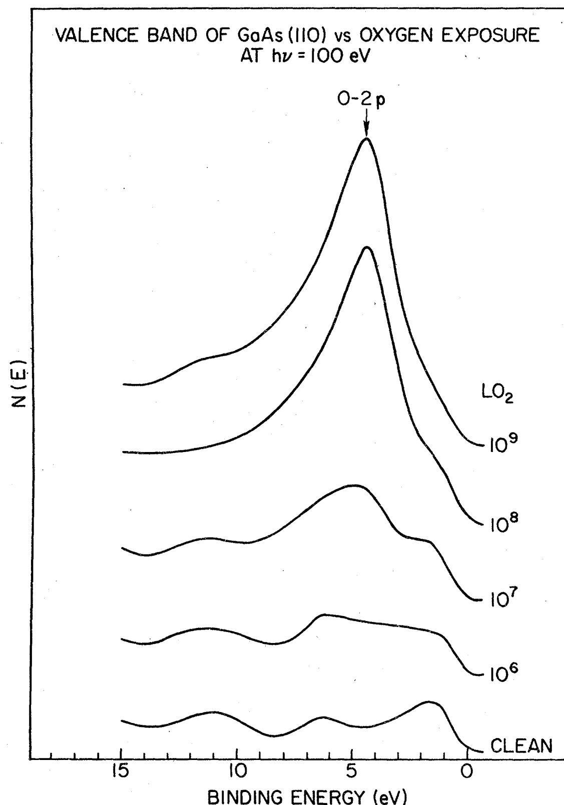

FIG. 4. Valence band of clean n-type GaAs(110) and the same surface exposed to the indicated exposures. These curves are blowups of the valence-band region of Fig. 2.

the total emission, so care must be used in separating out the oxygen contribution from that of the GaAs. These problems are seen rather clearly in Fig. 4 where we show a blowup of the GaAs valence band for various oxygen exposures. The coverage, as determined from the shifted arsenic level, gives a measure of the relative amount of oxygen that has chemically combined with the surface arsenic atoms. The coverage obtained form the O-$2p$ signal gives a measure of the *total* amount of oxygen sticking to the surface. Thus, comparison of the oxygen uptake determined in these two ways can be used to give additional information on the kinetics of the adsorption as well as the nature of the adsorbate. Our initial studies on sample LD3 indicate that the two methods give similar results. However, the 10^{12}-L O_2 exposure on sample LD1 shows that the number of shifted arsenic atoms has increased by a factor of 1.7, while the oxygen coverage has not changed appreciably from the coverage at 10^9-L O_2. This could be interpreted to mean that the oxygen has been adsorbed dissociatively because the higher pressure of the exposure has changed the adsorption kinetics. This is

a very interesting point, but we will not pursue it further here because more experimental work needs to be done on the exposures between 10^{10} and 10^{12}-L O_2 before definitive conclusions may be drawn. We will limit our discussion of chemisorption mechanisms to the exposures below 10^{10}-L O_2.

For this work, the significance of the curve for 10^{12}-L O_2 is that, even for this very large exposure (this corresponds to an exposure of 1 atm of O_2 for 20 min!), no major shift in the gallium $3d$ level is observed. The only effect on the gallium peak is a 0.4 eV broadening. Part of this broadening is due to a nonuniformity in work function across the face of the sample since the unshifted arsenic peak is broadened by 0.1 eV. For the exposure below 10^{10}-L O_2, the Ga-$3d$ broadens symmetrically by ± 0.12 eV, and the shift to higher-binding energy is *less than 0.03 eV.*

The oxidation of the GaSb (110) surface is shown in Fig. 5 for $h\nu = 100$ eV. As in the case of GaAs, all the spectral features of interest can be obtained at the same photon energy and in one spectrum, thus facilitating comparisons. The valence band extends approximately 12 eV below the valence-band maximum. The Ga $3d$ level is at a binding energy of 19.4 eV, the Sb $4d$ doublet is at 32.1 eV ($4d_{5/2}$) and 33.2 eV ($4d_{3/2}$). We are able to clearly see the spin-orbit splitting in the Sb $4d$ levels, whereas we were not able to see it at these energies for the Ga and As levels, primarily because the splitting of the Sb $4d$ levels is much larger than that of the $3d$ levels of As or Ga. We should also note that the As and Ga levels are $3d$'s, while that of Sb is a $4d$. This point is important for the choice of photon energy since the variation of cross section for the $4d$ levels versus photon energy is rather dramatic, as indicated in Fig. 6. Here, we show spectra of oxidized GaSb for several different photon energies. Note that almost all the intensity is lost from the $4d$ levels over a very small photon-energy range. The variation in cross section of the $3d$'s is not as dramatic, but is nevertheless also large.[32] Consequently, we are forced to use photon energies below about 120 eV.

As we oxidize the GaSb surface, we start to see changed in the spectra at about 5×10^5-L O_2. This is about a factor of 2 sooner than with the GaAs. But, more importantly, as we increase the exposure to 5×10^7-L O_2, we start to see a definite broadening of the Ga $3d$ level toward higher-binding energy. In fact, even by 5×10^8-L O_2, a definite shifted Ga $3d$ peak is seen ($\Delta E_B = 1.1$ eV). Of course, the shifted Sb $4d$ ($\Delta E_B = 2.5$ eV) level has also been growing at the expense of the unshifted level. The shifted peaks for both Sb and Ga completely dominate the unshifted peaks for exposures above 5×10^9-L O_2. In Figs. 2 and 5, we can see the obvious differences between the oxidation of

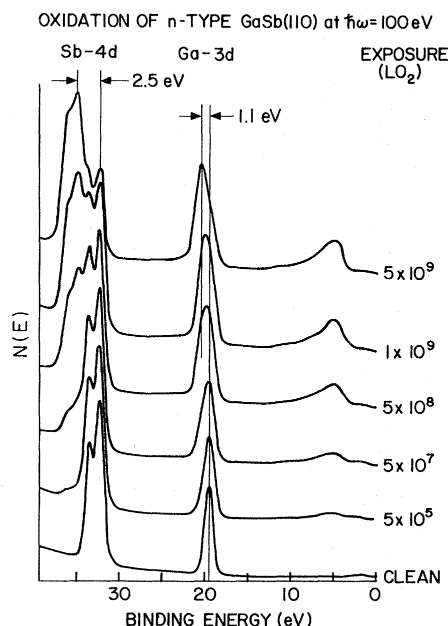

FIG. 5. Energy distribution curves of clean and oxygen-exposed n-type GaSb(110) at $h\nu = 100$ eV. Note that both the Ga and Sb shift simultaneously with increasing oxygen exposure.

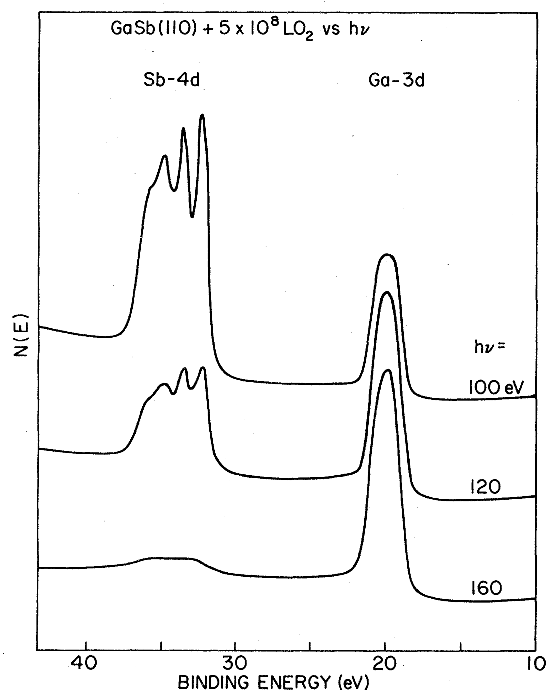

FIG. 6. Energy distribution curves of GaSb exposed to 5×10^8 - L O_2 for three photon energies showing the variation in the cross section fo the Sb $4d$ levels vs photon energy.

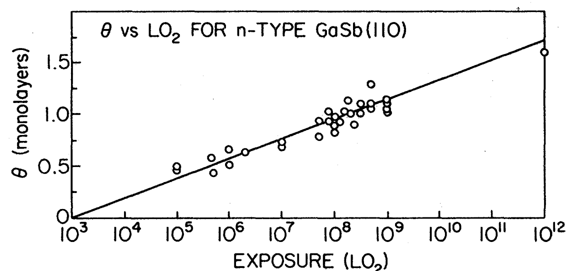

FIG. 7. Relative oxygen uptake of the GaSb (110) surface as a function of exposure, determined from the area under the O $2p$ level. The vertical scale is obtained by comparing the areas under the O $2p$ level in the spectra of Fig. 5 to the areas under the O $2p$ level in Fig. 2 for GaAs.

GaAs and GaSb. In GaAs, only the As peak is shifted while the Ga peak is broadened. In GaSb, both the Sb and Ga are definitely shifted, indicating that charge transfer from both surface Sb and Ga atoms to the oxygen has taken place. This implies that bonds are broken between neighboring surface Ga and Sb atoms.

Another striking difference is seen if the coverage (area under shifted Sb peak or O $2p$ level) is plotted with respect to exposure (Fig. 7). The rate of oxygen adsorption from Fig. 7 does not show the saturation behavior which is characteristic of the GaAs surface as seen in Fig. 3.

Spectra for the clean and oxygen-exposed p-type InP(110) surface are shown in Fig. 8. In this case, we used two different photon energies to optimize the surface sensitivity and cross section for the levels of interest. The P $2p$ levels are measured at $h\nu = 160$ eV and the In $4d$ levels at $h\nu = 80$ eV. The indium levels, being $4d$ levels, have the same general behavior versus photon energy as the Sb $4d$ levels. Therefore, they too have a rather large variation in cross section, forcing us to choose a photon energy not too high above threshold. As seen from Fig. 8, the InP (110) surface behaves like the GaAs (110) surface, with possible differences in the adsorption kinetics which will not be dealt with here. One subtle difference is that we are able to resolve the spin-orbit splittings in both the phosphorous and indium levels for the clean surface. However, they smear out upon oxygen adsorption. No shifts are observed in the In $4d$ levels, and a shifted P $2p$ level ($\Delta E_B = 4.4$ eV) is observed which grows with oxygen exposure. Similar results have been seen in InAs by Gudat and Eastman.[34]

All the previous exposures were done with unexcited molecular oxygen. In Sec. III, we will consider the effect of excited oxygen on the adsorption process.[20] In Fig. 9, we show what happens when the GaAs (110) surface is exposed to excited oxygen. In these spectra, the exposure was carried out in exactly the same way as the previous exposures except that the ion gauge was on during

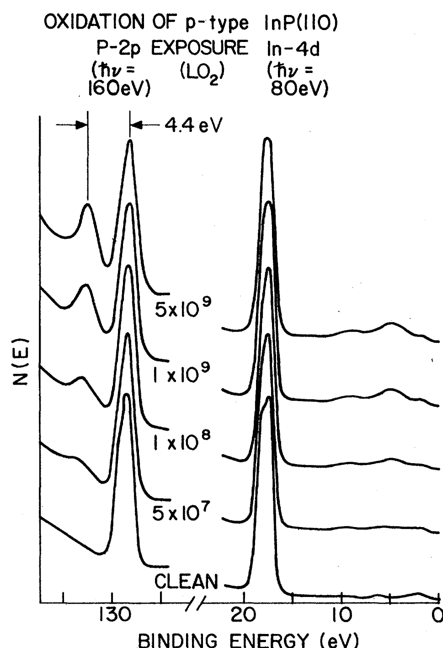

FIG. 8. Energy distribution curves of clean and oxygen-exposed p-type InP(110). The In $4d$ level was measured at $h\nu = 80$ eV and the P $2p$ level at $h\nu = 160$ eV.

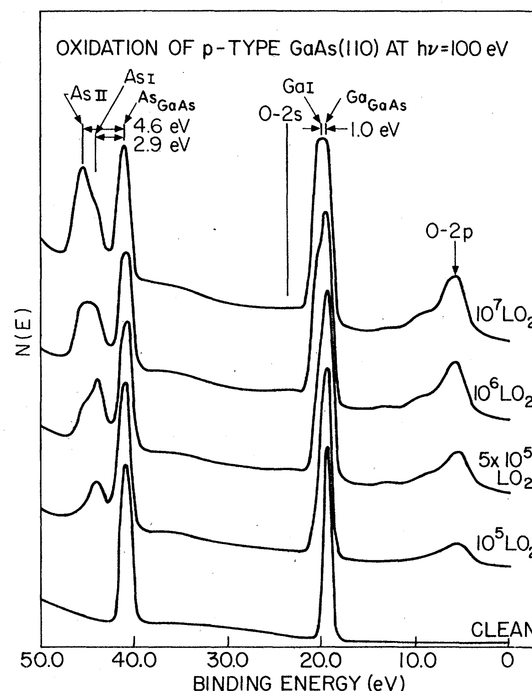

FIG. 9. Energy distribution curves of clean p-type GaAs(110) and the clean surface exposed to excited oxygen at $h\nu = 100$ eV.

the exposure with an emission current of 4 mA (the exposures at 10^6 and 10^7 L used an emission current of 0.4 mA). Comparing these spectra to those in Fig. 2, we see that the sticking probability has become much larger. It only takes an exposure of 10^5 L excited oxygen to give the same effect as an exposure of 5×10^7-L O_2. This is an increase in oxygen adsorption by a factor of 500! The fact that oxygen, which has been excited in some way, will stick more readily to semiconductor surfaces has been documented in the literature.[15,33] What has not been seen before is the change in chemical state due to bonding of such excited oxygen.[20] As we expose the surface to even more excited oxygen, a rather striking thing happens. At an exposure of 5×10^5 L excited oxygen, the first shifted peak ($\Delta E_B = 2.9$ eV) stops growing, and a second shifted peak with a binding energy shift of 4.5 eV starts to grow and soon dominates the first shifted peak. But, what is even more striking is that the gallium peak starts to broaden also at 5×10^5 L excited oxygen. At higher exposures, we can see that the initial broadening at 5×10^5 L excited oxygen is due to a shifted gallium peak ($\Delta E_B = 1.0$ eV) which grows concurrently with the second shifted arsenic peak.[13] This simultaneous growth is very much like what was seen for the oxidation of GaSb in Fig. 5. We also see in these spectra the O $2s$ at 24 eV and the O $2p$ at 5 eV below the valence-band maximum.

In Fig. 10, we give examples of the effects of very large doses of excited oxygen on the GaAs (110) surface. The top two curves are spectra for clean GaAs(110) and for the clean surface plus 10^{12}-L O_2. The spectrum labeled "heavily oxidized" was obtained by exposing the surface, which had previously been exposed to 10^{12}-L O_2, to 5×10^5 L excited oxygen with the ion gauge running at 0.4 mA emission current. Note that the binding energies of the peaks in this spectrum are the same as those of Fig. 9. There are two oxidation states of As, and there is a shifted gallium peak. The fourth spectrum of Fig. 10 labeled "very heavily oxidized" was obtained by exposing clean GaAs(110) to 5×10^5 L excited oxygen with the emission current of the ionization gauge (IG) set at 4.0 mA (giving a significantly larger amount of excited oxygen than in the previous case). In this case, we see no unshifted gallium peak; only the shifted one. There is no unshifted arsenic peak, but there are two other peaks shifted 0.4 and 3.2 eV with respect to the unshifted peak (if it were present). Note the drastic decrease in emission from the arsenic derived levels and that the emission from the O $2p$ and O $2s$ levels has gone down with respect to that in the second and third spectra.

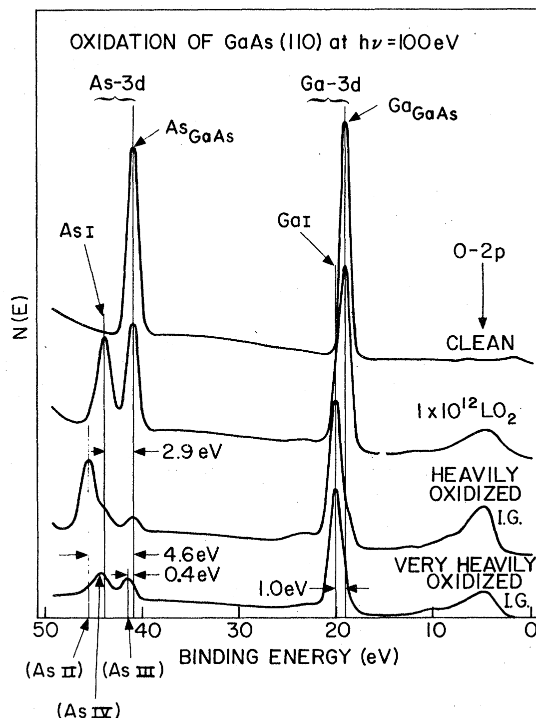

FIG. 10. Energy distribution curves of n-type GaAs (110), LD1, for the clean surface, the clean surface $+10^{12}$-L O_2, the previous surface+ 5×10^5-L excited oxygen with a 0.4-mA ion-gauge emission current ("heavily oxidized"), and the clean surface exposed to 5×10^5-L excited oxygen with 4.0-mA ion-gauge emission current ("very heavily oxidized").

The significance of these observations will be discussed in Sec. III, where we will present a model for the oxidation of the GaAs (110) surface from the chemisorption stage to the formation of bulk oxides. In Tables I and II, we summarize

TABLE I. Experimental binding energies referenced to the valence-band maximum. The experimental accuracy is estimated to be ±0.05 eV with the largest uncertainty being in the determination of the valence-band maximum. See text for discussion on difficulties in determining the binding energies with respect to the Fermi level.

Compound	Level	E_B (eV)
GaAs	Ga $3d$	19.0
	As $3d$	40.8
GaSb	Ga $3d$	19.4
	Sb $4d\,\frac{5}{2}$	32.1
	Sb $4d\,\frac{3}{2}$	33.2
InP	In $4d$	17.7
	P $2p$	128.4

TABLE II. Experimental binding energy differences (eV), from this work, between the shifted and unshifted Ga and As 3*d* levels for the clean and oxidized GaAs (110) surface. The entries were obtained by subtracting the binding energies of the levels in the top row from those in the leftmost column.

ΔE_B (eV)	As III	As II	As I	As_{GaAs}	Ga I	Ga_{GaAs}
As IV[a]	2.8	-1.4[c]	0.3	3.2	24.0	25.0
As III		-4.2	-2.5	0.4	21.2	20.2
As II			1.7	4.6	25.4	26.4
As I				2.9	23.7	24.7
As_{GaAs}[b]					20.8	21.8
Ga I						1.0

[a] The designations As I, As II, etc., refer to the labeling of Fig. 10.
[b] As_{GaAs} refers to As in GaAs; similarly, Ga_{GaAs} refers to Ga in GaAs.
[c] The negative shift means that As II has a larger binding energy than As IV.

the binding energies and chemical shifts (for GaAs) discussed above.

III. DISCUSSION

A. Interpretation of chemical shifts

In this section, we will concentrate on trying to determine which oxidation states of the As and Ga give rise to the chemically shifted peaks that are observed in the photoemission spectra. Considerable information can be obtained from the chemical-shift measurements by assuming that ligands of any given type each shift the core levels of the central atom by the same amount.[23] Thus, the total shift ΔE_{tot} is simply given as the sum of the individual ligand shifts ΔE_{ligand}, i.e.,

$$\Delta E_{tot} = \sum_{\substack{\text{all}\\ \text{ligands}}} \Delta E_{ligand} \,. \qquad (1)$$

The magnitude of the ligand shift may be determined by measuring the binding energies of several compounds containing different numbers of these ligands. In our case, this is very useful for the case of nonstoichiometric oxides. For stoichiometric oxides, the obvious thing to do is to use the bulk oxides as standards. Here, we will do both in order to determine the chemical species present on the surface after initial chemisorption and further oxidation.

In Table III, we present binding energy shifts for the Ga and As 3*d* levels in the compounds that will be used as standards. These values are taken from the literature and, rather than give absolute binding energies, we choose instead to give the binding-energy differences between the levels in the various compounds. This, in effect, avoids many of the problems in choosing an appropriate reference level when comparing the results from several sources. Through the work of Bahl *et al.*,[35] we were able to determine the 3*d* level binding energy shifts for As_2O_5 and As_2O_3 with respect to As. We then calculated the difference between the Ga and As 3*d* levels of As_2O_3, Ga_2O_3, GaAs, and Ga by referring to the work of Leonhardt *et al.*[36] The Ga_2O_3-Ga shift was found to agree with Schön's measurements to within 0.1 eV.[37] The binding energies of Ga_2O_3 and GaAs were also measured for us by an independent laboratory (using a Hewlett-

TABLE III. Experimental binding energy differences (eV), from the references cited, between the shifted and unshifted Ga and As 3*d* levels for various compounds of Ga and As. The data are presented in the same format as that of Table II.

ΔE_B (eV)	As_2O_3[a]	As_{GaAs}[b]	As[c]	Ga_2O_3[d]	Ga_{GaAs}[e]	Ga[f]
As_2O_5	1.7	4.9	4.3	25.7	26.6	27.0
As_2O_3		3.2	2.6	24.0	24.9	26.0
As_{GaAs}[g]			-0.6	20.8	21.7	22.8
As				21.4	22.3	23.4
Ga_2O_3					0.9	2.0
Ga_{GaAs}						1.1

[a] References 35 and 36.
[b] References 36, 38, 40, and 41.
[c] References 35 and 36.
[d] References 36–38.
[e] References 36, 38, 41, and 50.
[f] References 36 and 37.
[g] See text for the discussion about reliably determining the shifts between the semiconductor compounds and the other compounds in this table.

TABLE IV. Experimental ligand shifts of the Ga and As 3d levels for the compounds whose shifts were given in Table III.

Compound	ΔE_e (eV)[a]	ΔE_j (eV)[b]	n_j[c]	Ligand
As_2O_5	4.3	0.87	3	-O
		1.7	1	=O
As_2O_3	2.6	0.87	3	-O
As_{GaAs}	-0.6	-0.15	4	-Ga
Ga_2O_3	2.0	0.33	6	-O
Ga_{GaAs}	1.1	0.28	4	-As
As_{GaAsO_4}[d]	3.5	0.87	4	-O
Ga_{GaAsO_4}[d]	1.3	0.33	4	-O

[a] ΔE_e is the binding energy shift with respect to the free element.
[b] ΔE_j is the ligand shift referenced to the free element where $\Delta E_e = n_j \Delta E_j$, summed over all j.
[c] n_j is the number of ligands of the given kind.
[d] Note these are not experimentally determined shifts; these shifts are calculated for the ideal structures using the ligand shifts given in the rest of the table.

Packard 5950A ESCA spectrometer).[38]

The ligand shifts for the standard compounds may be calculated from the chemical shifts given in Table III. This is done in Table IV. In the first column of Table IV, we list the compounds. In the second column, we list the shifts of the As or Ga 3d levels in these compounds with respect to their binding energy for the free element. A positive chemical shift is defined as a shift to higher binding energy. Columns four and five give the number and type of ligand for the compounds in the first column. In GaAs, each gallium (or arsenic) has four arsenic (or gallium) ligands. As_2O_3 has three single oxygen single bonds per arsenic atom. Ga_2O_3 is coordinated by six oxygens. As_2O_5 has three oxygen single bonds and one oxygen double bond per arsenic. $GaAsO_4$ has a quartzlike structure[39] with the silicon atoms replaced by alternating Ga and As. This results in each gallium and arsenic having four oxygen ligands.

The ligand shifts ΔE_j are the shifts due to the particular ligand j and are obtained most simply by dividing the total shift (column two) by the number of ligands (column four). When there are two types of ligands in the compound in question, such as A_2O_5 which has three –O and one =O, we use another compound, As_2O_3 in this case, to determine one set of the shifts and then we solve for the second. In the last two rows of Table IV, we have calculated, using the experimentally determined shifts with Eq. (1), the shifts that we would expect from $GaAsO_4$. We should note, in comparing the ligand shifts of Table IV with those given in Table V of Ref. 35, that the shifts quoted here are only 3d shifts, whereas those used by Bahl *et al.*[35] are the average of the shifts of all the core levels. There will be a slight descrepancy if this point is not realized.

As mentioned in the previous discussion, when the GaAs (110) surface is exposed to unexcited oxygen, only one shifted arsenic peak, As I, is seen for all coverages. This implies that only a single site is involved in the chemisorption of unexcited oxygen. Thus, we must conclude that the As I peak, with a shift of 2.9 eV with respect to GaAs (2.3 eV with respect to elemental As), is due to one oxygen atom or molecule bonded to a surface arsenic atom. The shift of the As I peak is much larger than either the shift due to a single As-O bond (ΔE_B = 0.87 eV with respect to GaAs) or of an oxygen-arsenic double bond (ΔE_B = 1.7 eV with respect to GaAs). In fact, the experimentally determined shift of 2.9 eV is closer to the shift expected from three oxygens singly bonded to each surface arsenic atom, necessitating the breaking of back bonds. However, this latter situation implies that *three*, not one, chemically shifted As 3d peaks (ΔE_B with respect to GaAs ≈ –0.87, –2.04, and –3.06 eV) should be observed corresponding to the three possible oxidation states which the surface arsenic atoms would then have. We would expect to see the –0.87 and –2.04 eV peaks for low and intermediate coverages and the –3.06 eV peak almost exclusively for the high coverages. This is clearly *not* what we observe experimentally and, because of the high surface sensitivity of our measurement, we would be able to see such intermediate states. Therefore, we must conclude that the As I peak is due to a single arsenic-oxygen bond that gives a binding-energy shift three times larger than what is expected from an As-O bond in an arsenic oxide. In the case of As_2O_3, the oxygens are more electronegative than the arsenic, so there is an equal transfer of charge away from the arsenic along each ligand. In the case of oxygen chemisorbed to the GaAs surface, the gallium back bonds transfer charge *to* the arsenic so the oxygen is the only ligand in which there is charge transfer away from the arsenic. That is, the single oxygen ligand does not have any competition for the charge on the arsenic. Consequently, the oxygen ligand in this case could give a much larger shift than would be predicted by a simple ligand-shift analysis where the different electronegativities of the various ligands have not been taken into account. These same arguments, now used to estimate the shift of the Ga-3d due to a chemisorbed oxygen, would imply that the shift should be less than 0.33 eV (the ligand shift due to a single oxygen ligand in Ga_2O_3). Consequently, we would not expect to see a distinct chemically shifted peak for the case

of oxygen chemisorption on the surface gallium atoms. We would, however, expect to see an asymmetric broadening of the Ga $3d$ level. For exposures below 10^{10}-L O_2, as mentioned in Section III. A, there is no asymmetric broadening of the Ga $3d$ level to better than 0.03 eV. We can also exclude the possibility of bonding oxygen to the surface gallium atoms by breaking back bonds because, in this situation, we should definitely see an asymmetric broadening of the Ga $3d$ level along with intermediate oxidation states of the arsenic atoms, neither of which is observed experimentally.

The As II peak in the "heavily oxidized" curve of Fig. 10 is shifted 4.6 eV with respect to the arsenic in GaAs (or 4.0 eV with respect to elemental As). This value is bracketed by the experimentally determined value of 4.9 eV (4.3 eV with respect to elemental As) for As_2O_5 and the calculated value of 4.1 eV (3.5 eV with respect to elemental As) for $GaAsO_4$. The average of these two shifts gives 4.5 eV (3.9 eV with respect to elemental As), very close to the value measured in this work. This seemingly fortuitous result may be interpreted as follows. There are three single bonds and one double bond in As_2O_5, whereas $GaAsO_4$ contains four single bonds. The fact that the shift we measure lies between these two shifts is significant because, first, it indicates there are four oxygens bound to the As and, secondly, these bonds must have some double-bond character. In the rest of the discussion, we will simply refer to this compound as As_2O_5. There are, however, no peaks in the spectra corresponding to $GaAsO_4$. As mentioned above, with reference to Fig. 9, the gallium peak starts to shift as soon as the As II peak appears. The magnitude of the gallium shift is 1 eV which corresponds to Ga_2O_3 (compare Tables II and III). The fact that we start forming oxides of Ga and As at the same time clearly indicates that back bonds are being broken and true oxidation of the surface is occurring. We should note that we do not observe any intermediate oxidation states for the gallium.

In the "very heavily oxidized" spectrum of Fig. 10, the gallium peak, Ga I, is still shifted by 1 eV, indicating the presence of bulk Ga_2O_3. But, now, the peak labeled As III is shifted 0.4 eV with respect to the unshifted arsenic peak, As_{GaAs}. The shift we expect between free arsenic and arsenic in GaAs is 0.6 eV. Thus, this peak could be due to free As or, equally likely, arsenic bound to only one gallium atom (see the –Ga ligand shifts in Table IV for As_{GaAs}). The latter case would give a shift of about 0.4 eV. Therefore, it is plausible that this peak is due to either free arsenic or arsenic bound to, at most, one gallium atom.

The second arsenic peak in this spectrum, labeled As IV, is shifted 2.6 eV with respect to the As in GaAs. This is exactly the same as the shift observed for bulk As_2O_3 (Table III).

As mentioned above, InP behaves exactly like GaAs in the chemisorption stage. As in the case for the As I peak, the chemical shift in the P-$2p$ ($\Delta E_B = 4.4$ eV) is much larger than one would expect by simply adding an –O or =O group. The shifts in these two cases are 0.24 and 1.58 eV, respectively.[40] This larger shift is again probably due to increased charge transfer from the phosphorous to the oxygen because of the low electronegativity of the surrounding indium atoms. Thus, the same arguments used above for GaAs may be used here.

The case of GaSb(110) is much simpler than that of InP or GaAs. Both the Ga and Sb peaks shift simultaneously. Therefore, bonds are being broken in order to allow charge transfer from both the gallium and antimony atoms, resulting in the simultaneous formation of both gallium and antimony oxides. This difference in the mechanisms of oxygen adsorption is also reflected as a difference in the adsorption kinetics between GaAs and GaSb. This is most clearly seen by comparing the oxygen uptake curves of Figs. 3 and 7. We can immediately make two observations. First, the shapes of these two curves for oxygen coverage *versus* exposure are rather different and, secondly, the GaSb adsorbs oxygen more readily than the GaAs. The second observation can be understood by considering the ionicities of Ga, As, and Sb. There is a larger electronegativity difference between Ga and As than between Ga and Sb. This would imply that the GaAs bond is stronger than that of GaSb, giving a surface that is more resistant to chemisorption of oxygen. In view of this argument, we would expect that InP would behave like GaAs since the electronegativity difference between In and P is also large. This in indeed the case, as was shown above in Fig. 8. The dependence of oxygen uptake with electronegativity difference that we see here agrees with the work of Mark and Creighton[41] in which they observe a decrease in oxygen uptake with increasing bonding ionicity.

The difference in shape between the two curves in Figs. 3 and 7 seems to be very closely tied to the fact that oxygen chemisorbs to the GaAs surface, leaving it intact while, for GaSb, the oxygen actually breaks back bonds and forms oxides. Thus, for GaAs, we expect saturation at half monolayer coverage with the rate of oxygen uptake being a function of the coverage. For GaSb, on the other hand, the coverage does not stop at half monolayer, as seen by the vertical scale of

Fig. 7 (this scale was determined by comparing the oxygen coverages on the GaAs and GaSb spectra from the O $2p$ intensity and assuming half monolayer coverage at saturation for GaAs). In fact, the oxygen uptake for GaSb should be controlled mainly by diffusion of oxygen through the oxide layer to the unoxidized substrate.

At zero coverage, the approximate sticking coefficient is 2×10^{-4} for the GaSb surface and 8×10^{-10} for the GaAs surface. The measured sticking coefficient for GaAs is about five orders of magnitude smaller than what is reported in the literature for the cleaved GaAs (110) surface.[15] The larger sticking probability reported in the literature could possibly be due to the fact that the precautions exercised[15] to avoid effects of excited oxygen[20] were not sufficient or that the surfaces used were not perfect enough.[12,24] Furthermore, in the other studies, saturation is seen at 10^6-L O_2, whereas at this exposure we see less than 10% of saturation coverage (see Fig. 3).

B. Model for oxidation of GaAs(110)

The sequence of events leading to the formation of a thick oxide layer on GaAs may be summarized as follows: (i) the (excited or unexcited) oxygen is first chemisorbed on the surface As atoms with no breaking of back bonds; (ii) addition of excited oxygen leads to the breaking of bonds between the first and second layers in the crystal and the formation of less than two layers of As_2O_5 and Ga_2O_3; (iii) further exposure to oxygen (excited) causes the oxidation to proceed further into the bulk, allowing the newly formed arsenic oxides to sublime and leave an oxide layer mainly composed of Ga_2O_3 with small amounts of bulk As_2O_3 and free As.

The chemisorption step, which is identical for both excited and unexcited oxygen, seems to be a necessary precursor to the breaking of back bonds. In order to break the Ga-As back bonds, we not only need excited oxygen, but also the presence of an oxygen chemisorbed to the arsenic dangling bond. Therefore, the energy carried to the surface by the excited oxygen must be coupled to the strain energy due to the previously chemisorbed oxygen. In fact, if a saturation coverage of oxygen is preadsorbed on the surface and then that surface is exposed to excited oxygen, *two* layers of GaAs can be oxidized by an exposure *20 times less* than was necessary to gradually oxidize only the *top layer* (compare the top curve of Fig. 9 with the "heavily oxidized curve" of Fig. 10).

The initial oxidation results in the formation of the most oxygen-rich oxide of arsenic, satisfying all four of the possible arsenic bonds. This oxide, rather than As_2O_3, is formed because the part of the substrate being oxidized is in direct contact with the gaseous oxygen present in the chamber during exposure and enough oxygen is present to fully oxidize both the surface arsenic and gallium atoms. If the surface is oxidized even further, the substrate peaks are no longer visible, indicating that more than three or four molecular layers of oxide have been formed. This step in the oxidation is then the start of true oxide formation in which there is no longer a direct bonding between the GaAs lattice and most of the oxide and interface layer. In such a situation, as soon as a gallium or arsenic atom has broken its bonds to the underlying lattice due to oxidation of a neighboring site, it is no longer constrained to follow the chemistry of the GaAs surface. Instead, the gallium and arsenic atoms are now free to follow their elemental chemistries. In the case of gallium and arsenic, the formation of Ga_2O_3 is favored over arsenic-oxide formation, as seen by comparing their respective heats of formation.[42] Consequently, elemental gallium is oxidized more readily than elemental arsenic. Since there is now a layer of oxide through which the oxygen must diffuse in order to reach the substrate crystal, the amount of oxygen available for oxidation is limited and, consequently, the gallium will be oxidized first and then the arsenic. This is indeed the case, as seen by the fact that the thick oxide contains elemental arsenic as well as bulk As_2O_3. No elemental Ga is seen in the spectrum for the "very heavily oxidized" surface, indicating that the Ga may even be able to reduce As_2O_3 to elemental As. This could explain the presence of elemental As and no elemental Ga in the thick oxide. No As_2O_5 is present because oxygen is now scarce and the formation of the lower oxide of arsenic is more favorable. If the substrate were heated, resulting in a greater oxygen mobility through the oxide and, thus, a greater oxygen concentration at the interface, the situation would be much like that for the "heavily oxidized" spectrum, so As_2O_5 should then be present in the oxide layer.

Finally, there is very little arsenic (elemental or oxide) present in the thick oxide, indicating that the volatile As_2O_3 does sublime from the surface leaving an oxide rich in Ga_2O_3 with small amounts of As_2O_3 and elemental arsenic.

Caution should be exercised in trying to generalize these results to the polar faces or even (110) faces prepared by different techniques. For example, the work of Ranke and Jacobi[12] on the polar faces prepared either by ion bombardment and annealing or molecular-beam epitaxy suggests that oxygen sticks to the surface gallium atoms. However, the sticking coefficients repor-

ted in those studies were significantly higher than those for the cleaved (110) surface. These larger sticking coefficients were attributed to the presence of Ga atoms on the polar surface with unsaturated bonds.[12] From our results on the oxidation of GaAs(110) with excited oxygen, we saw that, as soon as a Ga-As bond is broken, i.e., as soon as an unsaturated Ga bond is created, the Ga atom immediately becomes oxidized. Thus, if the polar surfaces studied by Ranke and Jacobi do indeed have unsaturated Ga bonds, it is not al all surprising that oxygen bonds preferentially to the Ga atoms. In fact, it would be entirely consistent with the results of our work. Therefore, it seems clear that the chemisorption properties of the various faces are very dependent on the integrity of the surface which is a function of both the fundamental properties of the particular face as well as the surface preparation technique. The resistance to oxidation exhibited by the cleaved GaAs (110) surfaces compared to the other surfaces or (110) surfaces prepared by techniques other than cleavage implies that the cleaved surfaces are more intact, i.e., all the surface atoms have saturated bonds, since the resistance to oxidation is characteristic of a low density of unsaturated bonds.

C. Determination of the escape depth

The relative escape depth for electrons with kinetic energies between 20 and 200 eV may be determined from our experimental results quite simply and elegantly by merely plotting the ratio of the areas under the shifted and unshifted arsenic peaks as a function of photon energy. This curve is given in Fig. 11. The horizontal scale given the kinetic energies of the electrons in the crystal. The photon energies that were used for each point are obtained by adding 40 eV (the approximate As-3d binding energy) to the given kinetic energies. The right-most veritcal scale gives the actual ratio of the areas of the unshifted to shifted As 3d peaks as measured from the spectra of GaAs(110) +10^{12}-L O_2 for various photon energies. The minimum in the escape-depth curve occurs around 60-eV kinetic energy ($h\nu = 100$ eV). The error bars associated with the points are due to the uncertainties in measuring the areas under the peaks.

One assumption that allows us to calculate the *absolute* escape depth $L(E)$ is that there is one oxygen molecule (or atom, for this discussion the nature of the adsorbed species is irrelevant) per surface arsenic atom by an exposure of 10^{12}-L O_2. It seems adequately clear that saturation is reached at 10^{12}-L O_2, but we have yet done no mea-

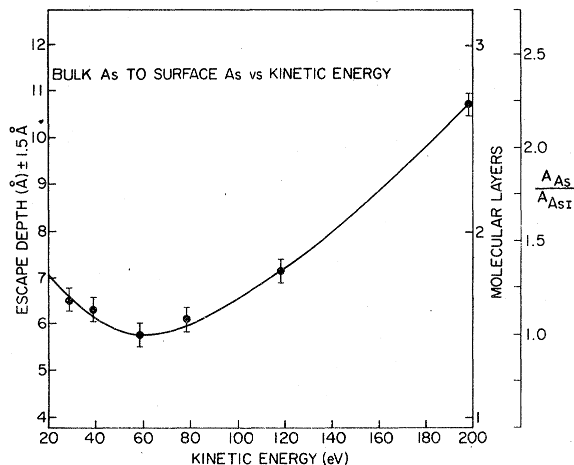

FIG. 11. Plot of the ratio of the unshifted to shifted As 3d levels as a function of electron kinetic energy for the GaAs (110) surface+10^{12}-L O_2 (rightmost scale). The other two scales give the escape depth in angstroms and molecular layers (see text).

surements to determine the actual oxygen coverage at this exposure. However, from the oxidation data of Fig. 2, it does seem to be a reasonable assumption. The major source of error is introduced into the calculation when we try to fix the absolute value of the escape depth. This entails estimating the thickness x_1 of the topmost GaAs plus chemisorbed oxygen layer. This one thickness will then allow us to give an absolute value to the escape depth.

Consider a system composed of two uniform layers, surface and bulk. Here, we neglect the fact that the surface layer is only one molecular layer and thus not uniform. But, in the spirit of the calculation, this assumption will not introduce an unreasonable amount of error. Assuming exponential attenuation of the emitted electrons and that the number of emitted electrons is proportional to the area under the appropriate peak in the photoemission spectrum, we may write

$$L(E) = \frac{x_1}{[\ln(A_{As}/A_{As\,I})]^{-1} + 1},$$

where A_{As} and $A_{As\,I}$ are the areas under the As and As I peaks, respectively. Using tabulated values for the radii of arsenic and oxygen, we let $x_1 = 4 \pm 1.5$ Å.[42] Inserting this into the above equation given the $L(E)$ scale on the left-hand side of Fig. 11. The second scale on the right-hand side of Fig. 11 giving the molecular layers is obtained by dividing the nominal escape depth by the distance between the (110) planes which is approximately 4 Å. At the minimum, the escape depth is 5.8 ± 1.5 Å or approximately 1.5 molecular layers, substantiating our claims of a very large sur-

face sensitivity. With this value for the escape depth, simple calculations show that a spectral feature from the bulk can no longer be seen if it is more than five molecular layers from the surface (this assumes a detectability limit of about 2% for well-separated peaks; if the peaks are close together, we must assume a higher detectability limit).

D. Surface chemical shift

During the course of this work, we have studied the Ga $3d$ levels from the clean GaAs (110) surface over a wide range of photon energies ($35 \leq h\nu \leq 240$ eV). This photon-energy range enables us to probe between approximately 1.5 and 3 molecular layers giving, first, primarily surface and, second, more bulk contributions to the spectra. If an appreciable chemical shift in the core levels between the atoms on the surface and in the bulk were present, it would definitely show up as a change in the full width at half maximum of the Ga $3d$ levels when a photon energy corresponding to a different escape depth was used. The fact is that we see no such effect to better than ±0.1 eV. In view of the surface state model of Fig. 2, these results indicate that there must be enough redistribution of charge along the back bonds, possibly involving several molecular layers, to keep the total charge densities around the surface atoms the same as in the bulk. This charge redistribution may, in fact, be one of the reasons for the smearing of the spin-orbit splitting of the Ga and As $3d$ levels.

The lack of chemical shift between the surface and bulk atoms also implies that the ligand shifts due to each back bond, i.e., the bonds connecting the surface layer to the rest of the crystal, will be $\frac{4}{3}$ larger than the shifts due to the bonds in the bulk. The reason for this is, of course, that the same shift is due to three bonds for the atoms at the surface compared to four in the bulk. This again fits in well with the surface state model of Fig. 1 since the arsenic atoms at the surface must have more charge and the gallium atoms less than the corresponding atoms in the bulk.

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