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STUDY OF THE ELECTRONIC SURFACE STATES OF III-V COMPOUNDS

Semi-Annual Technical Progress Report

1 October 1978 - 31 March 1979

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SUMMARY

In the past six months, work has proceeded on studies of Schottky-barrier formation, oxygen adsorption, and metal-oxygen coadsorption on GaAs (110) surfaces. The overall aim of these studies is to provide fundamental understanding of the interfacial states formation in both the metal-semiconductor and the oxide-semiconductor system. The practical implications will be to engineer devices based on Schottky barriers and to overcome difficulties in passivating III-V compound semiconductor surfaces. These studies also contribute to a particular type of devices, the negative electron affinity photocathodes which involve coadsorption of a metal (Cs) and oxygen on semiconductor surfaces in the fabrication process.

We have deposited group III metals (Al, Ga, and In) on both n- and p-type GaAs (110) surfaces and investigated the Fermi level pinning behavior in detail. We found a systematic difference in the Fermi energy stabilization in the gap with p-type samples pinning 9.25 eV below n-type samples. Since one of the constituents of the substrate material is also in group III, the present results provide further insights into a defect mechanism of Fermi level pinning which we have proposed previously.

We found that, in addition to a shifted As-3d peak, there is asymmetrical broadening of the Ga-3d level toward high binding energy when GaAs (110) is exposed to nonexcited molecular oxygen. The percentage of shifted Ga and shifted As is about equal. However, when a sputtered surface was exposed to oxygen, there was preferential adsorption on the Ga, indicating that the surface condition is important in controlling the final oxidation product.

We found greatly enhanced oxidation of GaAs when it is covered with a thin layer of cesium, in contrast to the cesiated surface, aluminized surfaces oxidize slower than bare surfaces. These results are important in the context of GaAs passivation, Schottky barriers, and negative electron affinity photocathodes.

CONTENTS

I. INVESTIGATION OF THE MECHANISM FOR SCHOTTKY-BARRIER FORMATION BY GROUP III METALS ON GaAs (110)

INTRODUCTION

Although several theories of Schottky-barrier formation have been proposed, none has emerged as the correct general theory which elucidates the mechanism responsible for the barrier formation. Indeed, there may be no such general theory and, at the present time, it seems more appropriate to study limited classes of semiconductor materials. We have chosen the 3-5 compounds for both theoretical and practical reasons. The cleavage faces of GaAs, GaSb, and InP have the advantage that there are no intrinsic surface states in the band gap.[1-4] This is in contrast to the more familiar column 4 semiconductors which do have intrinsic surface states in the band gap upon cleaving.[5,6] It was this concept of intrinsic semiconductor surface states in the gap which was used by Bardeen to explain Schottky-barrier formation on Si.[7] However, the presence of these intrinsic surface states in the gap on the clean cleaved Si (111) surface does not rule out the possibility that other mechanisms may be responsible for surface Fermi energy stabilization after deposition of an overlayer. It is well known, for example, that oxygen chemisorption or SiO_2 formation can be effective in removing the intrinsic surface states from the gap to the point where the surface becomes unpinned. The effect of a metal overlayer on the intrinsic states in the gap is less certain, and thus the presence of intrinsic surface states in the gap does, in effect, complicate matters. The situation is simpler with GaAs, GaSb, and InP since one may begin with a band gap at the surface free from states and then follow the Schottky-barrier formation as the metal is deposited. GaAs is particularly convenient to study since the pinning tends to stabilize the Fermi energy near mid-gap.[8] Thus, barrier formation on both n- and p-type materials is easily followed by photoemission techniques. Since we are able to follow the pinning beginning with submonolayer coverages of metal, our data has a direct bearing on many of the current Schottky-barrier theories.

EXPERIMENTAL CONSIDERATIONS

An advantage of the photoemission technique is that both chemical information and changes in the semiconductor surface Fermi energy are obtained with minimum disruption of the surface under study. This investigation was done using nearly monochromatic soft x-rays ($40 \text{ eV} \leq h\nu \leq 300 \text{ eV}$) from the 4° beam line[9] and ultraviolet light ($10.2 \text{ eV} \leq h\nu \leq 32 \text{ eV}$) from the 8° beam line at the Stanford Synchrotron Radiation Laboratory.[10] The experiments were performed in a standard ultrahigh vacuum system (base pressure 10^{-10} torr) equipped with 200 1/s ion pump, Ti sublimator, and LN_2 cryopump. The GaAs crystals used in the column 3 metal overlayer experiments were degenerately doped n-type (5×10^{17} cm^{-3} Sn, Varian) and nearly degenerate p-type (2×10^{18} cm^{-3} Zn, Laser Diode). Clean GaAs (110) surfaces were prepared by cleaving under vacuum with no hot filament ion gauges operating,[11] producing a surface with low defect density.[1,12] Synchrotron radiation was incident on the GaAs surface at an angle of 14°, and a PHI 15-255G double-pass CMA with axis normal to the (110) surface was used for electron energy analysis.

Al and In were evaporated from small bead sources, while Ga was evaporated from a quartz crucible. The evaporation rates were measured with a Sloan quartz crystal thickness monitor positioned alongside the evaporators, and dosing of the samples was controlled with a shutter positioned between the evaporators and the semiconductor surface. The rate monitor described above was calibrated against a second-rate monitor placed in the sample position in a separate experiment, and thus our estimates of the absolute coverage (assuming bulk metal parameters) should be good to within a factor of two, while estimates of relative coverages are probably better. Deposition rates were always less than 30×10^{14} atoms/cm^2/minute (~5Å/minute), and the use of a small shuttered source minimized the heating of the GaAs surface. All sources were outgassed before cleaving the GaAs crystal. The type and amount of gases present at the sample during evaporation was measured by placing a mass spectrometer head at the sample position in a separate experiment. The increase in partial pressure of O, H_2O, CO, or CO_2 was less than a factor of two for any of the sources following a careful outgassing (base pressure 3×10^{-10} torr). The Ga crucible evaporator was, by far, the worst offender of the three sources and the In bead the cleanest.

Measurement of coverage with a quartz crystal gives the mass adsorbed onto the surface which, for thick films, is easily converted to a thickness by means of the bulk density of the adsorbate. Some difficulty arises in determining the average thickness of an overlayer when the coverage is on the order of a monolayer on a crystaline surface, since the adsorbate may or may not lie in registry with the substrate. Comparison of the atomic density at the GaAs (110) surface (0.89×10^{15} atoms/cm^2) to the atomic density of the bulk metal to the two-thirds power (Ga metal: 1.4×10^{15} atoms/cm^2) gives a measure of the errors that may be expected by assigning a fixed number of atoms/cm^2 as one monolayer with a given thickness. We, therefore, use the number of atoms adsorbed per unit area as a description of coverage. Unity sticking coefficients are assumed for column 3 metals, thus equating dosage with atoms adsorbed per unit area.

BAND-BENDING DETERMINATION

Due to the central role played by semiconductor band bending in this study, a brief description of the band-bending determination will be given. Emission from the Fermi surface of a metal which is electrically shorted to the semiconductor sample is used to establish the Fermi energy (E_F) of the system (see Fig. 1, right-hand side). The photoelectron kinetic energy (at a given $h\nu$) which corresponds to the system Fermi energy is seen to be obtained directly from the metal (Au) EDC (energy distribution curve), independent of the metal work function. The kinetic energy of photoelectrons originating from features in the semiconductor valen-e band are obtained in the same way, independent of the semiconductor's work function. When the semiconductor bands are bent near the surface, it is important to note that the escape depth (L_e^s) of the photoelectrons used for band-banding determination is short (< 20 Å)[13] compared to the band-bending length ($\gtrsim 200$ Å). Thus, the relationship of senucibdyctir vakebce babd features to the system Fermi energy can be measured by UPS techniques. To ensure accurate band-bending determination, several strong semiconductor valence band features are routinely used. An analogous technique can be used with our soft XPS data, with core levels taking the place of valence band features.

The exact position of the semiconductor VBM, and thus its energy relative to E_F, is subject to definition by the experimenter. At 10.2 eV, the matrix elements for emission from the GaAs VBM are strong, and the VBM is easily derived from the EDC.[14] At higher photon energies, the matrix elements are weaker and the VBM is not so well defined. Absolute identification is made when degenerately doped p-type GaAs is cleaved and no band bending occurs. The flat-band condition is verified by cleaving degenerately doped n-type GaAs without pinning and noting that the shift of the valence band relative to E_F is equal to the band gap. This condition was nearly met in this series of experiments, and thus our absolute determination of E_{FS} relative to the VBM is probably good to ±0.1 eV (see Fig. 4, zero coverage). Note that the four data points for the as-cleaved p-type GaAs samples are scattered over a 0.24 eV range. This created some temporary confusion in the data analysis since, in our past experience, it had appeared that p-type GaAs was always unpinned.[14] However, Huijser et al[2] reported that pinning was observed on some rough cleaves on p-type GaAs. It is thought that the variation in pinning behavior may be due to crystal quality. In this analysis, we do not assume that p-type or n-type GaAs is unpinned but, instead, follow the method outlined above. Bachrach et al[15] have assumed unpinned p-type GaAs (110) surfaces in their Ga overlayer experiments, and thus their observation using XPS of no change in band bending after deposition of Ga on p-type GaAs (110) is not conclusive proof of the absence of a barrier.

DEFECT MODEL

In a paper presented at last year's PCSI conference, Lindau et al[16,17] reported on a series of experiments with Au overlayers on GaAs, GaSb, and InP (110) surfaces. The results can be summarized as follows: emission from the core levels of the 3-5 compound was monitored as an Au overlayer was built up stepwise, beginning with ~0.2 monolayer coverage. E_{FS} was essentially stabilized at the final pinning position by ~0.3 monolayers. After the Au overlayer thickness had been increased to the point where emission from semiconductor core levels should be essentially zero, core level emission from one or both semiconductor elements was still observed. In the case of Au on GaSb (110), emission from the Ga-3d core level was absent at high Au coverages, indicating that Au had covered the GaSb fairly uniformly, yet strong Sb-4d core level emission was evident, indicating segregation of the Sb to the surface of the Au overlayer. In the cases of GaAs and InP, both constituents were seen with thick Au overlayers.

UPS measurements were performed on the same system, and several important features of Schottky-barrier formation on these surfaces were seen. The Au-5d valence band peaks were observed to have a splitting that is characteristic of dispersed Au at submonolayer coverages. Constant final state (CFS) spectra were useful for observation of the empty surface states. In the case of GaSb (n-type), the transitions from the Ga-3d core level into empty surface states fade out with no apparent shift as the Au coverage is increased from zero to approximately one monolayer. Thus, E_F pinning was stabilized at ~0.2 monolayer coverage, no apparent movement of intrinsic semiconductor surface states into the gap was observed, and at high coverages it is evident that disruption of the 3-5 compound at the interface has occurred.

A most important observation concerning Fermi energy stabilization on 3-5 compounds was that the pinning position on a given 3-5 semiconductor was only slightly, if at all, different for metal overlayers of extremely different electronegativity (i.e., Cs and Au) and also for oxygen overlayers. In all cases, pinning was established at approximately the same position with only a small fraction of a monolayer of adsorbate. This required a model of Fermi energy stabilization which was independent of the overlayer. On this basis, a model for Schottky-barrier formation was proposed in which the new electronic states in the band gap were associated with semiconductor defects.

NEW RESULTS

The model outlined in the previous section provided motivation for forming a metal-semiconductor junction using one of the semiconductor constituents. By forming the junction with, for example, Ga on GaAs, the density of the pinning states which may be associated with a Ga deficiency at the interface might be reduced to the point where the barrier height was significantly decreased. Experiments were undertaken to examine the barrier formation on atomically clean GaAs (110) surfaces using Al, Ga, and In overlayers. Both n- and p-type substrates were used in an attempt to identify defect levels as either donor or acceptor type.

Stepwise deposition of the metal overlayer, beginning with (in most cases) less than 10^{14} atom/cm^2, allowed the evolution of the band bending and electronic states to be observed as the coverage was increased. EDCs taken during a series of Ga depositions on n-type GaAs using $h\nu$ = 21 eV are shown as an example which is typical for the column 3 metals on (110) GaAs (see Fig. 2). The position of the Fermi energy was determined from an EDC taken at the same photon energy of an Au substrate which was electrically shorted to the semiconductor samples. The EDC of the clean surface shows that the initial degree of band bending is small (~0.1 eV) and that the structure over the entire valence band, which is approximately 14 eV wide, is slightly smeared. This smearing can be due to both strain at the surface and nonuniform pinning.[18] The EDC structure is sharper on well-cleaved surfaces of p-type GaAs. The valence band structure had sharpened considerably[19] after deposition of only $0.05 \times 10^{15}/cm^2$ Ga, indicating that the surface Fermi energy was uniform and the strain reduced by the metal. An increase of 0.2 eV in the band bending was produced by $0.05 \times 10^{15}/cm^2$ Ga, but emission from states in the band gap was not yet evident. The next Ga deposition increased the total coverage to $0.5\ 10^{15}/cm^2$ and increased the band bending to 0.5 eV in a continuation of the trends seen after the first deposition. Note that some weak emission is seen from states between the GaAs valence band maximum and the Fermi energy. Further increases in Ga coverage did not produce appreciable changes in the band bending. At two monolayers coverage, the GaAs valence band structure is somewhat attenuated, and the emission from the states above the GaAs valence band maximum is stronger and resembles emission from Ga metal.

Constant final state (CFS)[20] spectra were obtained from the same surface (see Fig. 3). The strong peak at $h\nu = 28.6$ eV on the clean surface is due to excitation of the Ga-3d core level into the energy window of the CMA, which was centered at 4 eV kinetic energy. The two small peaks at 19.5 and 20.0 eV are produced by excitation of Ga-3d electrons into excitonic levels associated with empty surface or conduction band states.[21] The difference in energy of these two peaks (0.5 eV) is just the spin-orbit splitting of the Ga-3d core level. After $0.5 \times 10^{15}/\text{cm}^2$ of Ga was deposited on the surface, the Ga-3d peak position shifted by 0.4 eV due to band bending, as seen in the valence band EDCs (Fig. 2). The overlap between the metallic Ga-3d (3/2) and the semiconductor Ga-3d (5/2) makes the Ga-3d peak unreliable for determination of the E_F shift at the highest coverage. The peaks associated with the empty states near the conduction band minimum are of greatest interest here since movement of surface states into the band gap would produce pinning on n-type material. As the Ga overlayer thickness is increased, the excitonic peaks are reduced in amplitude until they are nearly gone at two monolayers coverage. No movement of these states toward the band gap is evident. The excitonic states are also stationary in the cases of O_2[1] and Au.[16,17] However, the peaks are eliminated at coverages of less than one monolayer Au and at less than one-half monolayer O_2. The weak persistence of the excitonic peaks with column 3 metal overlayers at ~ monolayer coverage may be due to a small percentage of uncovered Ga sites or related to the lack of strong disordering (as evidenced by sharp valence band structure) with these overlayers.

Changes in the band bending were measured to examine the trends in the position of the semiconductor surface Fermi energy (E_{FS}) within the band gap as a function of metal type, coverage, and bulk doping of the semiconductor. Degenerately doped n-type and nearly degenerate p-type GaAs were chosen so that the lowest acceptor levels and the highest donor levels (relative to the valence band maximum) could be determined for each metal. Data points for the as-cleaved surface are shown at zero metal coverage (see Fig. 4).

The variation of E_{FS} at submonolayer coverages is critical to the evaluation of different models for Schottky-barrier formation. Here, we see that the trend for barrier formation at low coverages is similar for Al, Ga, and In: the pinning is fairly well stabilized by a coverage of $0.2 \times 10^{14}/\text{cm}^2$ on both n- and p-type GaAs and seems to approach a common value for a given bulk doping, regardless of whether the surface was originally unpinned or partially pinned. Some variation is seen in the coverage at which the pinning becomes stabilized, but it is not clear whether any systematic trend in this regard can be extracted from the data. For example, In appears to produce stabilized pinning at a lower coverage than Ga or Al in general, but also note the large variation of the Ga coverage at which stabilization of the pinning occurs on p-type GaAs. This latter effect may be due to the interaction of Ga with defects produced at the surface by metal deposition.

A general picture of the sequence of events as the metal coverage is increased from zero can be constructed from this data. At coverages on the order of $0.1 \times 10^{15}/\text{cm}^2$, UPS data show that some strain which may be present at the interface is relieved and the pinning becomes fairly uniform across the surface. Pinning is usually stabilized at or below $0.2 \times 10^{15}/\text{cm}^2$ coverage between 0.75 and 0.85 eV on n-type and 0.5 to 0.6 eV on p-type GaAs. As the coverage is increased up to two monolayers, EDC structure remains sharp but becomes attenuated, while the excitonic structure in the CFS data almost disappears.

DISCUSSION

Several theoretical models of Schottky-barrier formation can be briefly reviewed[22] in the light of the paper last year of Lindau et al[16] and the results given above. The classic model of Bardeen explained Schottky-barrier formation on Si in terms of intrinsic surface states.[7] These states were later observed experimentally at the Si (111)-vacuum interface.[5,6] However, it is now well accepted that the (110) cleavage faces of many 3-5 compounds, including GaAs, GaSb,[2] and InP, do not contain intrinsic surface states in the band gap. In this case, some mechanism is needed to introduce extrinsic states into the gap or move intrinsic states into the gap.

Heine has proposed that bulk metallic states may tunnel into the semiconductor with decaying amplitude,[23] with a sufficient density of states within the band gap to pin the Fermi energy. Louie et al have also concluded that extrinsically-induced metal states were the determining factor in Fermi level stabilization,[24] based on pseudopotential calculations using a periodic jellium-semiconductor sandwich. In the theory by Inkson, it is proposed that the semiconductor band gap narrows at the surface due to dielectric screening differences between the metal and the semiconductor at the interface.[25] The narrowing pins the Fermi level and thus determines the barrier height. A model has been proposed by Brillson[26] in which both the band bending and the interfacial dipole resulting from some ionicity in the chemical bond between metal and semiconductor atoms contribute to the barrier height. Rowe et al have determined experimentally that Fermi energy stabilization can be completed with metal coverages of one monolayer (~ 2 Å) of column 3 metals on Si[27] (which has intrinsic surface states) and with submonolayer coverages of In on compound semiconductors[28] (no intrinsic surface states). They concluded that the E_F stabilization position within the gap is determined by the new distribution of interface states in the gap.[27]

The observed phenomena of Fermi energy stabilization in the band gap at coverages well below one monolayer, together with a lack of band-gap emission from other than metallic states, does not seem completely consistent with these models. Lindau et al[16,17] have presented detailed evidence which demonstrates that E_{FS} can be stabilized before bulk metallic states are formed. The trend for Fermi energy pinning near the valence band maximum in GaSb or near the conduction band minimum in InP does not seem to follow from the band narrowing theory by Inkson.[25] In regard to the model by Brillson,[26] the interfacial dipole may be expected to affect the work function at coverages below a couple of monolayers but should not contribute to the macroscopic Schottky barrier due to the high probability of tunneling through a spike in the microscopic potential which is on the order of a few angstroms wide in the data given above. The photovoltaic method of obtaining the band bending by Brillson[26] is also open to question since photoemission techniques, which give the band bending directly, have shown different results. Neither a high density of filled nor empty interfacial states (i.e., metal-semiconductor bonds) was observed in the band gap of GaAs following deposition of column 3 metals, but only metal-like emission, and therefore the suggestion of E_F stabilization by a high density of interfacial states in the band gap of Si by Rowe et al[27] cannot be extended to GaAs.

A defect mechanism for Schottky-barrier formation seems the best contender based on previous and current work presented here. Lindau et al[16,17] have suggested that the formation of defects in the semiconductor lattice may be driven by the energy released upon chemical bond formation between semiconductor and metal atoms. The probability of formation of a pinning defect certainly depends on the energy released during chemisorption of the metal and is probably less than unity in most cases. It is important to realize that the kinetic energy of the metal atom is insignificant compared to the chemisorption energy and consequently does not play a role in this model. Evidence for this mechanism is discussed by Spicer et al[29] in these proceedings.

The suspected role of defects in Fermi energy stabilization motivated a study of column 3 metals on GaAs to determine if Ga could reduce the surface vacancy density and in any way affect the Fermi energy stabilization. The behavior of the Fermi energy stabilization and intrinsic surface states with column 3 metal coverage follows the trends outlined by Lindau et al:[16,17] the pinning is essentially completed at coverages on the order of one to several tenths of a monolayer, and intrinsic or extrinsic semiconductor surface states are not evident in the band gap at any point in the metalization.

However, important new information concerning the role of defects in Fermi energy pinning is obtained from measurements of the Fermi energy position within the band gap as a function of semiconductor bulk doping. The observed trend is for the Fermi energy to be pinned 0.75 to 0.85 eV above the valence band maximum on n-type samples, but the pinning stabilizes between 0.5 and 0.6 eV on p-type GaAs. This evidence for discrete acceptor and donor levels is readily explained in a defect model picture, as discussed by Spicer et al.[29] These results are in disagreement with the well-known results of Mead and Spitzer,[8] in which the pinning positions within the band gap on n- and p-type GaAs were the same within 0.1 eV for Au and Al overlayers, roughly 0.5 eV above the VBM. These results are also not in agreement with the finding of zero-barrier height for Ga on p-type GaAs reported by Bachrach.[15] These differences may be related to the details of metal deposition and, in particular, to the deposition rate (surface heating may result from high rates) and radiative heating from the source. Since the possibilities for defects and compound formation are numerous, care must be taken to minimize the formation of defects. Other data[30] indicates that our techniques have less tendency to induce compound formation than those of Bachrach. Also, Bachrach assumed an absence of band bending after cleaving in the interpretation of his XPS data.

Some information regarding the density and type of defects may be inferred from the data presented here. A minimum of 4×10^{12} surface charges/cm^2, 1 percent of the number of surface Ga atoms, is required to compensate charge in the depletion region for a band bending of 0.5 eV with a bulk doping of 2×10^{18} cm^{-3}. The defect density is probably not as large as the number of surface atoms, based on the degree of structure sharpness seen in the valen-e band UPS data and the lack of sharp defect level emission in the gap when E_{FS} is pinned after deposition of metal. The association between EDC structure sharpness and surface order has been demonstrated by a comparison of cleaved, heat cleaned, and sputtered and annealed surfaces.[12] The occurrence of pinning on freshly cleaved n-type GaAs surfaces with sharp EDC structure but never a case of smeared structure on an unpinned n-type GaAs surface indicates that Fermi energy pinning is a more sensitive indicator of surface disorder than EDC structure.[12,18] Thus, the occurrence of both pinning and structure sharpening are not inconsistent.

That the Fermi energy stabilization can result from the deposition of a fraction of a monolayer of metal, together with other considerations already discussed, suggests that point defects at the surface may be responsible for the pinning. The possibilities include monovacancy, interstitial, and antisite defects. Deposition of Ga onto the surface should greatly reduce the density of surface Ga vacancies formed by means of the energy released when the metal atom chemisorbs onto the semiconductor. If surface Ga vacancies were associated with the pinning levels, the band bending should decrease with the annihilation of the Ga vacancies. Al and In should be nearly as efficient as Ga metal in eliminating surface Ga vacancies, since ternary compounds of $Al_xGa_{1-x}As$ and $Ga_{1-x}In_xAs$ (with $x << 1$) are not significantly different from GaAs in lattice dimensions and band gap. The very similar barrier heights seen in every case reported here on n- and p-type GaAs suggests that surface Ga vacancies are not likely to be responsible for the observed barrier formation. Neither do surface interstitial defects seem a likely choice due to the instability that would be expected for an interstitial atom in the surface lattice. Surface anti-site defects, or other defects beneath the surface, are likely to be produced by metal deposition even though a column 3 metal is used.

Last year, in these proceedings, our group tentatively suggested that the pinning on GaAs was due to Ga vacancies based on the results reported by Bachrach[15] and Amith et al[31] at the Fifth PCSI Meeting. At this meeting, we have presented a much more detailed and comprehensive model for both Schottky-barrier pinning and interface states on MIS structures.[32] In this, we tentatively suggest GaAs defect levels at 0.8 and 0.55 eV due to As and Ga anti-site defects: the 0.8 eV level being due to Ga on an As site producing an electron acceptor and the 0.55 eV level an As on a Ga site producing an electron donor. However, we emphasize that the detailed nature of the defect is rather speculative, e.g., a vacancy might be associated with the anti-site defect. Further, it is recognized that the defect may lie partially or entirely below the surface. A more detailed model, in which the heat of chemisorption provides energy for the creation of pinning defects, is given in the paper by Spicer et al.[29] On the basis of that model, net out-diffusion of both As and Ga from below the surface may be possible even though a column 3 metal is deposited. Thus, it appears that the present data is consistent with our new model of defect formation by metal deposition. However, more work must be done to uniquely establish this model. In addition, Williams[33] has shown that the type and behavior of pinning defects is more complex when highly reactive materials are involved.

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FIGURE CAPTIONS

1. Determination of the relative energies of the semiconductor valence band and the Fermi energy. A highly schematic band diagram of the metal reference is shown in the lower right-hand corner, and above the band diagram is the corresponding photoemission EDC obtained using $h\nu = 21$ eV. A similar set of diagrams is given for the semiconductor; in this case, with E_F at the CBM in the bulk and pinned at approximately mid-gap at the surface. The relative energies of the VBM and E_F are obtained directly from the photoemission measurements. Note that the vacuum level at the sample surface may change without affecting peak positions in the EDCs: this is due to all energies being measured relative to E_F.

2. Valence band EDCs at sequential stages of Ga deposition on n-type GaAs. Emission from metallic states is weak due, in part, to the photon energy being greater than the metal plasma frequency. Since the Fermi energy is taken as the zero of energy in this figure, the band bending is obtained from the position of sharp structure in the valence band such as the peak at about -8 eV. Dosage (D) is given in units of $10^{15}/cm^2$.

3. Constant final state (CFS) spectra of the same surfaces for which EDCs were shown in Fig. 3. Reduction of structure at ~550 Å wavelength and 0.05 Ga coverage is due to orbit change in the synchrotron. The indicated shift in Fermi energy corresponds to the open circles at zero coverage and at 0.5 coverage in Fig. 4. The structure at 19.5 and 20.0 eV is due to excitons involving the lowest

intrinsic empty state. The lack of movement of these peaks suggests that the empty surface states associated with the excitons do not drop into the band gap. *Dosage (D) is given in units of* $10^{15}/cm^2$.

4. Variation of band bending as a function of metal coverage for Al, Ga, and In on n- and p-type GaAs (110). Points with a slash line indicate a second run on a new cleaved surface. Note the difference in pinning position on n- vs p-type samples; the acceptor levels on n-type GaAs are 0.25 eV above the donor levels seen on p-type GaAs. Error bars for absolute energy position are ±0.1 eV and probably smaller for relative energy position. The p-type samples were non-degenerate, and hence the VBM is slightly below E_{FS} *on the unpinned* p-type surface. The data was obtained from valence band data with $h\nu = 21$ eV such that the surface sensitivity is within the limits described under Band Bending Determination.

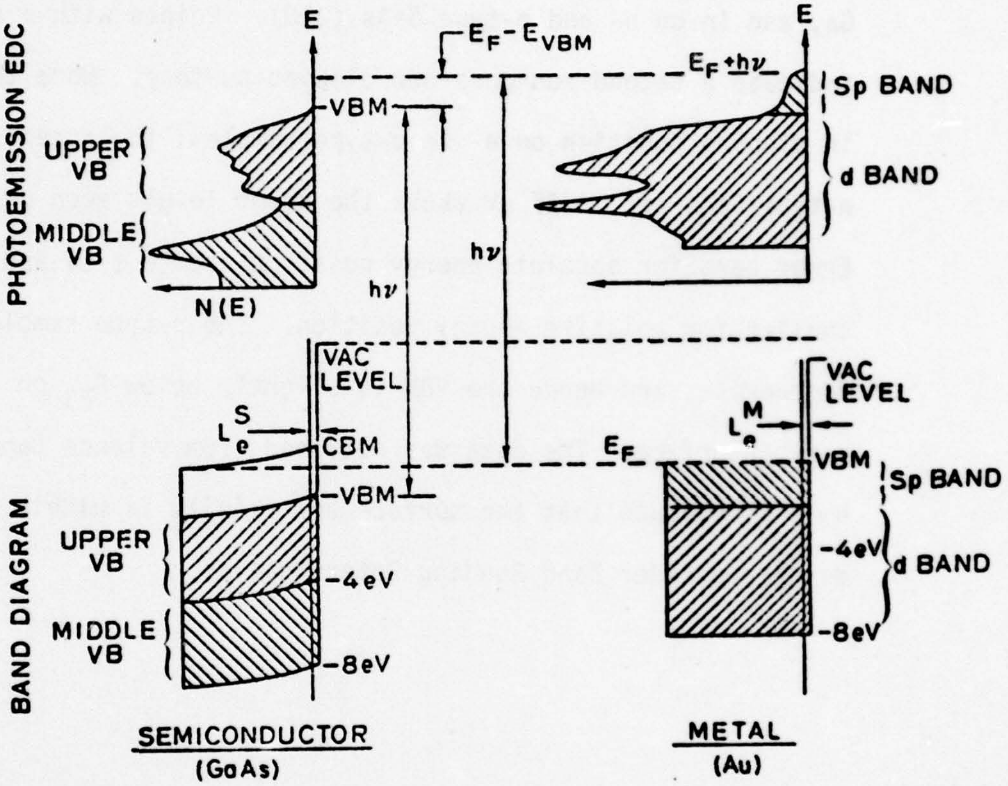
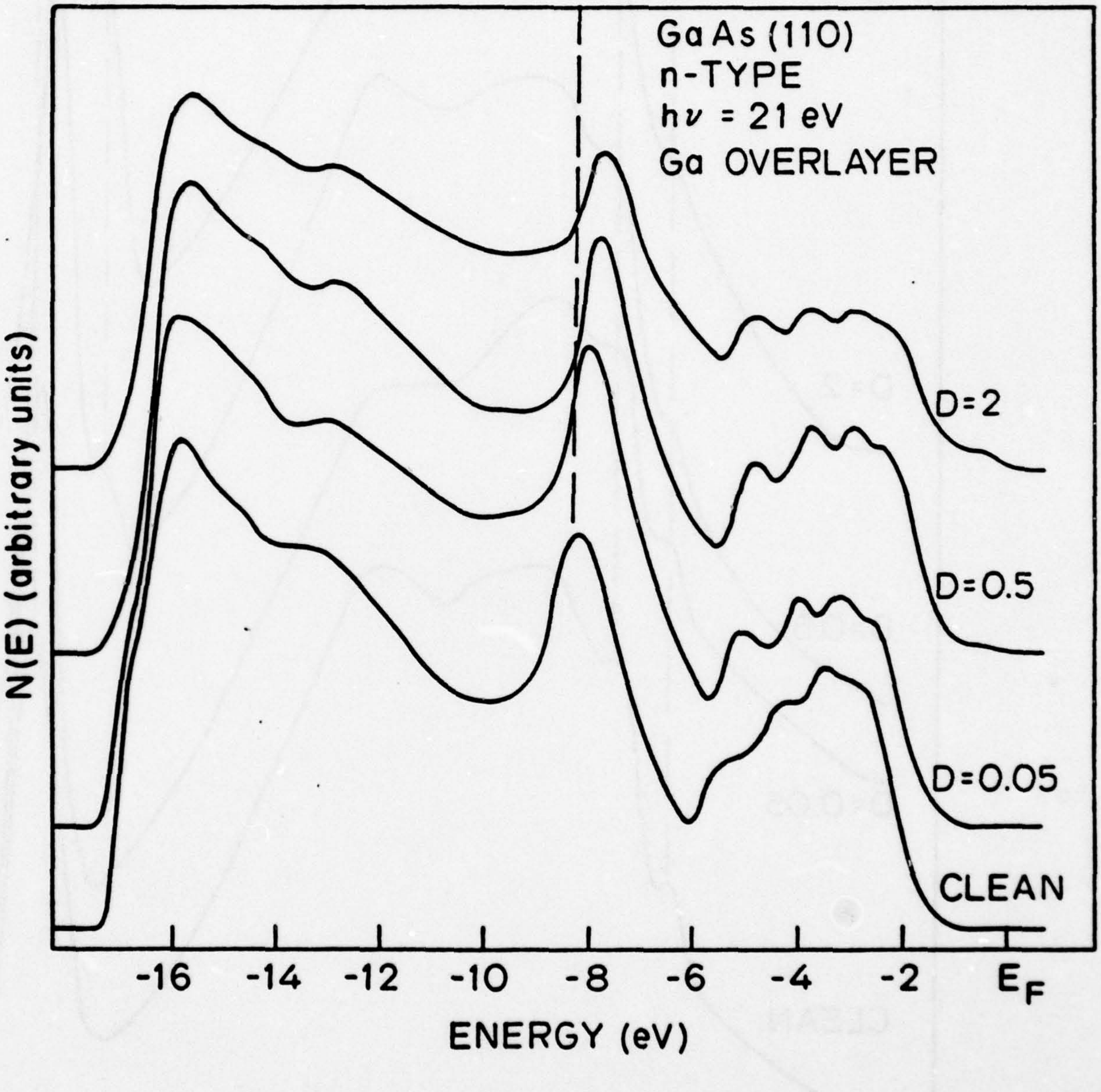
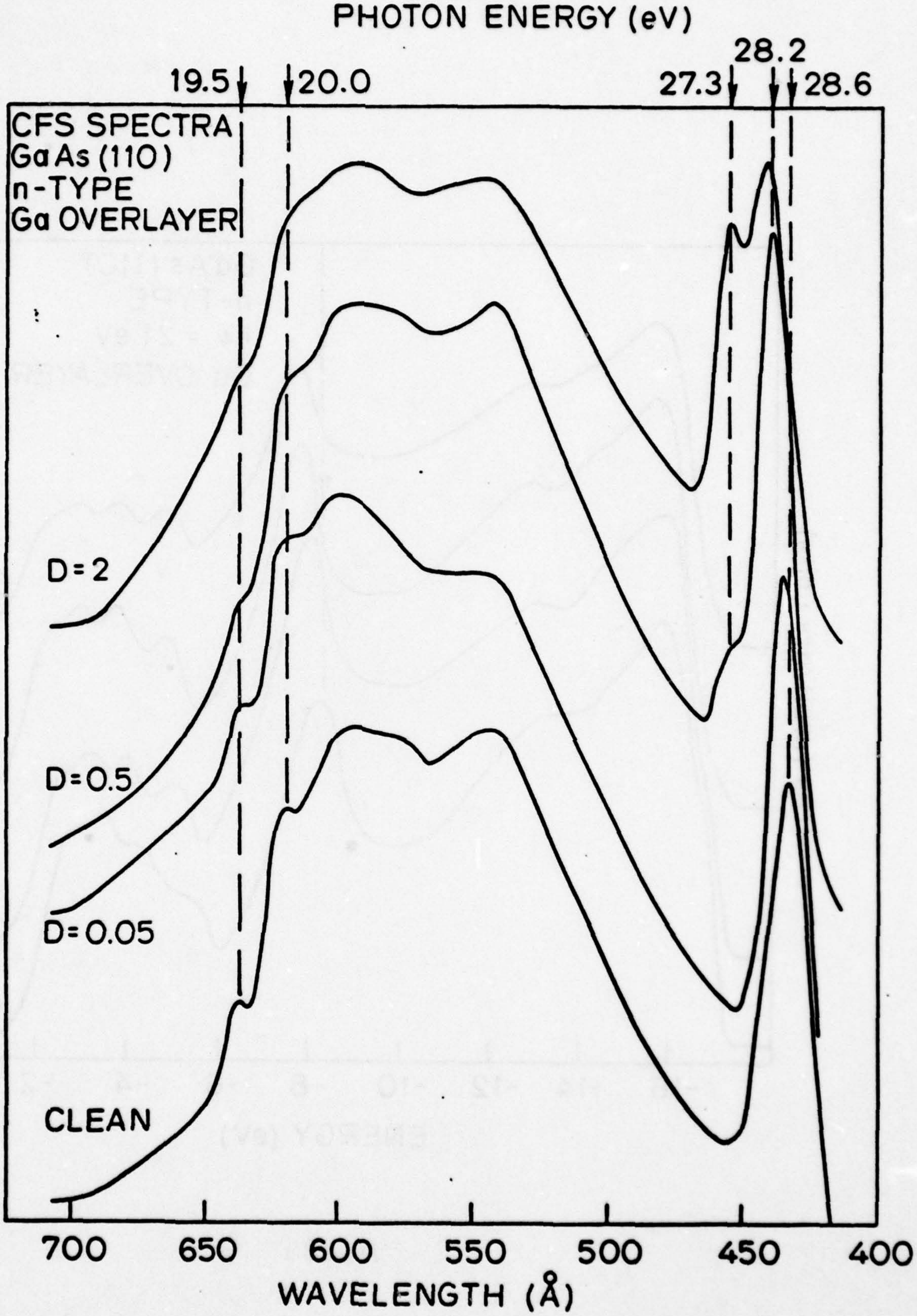

PHOTOEMISSION EDC
E
$E_F - E_{VBM}$
E
$E_F + h\nu$
Sp BAND
VBM
UPPER VB
d BAND
MIDDLE VB
$h\nu$
$h\nu$
N(E)
VAC LEVEL
VAC LEVEL
L_e^S
L_e^M
CBM
E_F
VBM
Sp BAND
VBM
UPPER VB
-4eV
d BAND
-4eV
MIDDLE VB
-8eV
-8eV
BAND DIAGRAM
SEMICONDUCTOR (GaAs)
METAL (Au)

Figure 1



Ga As (110)
n-TYPE
hν = 21 eV
Ga OVERLAYER
D=2
D=0.5
D=0.05
CLEAN
N(E) (arbitrary units)
-16
-14
-12
-10
-8
-6
-4
-2
E_F
ENERGY (eV)

Figure 2



PHOTON ENERGY (eV)
19.5
20.0
27.3
28.2
28.6
CFS SPECTRA
Ga As (110)
n-TYPE
Ga OVERLAYER
D=2
D=0.5
D=0.05
CLEAN
700
650
600
550
500
450
400
WAVELENGTH (Å)

Figure 3

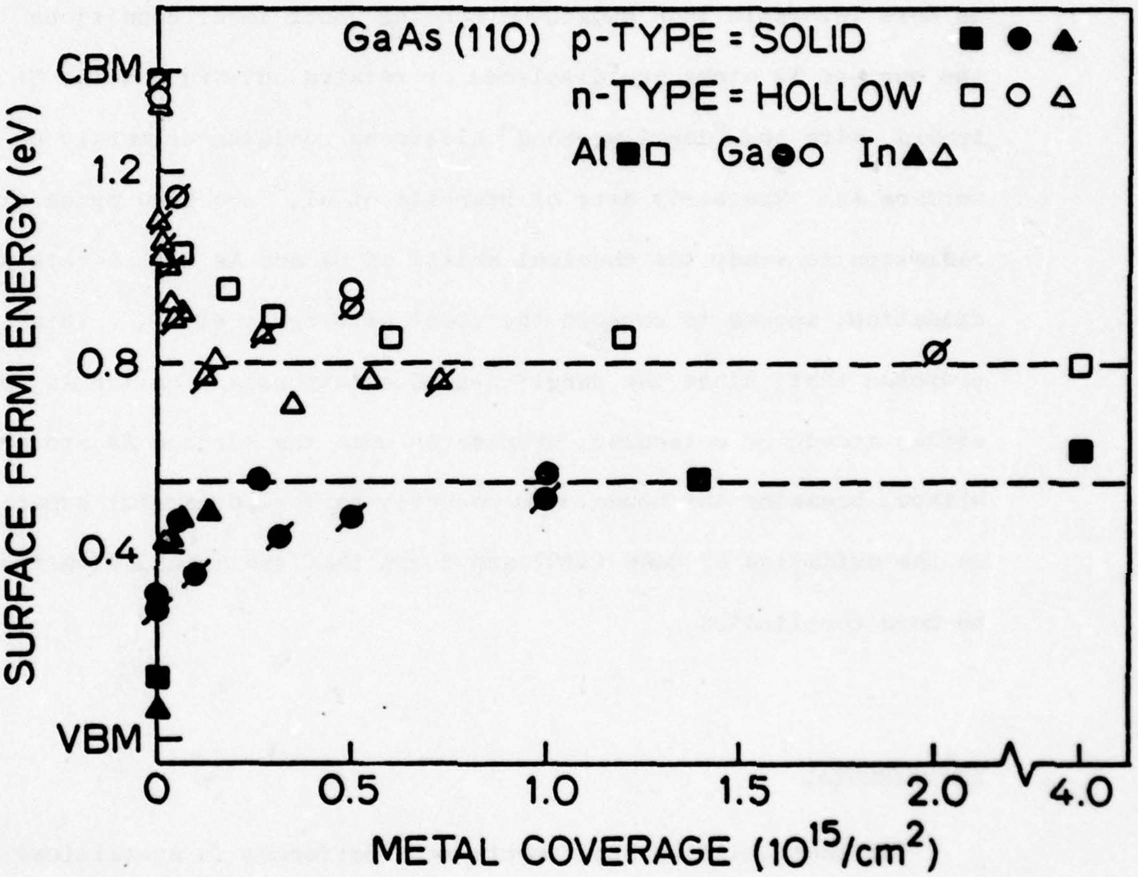

GaAs (110) p-TYPE = SOLID ■ ● ▲
n-TYPE = HOLLOW □ ○ △
Al ■□ Ga ●○ In ▲△
CBM
1.2
0.8
0.4
VBM
SURFACE FERMI ENERGY (eV)
0
0.5
1.0
1.5
2.0
4.0
METAL COVERAGE ($10^{15}/cm^2$)

Figure 4

II. THE OXIDATION OF ORDERED AND DISORDERED GaAs (110)

INTRODUCTION

The physics of the initial stages of oxidation of GaAs (110) has been under investigation for some time. Recently, some agreements have emerged for the cleaved (110) surface. For example, oxygen-As bonding is more favorable than oxygen-Ga bonding under ideal conditions[1,2] since the surface As atoms are displaced or rotated outward and the Ga atoms inward, with the "dangling-bond" electrons residing primarily on the surface As. The early data of Pianetta et al,[3] who used synchrotron radiation to study the chemical shifts of Ga and As core levels upon oxidation, appear to support the model of Gregory et al.[1] This model proposes that, since the dangling-bond electrons are on the As, oxygen, either atomic or molecular, chemisorbs onto the surface As atoms only, without breaking any bonds. We recently performed careful experiments on the oxidation of GaAs (110) and found that the actual situation may be more complicated.

EXPERIMENTAL

The photoemission experiments were performed in a stainless steel vacuum chamber (base pressure ~10^{-10} torr), with synchrotron radiation from the SPEAR storage ring as the excitation source.[3] Clean GaAs (110) surfaces were prepared by cleaving in situ. During all oxygen exposures, precautions were taken to avoid excitation of the gas.[3] Ion pumps were valved off, cold cathode or thermocouple gauges were only used to measure the initial and final pressures, and the high voltage cables to the double-pass cylindrical mirror analyzer (CMA) were removed. The batteries in the CMA controller can generate a plasma discharge at certain pressures and cause heavy oxidation of the samples. Details of the experiment are given elsewhere.[4]

RESULTS AND DISCUSSION

Figure 1 shows photoemission spectra at $h\nu = 100$ eV from a GaAs (110) surface exposed to 10^{13} L (1 Langmuir = 10^{-6} torr-sec) oxygen. In these curves, one can observe emission from the Ga-3d and As-3d core levels. There is a clear 3.0 eV chemical shift on the As-3d towards higher binding energy (BE), indicating bonding of oxygen to the As atoms. The situation on the Ga-3d is less clear since a resolvable chemical shift is absent, although there is a broadening of this level. The broadening of the Ga-3d core level is displayed in great detail in Fig. 2. The statistics in these spectra are better than those of Pianetta et al.[3] Analysis was also aided by having the data stored on tape.

The set of Ga-3d levels at various oxygen exposures are normalized to the same peak height (Fig. 2). These are aligned by referencing to the unshifted As-3d with the assumption that BE(As)-BE(Ga) of the unshifted levels remains constant with surface treatment. One notices that, with increasing oxygen exposure, there is asymmetrical broadening of the line, with a significant amount of broadening to the higher BE side. The amount of broadening may be estimated by deconvolution of the Ga level. Our procedure was to fit the asymmetrical peak with three skewed Gaussian components, one unshifted (which retains the same BE relative to the As-3d as on the clean surface) and two shifted (towards higher and lower BE). We have also tried to fit the Ga-3d using two components, one "unshifted" and one shifted towards higher BE. In this case, however, the position of the "unshifted" component is also permitted to vary in the curve-fitting procedure. The total amount of shifted Ga (expressed as percentage of total Ga-3d emission) is roughly the same in the two procedures. Further details of the deconvolution will be reported elsewhere.[4]

Table I lists the results of the deconvolution using three components. The amount of shifted As is shown as a percentage of the total As-3d emission (the area under the shifted and unshifted peaks). Also listed is the amount of shifted Ga-3d, expressed as a percentage of the total Ga-3d emission. From this table, we observe the following.

(1) For all exposures on the ordered surface with nonexcited oxygen, the percentage of the total shifted Ga-3d is roughly the same as the As-3d.

(2) For the sputtered surface, there is a large shifted Ga-3d component even at 10^9 L (about the same as for 10^{13} L of nonexcited oxygen on an ordered surface), but the shifted As-3d is much less than on the unsputtered surface at the same exposure.

The present data show unambiguously that a component shifted (by ~0.9 eV[4]) towards higher BE is present in the Ga-3d when GaAs is exposed to oxygen. However, it is not clear what the nature of this shifted component is. While it is located near the position of Ga-3d in Ga_2O_3, suggesting that Ga_2O_3 or a Ga suboxide is formed, recent calculations by Goddard[5] show that the expected Ga chemical shift for oxygen chemisorbed on the As is 0.8 eV, so that it is possible that oxygen is chemisorbed on the surface As only, with the surface Ga atoms not directly involved. The observed percentage of shifted As-3d is roughly the same as the percentage of shifted Ga at all coverages if the initial surface is undamaged and unexcited oxygen is used. Since each surface As is bonded to three Ga atoms, it appears that, in a chemisorption-on-As picture, initially, the percentage of shifted Ga should be much larger than the percentage of shifted As unless there is a nucleation mechanism so that the chemisorption occurs in patches; another possibility is that chemisorption causes loss of symmetry, i.e., causing As and Ga to pair up. A more definitive test of the simple chemisorption on the As model is to obtain the relative amounts of oxygen and shifted As from the emission intensity of oxygen and As levels after correction for the cross sections. For simple chemisorption of atomic oxygen on As only, there should be one oxygen for every shifted As. From his XPS data, Brundle[6] has estimated the amount of oxygen relative to the shifted As on GaAs (110) exposed to unexcited oxygen and obtained values close to three oxygens for each shifted As. He suggests formation of Ga_2O_3 and As_2O_3. Su[4] has also made a preliminary estimate of the oxygen/shifted As ratio and obtained values between 3 and 4. If these estimates are correct, simple chemisorption on the surface As alone is not likely. One then would have to invoke bonding to the Ga atoms as well. Possibilities are Ga_2O_3 and As_2O_3, suggested by Brundle,[6] although it is difficult to see how these would passivate the surface. Another possibility is $GaAsO_4$. Ludeke[7] has proposed a model suggesting formation of a distorted (111) layer of $GaAsO_4$ which apparently explains the surface passivation and disordering. His model predicts 1.5 monolayers of oxygen at saturation or three oxygens per shifted As. The present data are not inconsistent with his model, although he predicted only a 0.2 eV chemical shift on the Ga (compared to the 0.9 eV observed experimentally in our data). However, since Goddard predicts a 0.8 eV shift on the Ga even without direct bonding to the Ga, it is likely that the prediction of the 0.2 eV shift by Ludeke is on the low side.

Once the GaAs (110) surface is disordered by sputtering, the percentage of shifted Ga with oxygen exposure is increased substantially. The opposite is true for the As (see Table I), although, on an ordered surface, the amount of shifted As with oxygen exposure is about equal to the amount of shifted Ga. This shows that the As atoms are able to compete strongly for oxygen on an ordered (110) surface produced by cleaving. From the quantitative data in the previous paragraph, it is likely that oxygen bonds to the Ga as well. Thus, it appears that bonding of oxygen to the As may perturb the surface sufficiently to promote bonding to Ga sites. On the other hand, once the surface is disordered by sputtering (or has defects produced in other ways), there is much more oxygen bonding to Ga than to As. The arguments based on bulk thermodynamics, namely, that Ga oxides form more readily than As-oxides, can now be applied.

Mark et al[8,9,10] have suggested that the oxidation on GaAs (110) commences on residual defect sites and produces additional disorder owing to the release of exothermic adsorption energy, so that, as the oxidation progresses, the entire surface becomes disordered. In the present case, on the ordered, cleaved (110) surface, the role of defects is not clear. If oxygen adsorbs only on native and subsequently generated defect sites, then one would expect to observe roughly equal percentages of shifted As and shifted Ga on both ordered (cleaved) and disordered (sputtered) surfaces. Possibly, the defects play a more complicated role, e.g., catalyzing the dissociation of O_2 as suggested by Goddard et al.[11]

Mele and Joannopoulos[12,13,14] have made calculations of the local density of states for different configurations of oxygen chemisorbed on GaAs. Some of the data of Pianetta et al[15,16] on the valence band structure of GaAs after oxygen adsorption, when compared to these calculations, appear to support a picture of molecular oxygen chemisorbed on the surface As[12,13,14] because of detailed structure. In addition, a shift towards higher BE (from 11 to 13 eV) of the As-4s band was taken as evidence for chemisorption of oxygen to the As. However, this shift is not present in most of Pianetta et al's data. We have studied the adsorption of oxygen on GaAs using higher photon energies, where the As-4s like bands can be observed more easily. The results are shown in Fig. 3. No shift of the As-4s band towards higher BE was seen in this set of data. The absence of the shift for the As-4s predicted by Mele and Joannopoulos[12,13,14] indicates that a simple chemisorbed configuration may not be an adequate description of the actual situation. Though simple chemisorption to the surface As may occur in some cases, more complex bonding generally prevails. The chemical shift data presented above show that bonding to surface Ga's very likely also occurs. The dominance of one oxygen derived structure in these spectra suggest atomic rather than molecular oxygen adsorption.[12,13,14]

In summary, the present data support a model that on the cleaved (110) surface oxygen bonds to both the surface As and the surface Ga, although alternative explanations exist. If bonding is to both Ga and As, it must be in such a manner that roughly a monolayer coverage gives a protective layer. It is hard to reconcile this with bulk Ga_2O_3 and As_2O_3 forming. For a surface which has been disordered by sputtering, bulk thermodynamics takes over and preferential bonding of oxygen to Ga is observed.

Table I

Treatment	Percent Shifted As	Percent Shifted Ga
10^7 L O_2	9	12
10^8 L O_2	23	22
10^9 L O_2	27	26
10^{10} L O_2	34	28
10^{13} L O_2	52	47
sputtered surface + 10^9 L O_2	11	48

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FIGURE CAPTIONS

1. Photoemission spectra at $\hbar\omega = 100$ eV for GaAs (110) exposed to 10^{13} L oxygen.

2. Photoemission spectra at $\hbar\omega = 100$ eV of the Ga-3d core level for GaAs (110) at different oxygen exposures.

3. Photoemission spectra at $\hbar\omega = 30$ eV for GaAs (110) at different oxygen exposures.

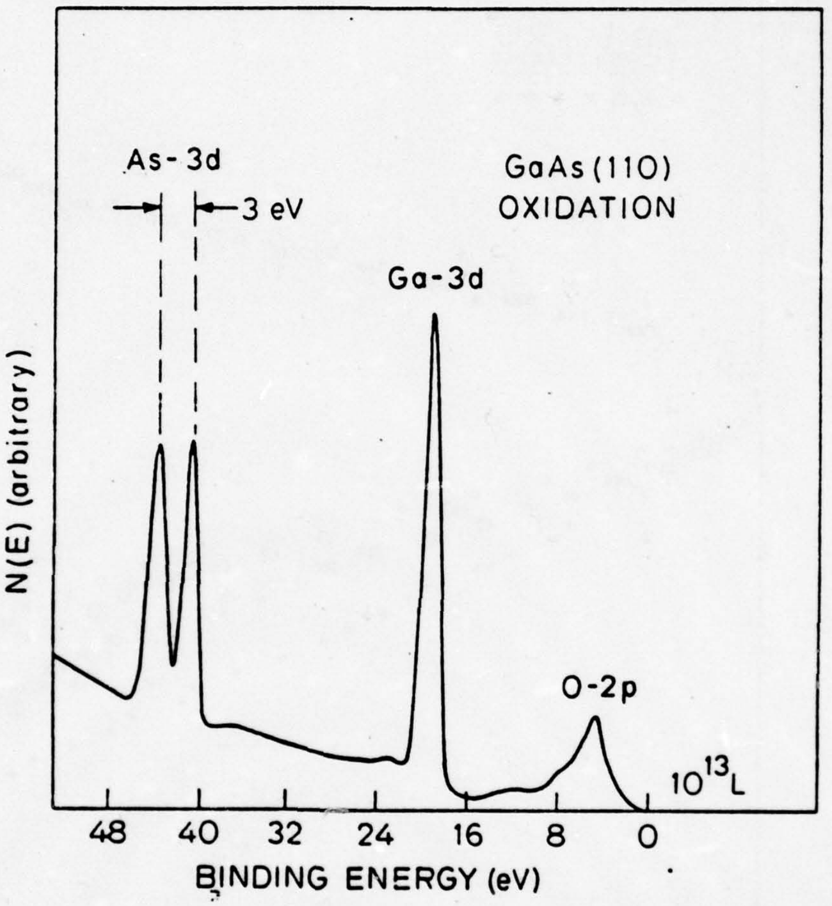

As-3d
3 eV
GaAs(110)
OXIDATION
Ga-3d
O-2p
10^{13}L
N(E) (arbitrary)
48
40
32
24
16
8
0
BINDING ENERGY (eV)

Figure 1

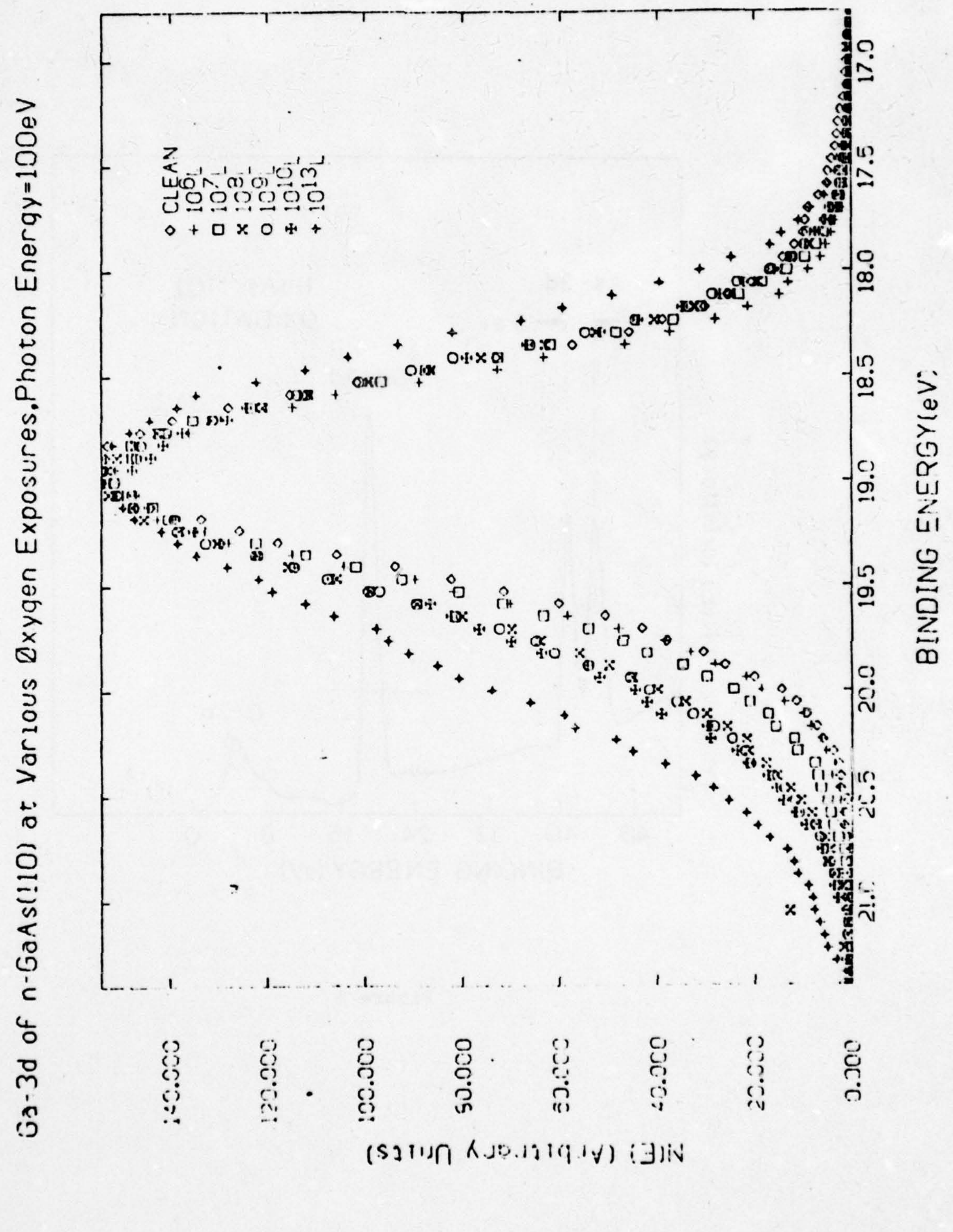
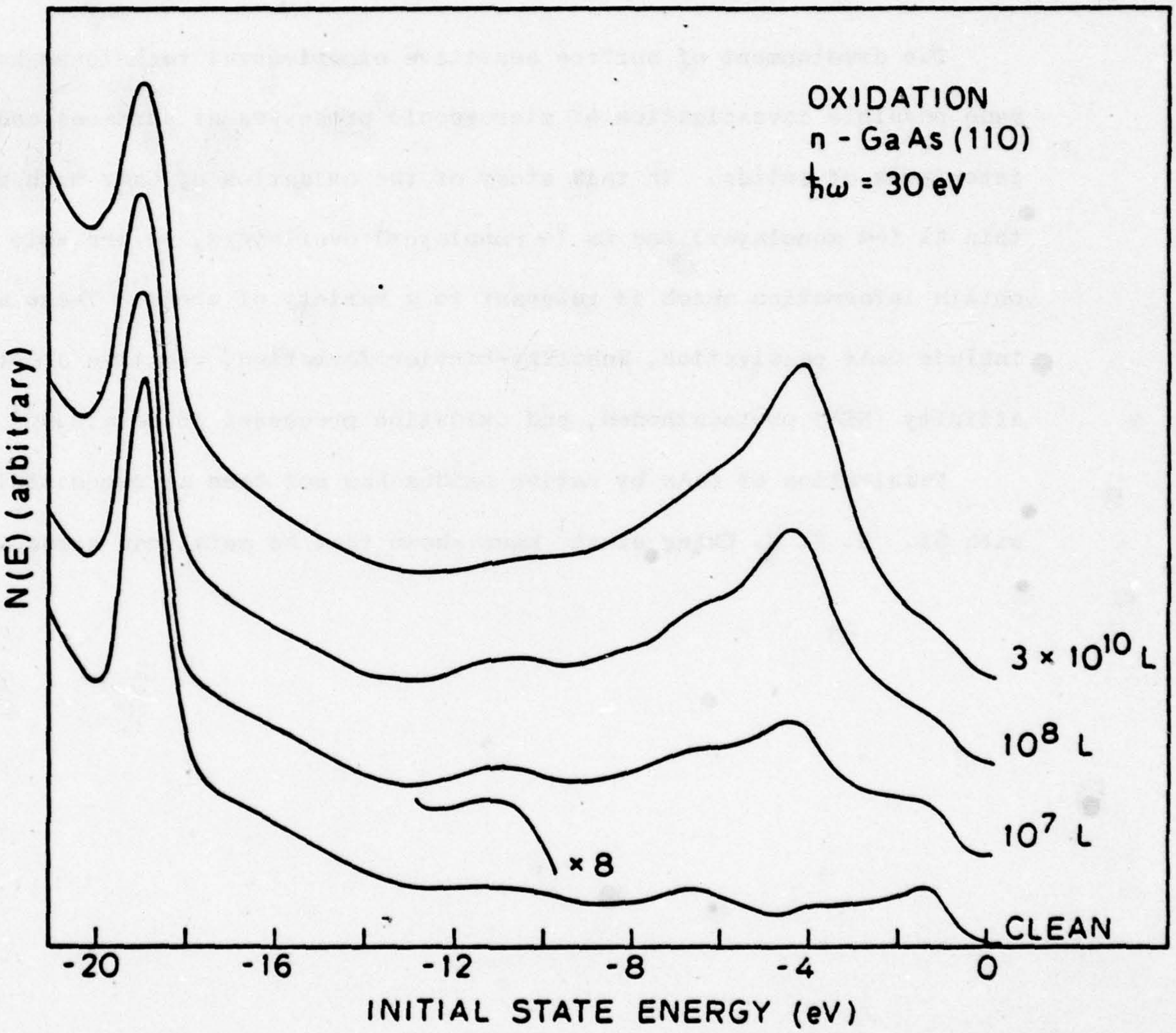

Ga-3d of n-GaAs(110) at Various Øxygen Exposures, Photon Energy=100eV
◇ CLEAN
+ 10^6 L
□ 10^7 L
X 10^8 L
○ 10^9 L
✣ 10^10 L
+ 10^13 L
N(E) (Arbitrary Units)
0.000
20.000
40.000
60.000
80.000
100.000
120.000
140.000
BINDING ENERGY(eV)
21.0
20.5
20.0
19.5
19.0
18.5
18.0
17.5
17.0

Figure 2



OXIDATION
n - GaAs (110)
$\hbar\omega$ = 30 eV
N(E) (arbitrary)
3 × 10^10 L
10^8 L
10^7 L
CLEAN
× 8
-20
-16
-12
-8
-4
0
INITIAL STATE ENERGY (eV)

Figure 3

III. COMPARATIVE STUDIES OF OXYGEN ADSORPTION ON GaAs (110) SURFACES WITH THIN ALUMINUM AND CESIUM OVERLAYERS

INTRODUCTION

The development of surface sensitive experimental techniques has made possible investigation of microscopic processes at surfaces and interfaces of solids. In this study of the oxidation of GaAs with very thin Al (~4 monolayer) and Cs (~ monolayer) overlayers, we are able to obtain information which is relevant to a variety of areas. These areas include GaAs passivation, Schottky-barrier formation, negative electron affinity (NEA) photocathodes, and oxidation processes in metals.

Passivation of GaAs by native oxides has not been as successful as with Si. R. P. H. Chang et al[1] have shown that As metal can accumulate at the semiconductor-oxide interface in plasma-grown oxides. An alternative approach to passivation is to form a nonnative oxide (or nitride) on the semiconductor. M. Hirose et al[2] have oxidized Al as it was deposited on a GaAs wafer to produce an Al-Al_2O_3-GaAs structure. A large density of interfacial states ($>10^{13}$ states/cm^2-eV at 0.5 eV above the valence band maximum) was observed, which Hirose et al attributed to the thin native oxide initially present on the GaAs. In the present investigation, an atomically-clean unpinned surface was prepared by cleaving under ultrahigh vacuum. Use of photoemission techniques allowed monitoring of the pinning[3] as the Al was deposited and then oxidized.

Most theories of Schottky-barrier formation on 3-5 compounds rely on the interaction of bulk metal states with the semiconductor.[4] In previous experimental work, we have sought to test the role of bulk metallic states in Fermi energy stabilization by measuring the pinning as a function of metal coverage.[5] As a result of that investigation, a defect model for Schottky-barrier formation was proposed.[5] A novel alternative approach to explore the relationship between metallic states and pinning has been used in this work: the pinning was monitored as a very thin metal overlayer was oxidized to eliminate the metallic states. As will be shown, this approach is much more easily implemented with Al on GaAs than with Cs on GaAs, due to the vastly different oxygen uptake by the GaAs in these two cases.

EXPERIMENTAL CONSIDERATIONS

An advantage of the photoemission technique is that both chemical information and changes in the Fermi energy near the semiconductor surface are obtained with minimum disruption of the semiconductor surface. This investigation was done using nearly monochromatic soft x-rays ($40 \text{ eV} \lesssim h\nu \lesssim 300 \text{ eV}$)[6] and ultraviolet light ($10 \text{ eV} \lesssim h\nu \lesssim 32 \text{ eV}$) at the Stanford Synchrotron Radiation Laboratory.[7] The experiment was performed in a standard ultrahigh vacuum chamber (base pressure 3×10^{-10} torr). Clean GaAs (110) surfaces were prepared by cleaving under vacuum with no hot filament ion gauges operating. The GaAs crystal used in the overlayer studies was degenerately doped n-type (5×10^{17} cm^{-3} Te). Synchrotron radiation was incident on the GaAs surface at an angle of 14°, and a PHI 15-255G double-pass CMA was used for electron energy analysis. Al, Ga, and In evaporation sources are described elsewhere,[3] and the evaporation rate was monitored with a quartz crystal thickness monitor. Cesium was evaporated from a channel-type source and monolayer coverage was assumed when saturation of the surface occurred. All oxidations were carried out at room temperature by admitting oxygen into the chamber through a leak valve. Pressures were monitored with a cold cathode gauge (unless otherwise noted) to avoid the excited oxygen effects seen with hot filament ion gauges.[8]

RESULTS

Evaporation of Al onto the cleaved GaAs (110) surface yielded a thin (~8 Å) metallic Al overlayer containing a small amount of Ga due to replacement of some surface Ga with Al.[9] Photoemission energy distribution curve (EDC) structure associated with the GaAs substrate was uniformly attenuated as the Al overlayer thickness was increased. Emission from the Ga-3d core level was broadened due to the presence of metallic Ga, but the As-3d core level was not broadened (see Fig. 1). The weak valence band emission from the aluminized surface was due mainly to the GaAs substrate.

Exposure of the aluminized surface to unexcited oxygen resulted in the chemisorption of oxygen onto the Al followed by rapid oxide formation similar to reports in the literature on the oxidation of bulk Al.[10] Oxidation of the Al overlayer was completed between 10^3 and 10^4 L O_2, but the lack of a shifted As-3d peak was evidence that oxidation of the GaAs had not occurred. Further exposure to unexcited oxygen (up to 10^8 L) resulted in the oxidation of a small amount of Ga, roughly equal to the metallic Ga contained in the Al overlayer. The weak emission which extends out to approximately 3 eV beyond the As-3d peak on the high binding energy side is probably due to chemisorption of oxygen on a small fraction of the surface As.

Oxygen exposures were then begun with an ionization gauge operating in the chamber (I_{EM} = 4 mA) for production of excited oxygen.[8] At an exposure of 10^6 L excited O_2, a new shifted As-3d peak began to appear and was well established by 10^7 L excited O_2 ($\Delta E = 4.8$ eV). This is in good agreement with a shift which has been associated by Pianetta (using a ligand analysis) with As coordinated by four oxygen atoms.[11]

The Fermi energy, which was near the conduction band minimum (CBM) in the bulk of the GaAs, was pinned 0.8 ± 0.15 eV below the CBM due to Al deposition.[9] The change in band bending following oxidation with a column 3 metal overlayer present was found to be slight using the photoemission technique.[3] In the case of the aluminum overlayer, the band bending appeared to relax by ~0.1 eV following exposure to 10^8 L unexcited oxygen. Similar relaxations were observed with the other column

3 metals: a relaxation of ~0.05 eV at a Ga covered (~1 monolayer) surface after an exposure to 10^5 L unexcited oxygen and a relaxation of ~0.15 eV at an In covered (~1 monolayer) surface after an exposure to 3×10^6 L unexcited oxygen.

DISCUSSION

It is well established that careful exposure of the clean GaAs (110) surface to small amounts of oxygen results in a chemisorption state in which the back bonds of the surface Ga and As atoms are not broken.[8,11,12,13] If precautions are taken to avoid production of excited states of the oxygen molecule,[8] then even very large oxygen exposures (10^{12} L = 1 atm for ~22 m) produce only the chemisorbed stage of oxidation.[13] Thus, there is obviously a strong activation barrier for the formation of oxides by unexcited oxygen on a GaAs surface with a high degree of surface perfection. In Fig. 2, we show a typical set of spectra (obtained by Piannetta[8,14]) from different oxygen exposures of the bare surface. An exposure of 10^7 L O_2 produced only a small shoulder on the As-3d, but 5×10^7 L O_2 resulted in a distinct peak ($\Delta E = 2.9$ eV) which has been associated with the chemisorption of oxygen on surface As atoms. In the case of the aluminized surface, only 10^4 L unexcited O_2 was required to oxidize the Al overlayer, but a total exposure of 10^8 L unexcited O_2 yielded only a small shoulder on the As-3d core level. This shoulder is probably due to oxygen chemisorption on a small fraction of As at the semiconductor surface. However, at least an order of magnitude greater oxygen exposure was necessary to produce a detectable shifted As-3d peak with the Al oxide overlayer as compared to the bare surface. One likely explanation is that oxygen transport to the semiconductor was impeded by the oxide. Another possibility is that most As dangling bonds at the semiconductor surface were involved in bonding to Al atoms in the oxide overlayer.

A comparison of spectra from the aluminized surface and bare surface after exposure to excited oxygen further demonstrates the slower oxidation rate for the aluminized surface. The excited oxygen spectra in Fig. 2 were obtained from a fresh surface which had not been previously exposed to unexcited oxygen. The oxidation of the bare surface begins with the appearance of a shifted As-3d peak (10^5 L O_2^*, $\Delta E = 3.1$ eV) similar to that which is observed using unexcited O_2 (5×10^7 L O_2, $\Delta E = 2.9$ eV) but, as the exposure is increased, a second shifted peak ($\Delta E = 4.6$ eV) grows to eventually dominate the first shifted As-3d peak, and broadening of the Ga-3d peak is observed. In the model given by Pianetta,[13] the first shifted As-3d core level corresponds to the chemisorption of oxygen on the surface As, and the second shifted As-3d core level corresponds to the breaking of back bonds and oxide formation. This sequence of events is not the same in the case of the aluminized surface. The only change in the As-3d core level is the appearance of the shifted peak corresponding to oxide formation with As coordinated by four oxygens.[11] This seems to indicate that the majority of the interfacial As atoms are in sites such that chemisorption of oxygen onto these As atoms cannot occur, i.e., the Al_2O_3 overlayer may be joined to the substrate by interfacial Al-As bonds.

A dramatic change in oxidation behavior of the GaAs (110) surface was seen after cesiation.[15] After only a 10 L exposure to unexcited oxygen, a chemically shifted As-3d peak which is characteristic of oxygen adsorbed on GaAs was evident (see Fig. 3). The shifted As-3d and O-2p peaks grow simultaneously as the surface is exposed to more unexcited oxygen until saturation is reached between 40 and 100 L. A striking contrast to the oxidation of the aluminized or the bare GaAs (110) surface is immediately apparent here: the oxygen uptake by the GaAs is many orders of magnitude faster on the cesiated surface. The spectrum after 20 L O_2 for the cesiated surface is comparable to the spectrum after 5×10^7 L O_2 for the bare surface.

The effect of oxygen on Cs is to shift the Cs core levels to lower binding energy with peak shapes unchanged. Accompanying the Cs core level shift is the continuous movement of the shifted As-3d peak to higher binding energy. Movement of both the Cs shifted As-3d peaks stabilizes after 40 L O_2, at which point the growth in strength of the shifted As-3d peak also slows down. This correlation indicates interaction between the oxidizing substrate and the Cs/O overlayer. The nature of this complex interaction is discussed elsewhere.[15] As far as we are concerned here, it is sufficient to point out that the shifted As-3d peak ($\Delta E = 2.9$ to 3.3 eV) represents the same chemisorption state of oxygen that is seen on the bare surface, with the variation of ΔE from 2.9 to 3.3 eV, due to the interaction between cesium and oxygen. As in the case of the aluminized surface, the stabilization of the Fermi energy within the band gap at the cesiated surface was essentially unaffected by oxidation.

Negative electron affinity (NEA) on semiconductors is currently thought to be a combination of semiconductor band bending and lowered work function.[16] Models of NEA photocathodes usually assume a structure consisting of a Cs oxide or suboxide on an intact semiconductor surface lattice. However, the rapid oxygen uptake by the surface As atoms indicates that a more complex structural model should be considered for NEA photocathodes.

A basic independence of the Fermi energy with respect to the type of metal adsorbed and with respect to oxidation of the metal is suggested by this data. This statement is consistent with the well-established result that the Schottky-barrier height on GaAs is only slightly, if at all, dependent on the type of metal used.[17] However, it is interesting to consider that the similarity in pinning position (within 0.3 eV) of metal and oxide overlayers may indicate that the pinning mechanisms in these two very different situations may be closely related or even the same.[18] In the case of aluminized GaAs, the pinning position remained the same within 0.1 eV for the sequential stages of aluminization ($\theta \gtrsim$ 2 Å), oxidation of the Al, and further oxygen exposure until oxidation of the semiconductor was accomplished with excited oxygen. The use of Cs instead of Al produced striking changes in the oxidation behavior of the GaAs, yet the pinning position was essentially the same throughout the oxidation.

A very brief comparison of the pinning mechanisms given in various theories of metal-semiconductor[19] and oxide-semiconductor[20] interfaces shows that little effort has been given to the concept of a common pinning mechanism for the two interfaces. However, Lindau et al[5] has proposed a model for Schottky-barrier formation on GaAs, GaSb, and InP which may apply equally as well to insulating overlayers on the 3-5 semiconductors. In this model, semiconductor defect states at the interface are associated with the electrical states which pin the Fermi energy. The driving energy for creation of defects on an initially clean unpinned surface comes from the thermal spike generated when an atom (metal or gaseous) chemisorbs on the semiconductor surface. A more detailed discussion of the pinning mechanism in metal-semiconductor and oxide-semiconductor interfaces is given by Spicer et al.[18]

It is possible that much new information on metal oxidation properties can be gained by microscopic oxidation studies based on techniques used here. Information which relates to oxidation processes in metals is obtained indirectly by observing the change in substrate oxidation behavior after deposition of a thin metal overlayer. As an example, the oxygen uptake by both Cs[21] and Al[10] is rapid compared to bare GaAs,[8,14] yet oxygen seems to readily penetrate through the Cs to the GaAs in contrast to the GaAs oxidation-impeding behavior of the Al overlayer. However, much more work is needed to establish definitive relationships between substrate oxidation and the oxidation properties of the metal overlayer.

SUMMARY

Exposure of bare and cesiated GaAs (110) surfaces to unexcited oxygen results in the same chemisorption state of oxygen on As, but the uptake rate is more than a factor of 10^6 faster. Aluminization is found to slow the oxygen uptake by the GaAs. The data also suggests that the oxidation products may be influenced by the metal oxide overlayer, in agreement with the results of R. P. H. Chang et al.[2] The lack of significant change in the Fermi energy pinning when the metal overlayer is oxidized suggests a related pinning mechanism for the two cases, for which a defect model is considered a strong candidate.[18]

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FIGURE CAPTIONS

1. Photoemission EDCs of aluminized GaAs (110) before and after exposure to unexcited oxygen (O_2) and then excited oxygen (O_2^*).

2. Photoemission EDCs of bare GaAs (110) before and after exposure to unexcited oxygen (O_2) and, on a different surface, excited oxygen (O_2^*). The shifted As-3d peak due to oxygen chemisorption appears on the bare surface after an unexcited oxygen exposure which is a factor of ten less than the exposure required to produce a similar shifted As-3d peak on the aluminized surface. From Refs. 8 and 14.

3. Photoemission EDCs of cesiated GaAs (110) before and after exposure to unexcited oxygen. Note that the shifted As-3d peak after only 10 L O_2 is comparable to the shifted As-3d peak after 10^7 L O_2 on the bare surface (see Fig. 2).

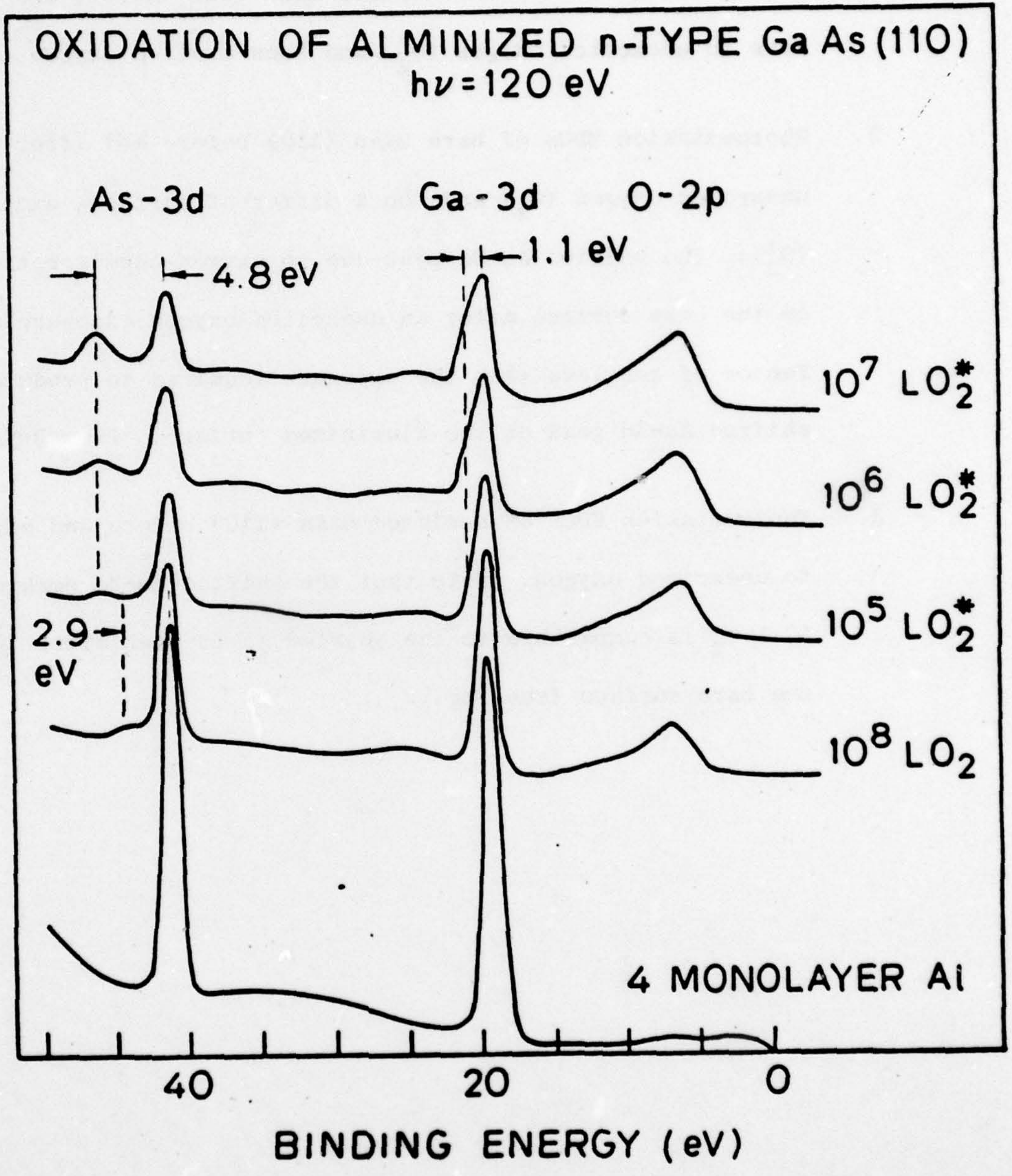
OXIDATION OF ALMINIZED n-TYPE Ga As (110)
hν = 120 eV
As-3d
Ga-3d
O-2p
4.8 eV
1.1 eV
2.9 eV
N (E) (arbitrary)
10⁷ LO₂*
10⁶ LO₂*
10⁵ LO₂*
10⁸ LO₂
4 MONOLAYER Al
40
20
0
BINDING ENERGY (eV)

Figure 1

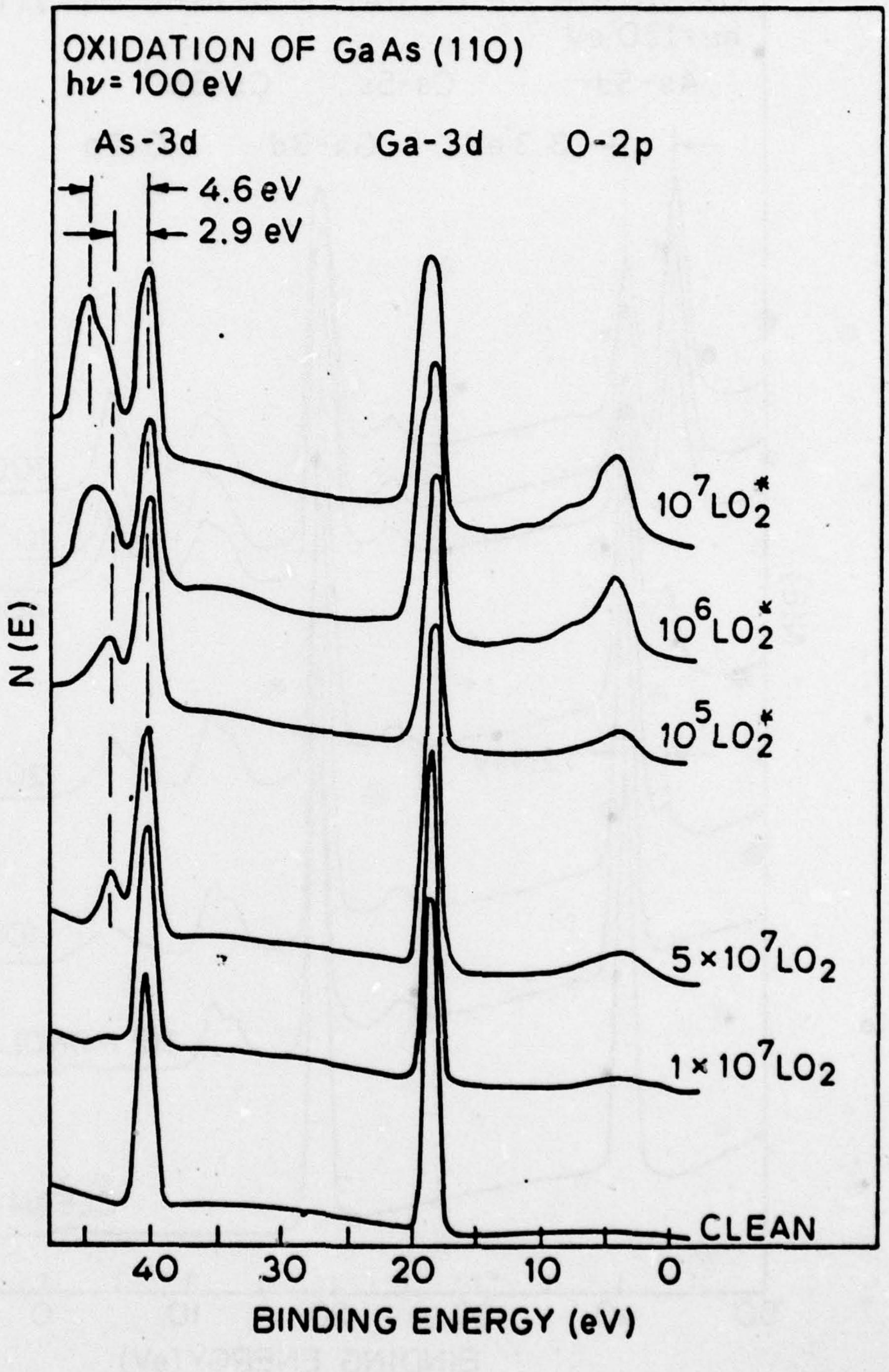
OXIDATION OF GaAs (110)
$h\nu = 100$ eV
As-3d
Ga-3d
O-2p
4.6 eV
2.9 eV
N(E)
10^7 LO$_2^*$
10^6 LO$_2^*$
10^5 LO$_2^*$
5×10^7 LO$_2$
1×10^7 LO$_2$
CLEAN
40
30
20
10
0
BINDING ENERGY (eV)

Figure 2

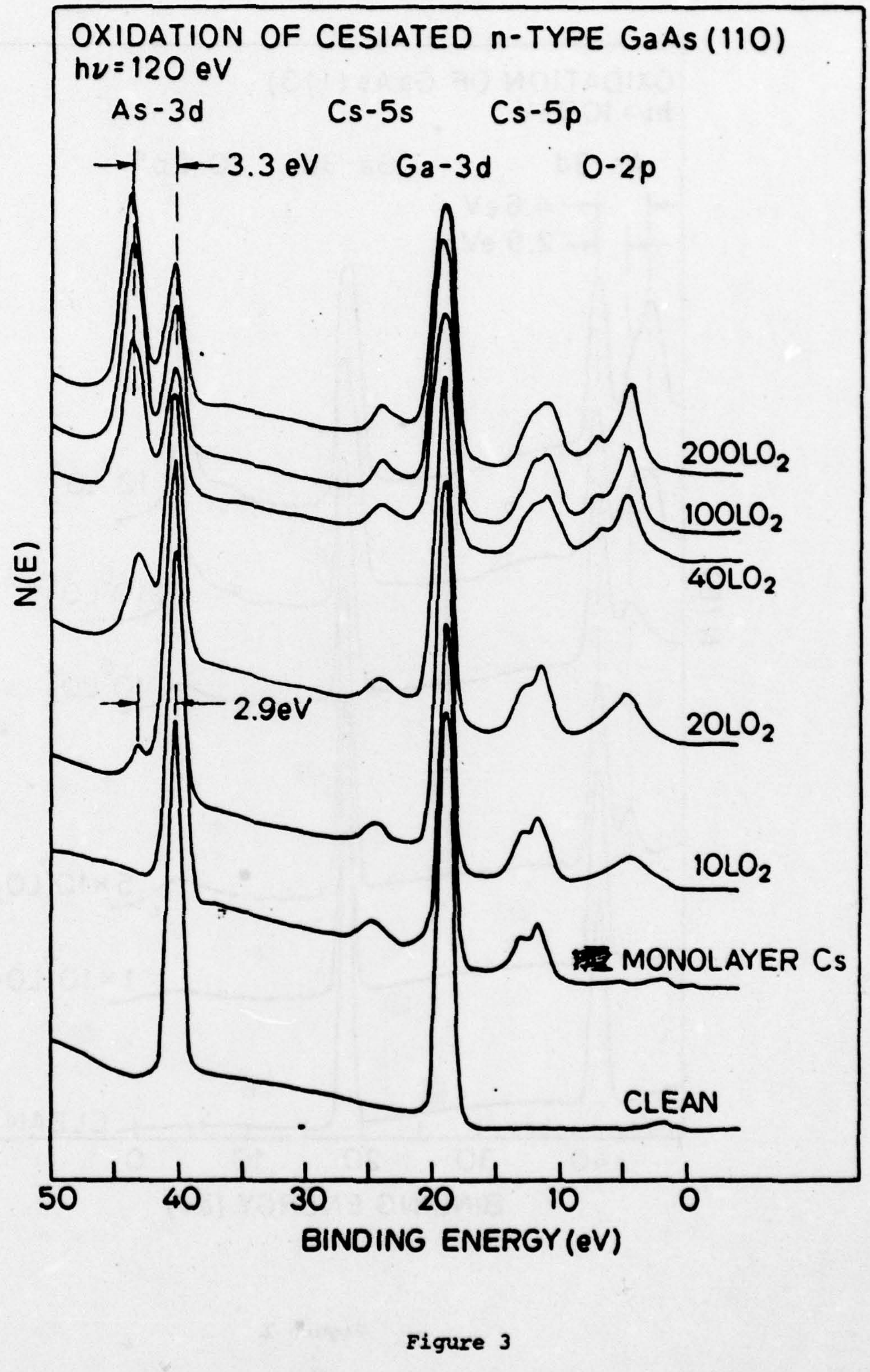
OXIDATION OF CESIATED n-TYPE GaAs (110)
hν = 120 eV
As-3d
Cs-5s
Cs-5p
3.3 eV
Ga-3d
O-2p
2.9eV
N(E)
200LO₂
100LO₂
40LO₂
20LO₂
10LO₂
MONOLAYER Cs
CLEAN
50
40
30
20
10
0
BINDING ENERGY (eV)

Figure 3