Determination of the Oxygen Binding Site on GaAs(110) Using Soft-X-Ray-Photoemission Spectroscopy*

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The first steps in the oxidation of GaAs(110) are examined through shifts in the As and Ga 3*d* levels as a function of oxygen exposure. We observe a large chemical shift in the As 3*d* levels (about 4 eV) while the Ga 3*d* levels were shifted by less than 1 eV. This gives direct evidence for oxygen bonding to arsenic at the GaAs(110) surface, and illustrates the change in chemical character which can take place in atoms at the surfaces of compounds.

In the past few years, a question has been raised concerning the binding site (or sites) of oxygen on gallium arsenide. The answer to this question is important not only because it will help clarify some aspects of the various GaAs surface-state models, but it will also help in the understanding of the passivation of practical GaAs surfaces. In addition it provides a test of the applicability of different techniques for studying the oxidation properties of other III-V compounds as well as semiconductors in general. Furthermore, the behavior of GaAs during oxidation illustrates the way in which the surface chemistry of a covalent compound can differ from that expected from bulk heats of reaction and thermodynamic arguments. The oxidation of GaAs has been studied extensively by ultraviolet photoelectron spectroscopy,[1] ellipsometry,[2] electron energy-loss spectroscopy,[3,4] Auger electron spectroscopy,[2,4] low-energy electron diffraction,[2] and flash desorption.[5] Recent work by Dorn, Lüth, and Russel,[2] Froitzheim and Ibach,[3] and Gregory *et al.*[1] on the nonpolar GaAs (110) cleaved surface suggests that oxygen binds preferentially to the surface arsenic atoms whereas studies on polar GaAs surfaces by Ludeke and Koma[4] and Arthur[5] imply that oxygen sticks to the surface gallium atoms. Since the reported results are from different surfaces and from surfaces prepared in different ways, caution must be exercised in generalizing the conclusions from one system to another.

It is a well known fact that inner core levels shift in energy as a function of chemical environment. This chemical shift has been used extensively in the field of x-ray photoemission spectroscopy as an aid in determining numbers of bonding states as well as the amount of charge transferred upon formation of various chemical bonds.[6] The results presented here use the chemical shift information from the 3*d* levels of gallium and arsenic to study the bonding states of the gallium and arsenic atoms during the oxidation of the GaAs (110) surface. Furthermore, the shorter escape depths for electrons photoemitted from the As and Ga 3*d* levels by photons in the range 80 to 350 eV give a significant increase in surface sensitivity over conventional x-ray photoemission techniques employing Al $K\alpha$ radiation.[7]

The apparatus used in these studies consists of an ultrahigh-vacuum system (base pressure $< 6\times10^{-11}$ Torr) with a double-pass cylindrical mirror analyzer, a multisample holder, a cleaver, Au and Cu evaporation sources, and gas-handling facilities. As a light source, we used synchrotron radiation at the Stanford Synchrotron Radiation Project emitted from the storage ring SPEAR at the Stanford Linear Accelerator Center. The general properties of synchrotron radiation as well as the relevant SPEAR parameters have been discussed elsewhere.[8] The monochromator that was used for these studies is of the grazing-incidence type and is also described elsewhere.[9] We were able to obtain useful radiation for photoemission experiments in the photon energy range from 32 to 350 eV at a resolution of 0.1 Å.

The GaAs samples were $5\times5\times13$ mm^3 with the long axis along the (110) direction. The p-type samples were Zn doped with $p=6\times10^{18}$ cm^{-3} and the n-type samples were Te doped with $n=3.5\times10^{17}$ cm^{-3}.

The measurements were done by first cleaving both the n- and p-type samples *in situ* ($p<1\times10^{-10}$ Torr) and taking a set of electron energy-distribution curves (EDC's) for different photon energies. Then, the samples were simultaneous-

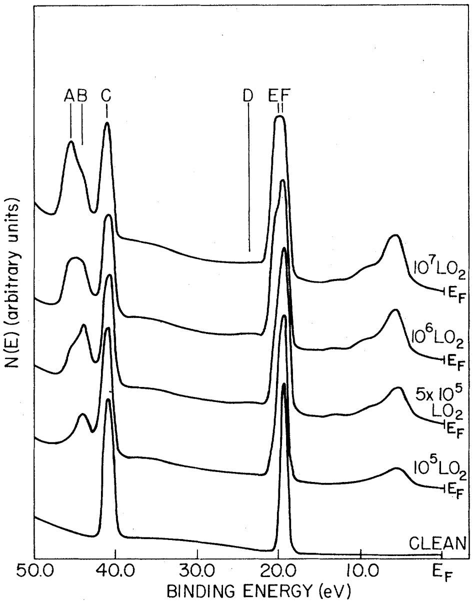

FIG. 1. Photoemission spectra of clean and oxidized GaAs(110) for 100-eV photon energy.

ly oxidized and a set of EDC's was taken after each exposure. Spectra from freshly evaporated gold films were routinely taken to determine the Fermi level of the GaAs. The samples were oxidized using ultrapure oxygen admitted through a bakable leak valve. The oxygen pressures during exposure ranged from 1×10^{-8} to 1×10^{-2} Torr depending on the exposure. In all cases the oxygen was pumped out before the measurements were made. We cleaved each sample and performed the oxidations three times to insure reproducibility. During studies of the clean and oxidized surfaces, the base pressure while open to the monochromator and storage ring was 6×10^{-11} Torr. The EDC's were taken using pulse counting and signal averaging. Each sweep was no longer than 50 sec to minimize any intensity fluctuations from the storage ring.

In Fig. 1, we show EDC's for the oxidation of p-type GaAs taken at a photon energy of 100 eV. The spectra extend from the Fermi level (taken as zero binding energy for the clean GaAs) to a binding energy of about 50 eV. The spectra for the oxidized GaAs were all referred back to the clean spectrum. We choose to illustrate the oxidation at 100-eV photon energy because the combination of cross-section and surface sensitivity are optimum for both the Ga and As $3d$ levels. The bottom curve shows the spectrum for clean GaAs (110). The Ga $3d$ level appears at a binding energy of 19.0 eV (peak F) and the As $3d$ at 40.8 eV (peak C). The binding energies could be determined to an accuracy of better than ±0.2 eV. Spin-orbit splitting of the Ga $3d$ level was not seen here because the resolution was 0.25 eV; however, it was clearly resolved at lower energies with an experimental resolution of 0.1 eV.[10] The sharpness of the Ga $3d$ levels in the high-resolution data provides evidence that there is no measurable shift (> 0.1 eV) between surface and bulk Ga $3d$ levels (see discussion on escape depth below). Little emission from the valence band, which extends down to 13 eV below E_F, is visible on the clean sample. The next curve shows the spectrum after an exposure of 10^5 L O_2 (1 L = 10^{-6} Torr sec). In this case, the two most striking features are the increase in the valence band emission, which will not be discussed here,[10] and the appearance of peak B on the high binding energy side of the As $3d$ level. This shift is measured to be 3 eV. Note, however, that the gallium peak remains less affected. Upon higher exposure, peak A appears, shifted from the As $3d$ level by 4 eV. Peak A first appears at 5×10^5 L O_2 and grows quickly until at 10^7 L O_2 it completely dominates peak B, which seems to stop growing as soon as peak A appears. As peak A appears, the Ga $3d$ level starts to broaden and at the highest exposures has split into the shifted peak E and the unshifted peak F. The best estimate for this shift is about 1 eV whereas Schön reports a shift of 1.9 eV for oxidized Ga.[11] The very small peak at 24 eV (peak D) has tentatively been identified as either O $2s$ or chemically shifted Ga $3d$ at a very low concentration. The n-type GaAs (110) showed the same qualitative behavior as the p type.[12] As mentioned above, 5×10^5 L O_2 is the exposure at which both peak A appears and peak E becomes discernible. This exposure also signals the beginning of the Fermi level pinning on p-type GaAs (110),[1, 10] as well as being the point at which a significant fraction of a monolayer starts to form on the surface of the sample.[2]

These spectra clearly show that at low coverages ($\leq 10^5$ L O_2), the oxygen bonds principally to the arsenic and leaves the gallium less affected. At higher coverages, the oxygen still bonds preferentially to the arsenic, but in a different way, as evidence by the appearance of peak A. One could speculate on the causes of these differences (e.g., O_2 versus O adsorption, interaction between adsorbed species at high coverage, etc.) and clearly an understanding of the details in Fig. 1 should ultimately give us detailed knowledge of the early steps in GaAs oxidation. However, the prinicpal focus at this time should be the fact that for all coverages studied, the As *d* shift is several times larger than the Ga shift. This provides definitive evidence that the oxygen bonds primarily to the surface As atoms at these exposures.

The bonding of oxygen primarily to As is in accord with and predicted by the surface-state model proposed by Gregory *et al.*,[1] in which the dangling-bond electrons are localized on the As atoms and only empty surface states are on the Ga atoms. This model has been well confirmed.[13,14] On the basis of thermodynamical arguments and the heats of oxidation of Ga and As,[15] one might expect that oxygen would preferentially attach itself to Ga even at the lowest possible exposures. This does not occur because the surface atoms are not in their elemental state as a result of bonding with their neighbors. Because of these bonds and the atomic potentials of Ga and As, it is the surface As and not Ga atoms which have "dangling-bond" electrons available for the oxygen.

Now the effects of escape depth will be discussed briefly with reference to the heavily oxidized GaAs (110) of Fig. 2. This figure shows spectra from 10^7 L O_2 on *n*-type GaAs as a function of photon energy from 80 to 240 eV. The effect of escape depth is most clearly seen by looking at the ratio of peaks *AB* and *C*, and by remembering that peaks *AB* have been shifted by surface oxidation and peak *C* is representative of the bulk. Peaks *A* and *B* are no longer resolved because these spectra were taken at a much lower resolution. The reason for concentrating on the ratio of peak *AB* to *C* is that the effects due to cross-section changes for different photon energies are minimized. Below 80 eV the As 3*d* cross section is reduced and the background of inelastically scattered electrons tends to obscure the As 3*d* emission. At 80 and 100 eV, peaks *AB* and *C* are approximately equal in height, indicating equal surface and bulk contributions since by 10^7 L O_2 a saturation coverage of about 0.5 monolayer has been reached. This coverage corresponds to one oxygen for each arsenic.[2] As higher photon energies are used, the surface contribution becomes smaller as indicated by the relative decrease in peak *AB* with respect to peak *C*. At even higher photon energies on the order of 1000 eV, it is known from escape-depth curves[7] that the surface contribution will appear to be negligible. This clearly illustrates the importance of being able to tune the photon energy to a range that will give minimum escape depths for the core levels being studied.

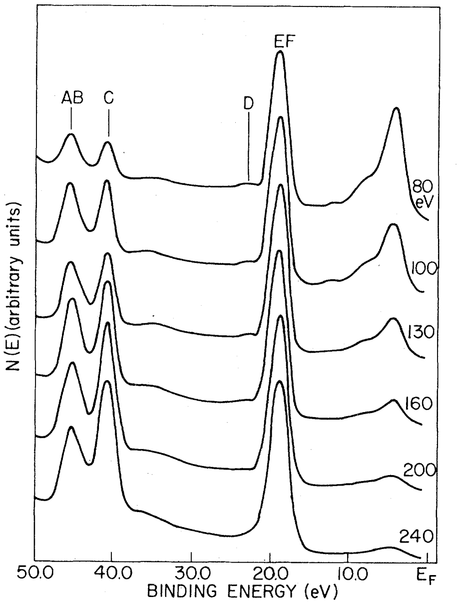

FIG. 2. Photoemission spectra of heavily oxidized (10^7 L) GaAs(110) as a function of photon energy.

We have studied the oxidation of GaAs (110) by looking for chemical shifts in the Ga and As 3*d* levels. We chose a photon energy to maximize the surface sensitivity of our measurement and observed a much larger chemical shift for the As 3*d* level than for the Ga 3*d* even at relatively low O_2 coverages. The larger As shift is attributed to predominant bonding of oxygen to the As surface atoms in chemisorbing the first half monolayer of oxygen on the GaAs (110) surface. These results illustrate a very important aspect of the surfaces of covalent compounds—the chemical nature of the surface atoms, as seen by adsorbed gases, can differ drastically from that of the elemental atoms. In the present case, because of the bonding of the surface atoms to the rest of the crystal, the chemistry of Ga and As surface atoms are reversed, i.e., As has excess electrons and is oxidized first, whereas the surface Ga has no excess electrons and behaves as a nonmetallic element. The results presented here also have shown the importance of tunable synchrotron radiation in studying various gas sorption and oxidation problems by choosing a photon energy for optimum cross section and surface sensitivity. These methods should be applicable to the study of adsorption on many other systems.

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Frequency Dependence of the Electron Conductivity in the Silicon Inversion Layer in the Metallic and Localized Regimes

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The conductivity of electrons in the inversion layer of silicon has been measured from 0 to 40 cm^{-1} at 1.2°K in the metallic and localized regimes. The correlation between $\sigma(T)$ and $\sigma(\omega)$ in the localized regime suggests that the drop in conductivity at low electron concentrations is caused by the appearance of a gap at the Fermi level.

Electrons in silicon inversion layers provide us with a two-dimensional[1] electron gas whose concentration can be varied by over two orders of magnitude. The relative ease with which the electron density can be varied has led to interesting studies of many-body effects on the electron mass[2] and g factor[3] and of "localization" of the electrons at low concentrations.[4-13] The latter has recently attracted much attention but a clear picture of the character of the electron states at the Fermi level in the localized regime has yet to emerge.

Following suggestions by Mott[11] and Stern[12] a number of investigators[4-10,13] have examined the behavior of the conductivity as a function of temperature and electron concentration n_s, and concluded that the conductivity near threshold may be described by the Mott theory of Anderson localization in a two-dimensional band tail. In devices with a large amount of disorder at the interface, the agreement with the Mott[14] theory is striking, especially with regard to variable-range hopping. In other devices which have considerably less disorder as measured by fixed oxide charge, Q_{ss}, the observation of localization is somewhat embarrassing. In these experiments or devices results are obtained that raise serious questions about the applicability of the Mott theo-