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O_2/GaAs(110) interface formation at 20 K: Photon-induced reaction and desorption

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High-resolution synchrotron-radiation photoemission studies of molecular O_2 condensed on GaAs(110) at 20 K show that oxidation is a consequence of photon irradiation. Core-level results for 2 L O_2 [1 langmuir (L) $\equiv 10^{-6}$ Torr sec] demonstrate that the topmost layer of As atoms is initially involved in a sequential, two-step reaction to produce As^{1+}- and As^{3+}-like oxides. These reactions are mediated by secondary electron capture by O_2 which then dissociates to form surface oxides. As^{5+}-like bonding configurations are formed when additional O_2 is condensed on the surface and exposed to photon irradiation. O_2-GaAs interface reactions slow as transport through the thickening oxides is impeded, and photon-induced desorption of oxygen becomes significant. Studies of Fermi-level movement into the gap as a function of O_2 exposure suggest that oxidation at 20 K produces acceptorlike states. Fermi-level evolution for *n*-type GaAs is strongly dependent on dopant concentration, O_2 dose, and light exposure, indicating band flattening for lightly doped samples due to surface photovoltage effects. These effects are not significant for *p*-type GaAs at 20 K, consistent with the formation of acceptorlike states. Together, these results show a complex dependence of surface chemistry on photon irradiation, but remarkably little dependence of the surface Fermi-level position on the reactions.

INTRODUCTION

Investigations of O_2/GaAs(110) interactions have been conducted for many years, and tremendous progress has been made toward understanding the interfacial chemistry.[1-10] These studies have been conducted under several distinct conditions, with most of the work being done at 300 K. Some experiments sought to elucidate the complex chemistry and morphology of the evolving oxides by examining the surface after exposure to increasing quantities of molecular oxygen in the dark.[1-7] Others focused on how surface oxidation could be enhanced and controlled via laser excitation of O_2 and the semiconductor.[7,8] Despite this progress, there remain fundamental questions concerning the initial stages of reaction, the donor and acceptor character of the oxygen-induced defects, and the correlation between the electronic states of the oxide and the Fermi-level evolution of the semiconductor.

Two groups have recently investigated the early stages of O_2/GaAs interactions at low temperature.[9,10] Stiles *et al.*[9] reported Ga oxidation that was greater at 100 K than at 300 K after equivalent doses, and they concluded that this was a consequence of increased O_2 sticking at low temperatures. Frankel *et al.*[10] showed O_2 physisorption on GaAs(110) at ~45 K and the conversion of physisorbed oxygen to chemisorbed oxygen upon warming the sample to 300 K. This observation of a change of state was supported by Berkovits *et al.*,[11] who showed that physisorbed oxygen could not be desorbed by low-temperature annealing ($T \leq 65$ K) without some oxygen being chemisorbed on the surface, thereby indicating that a delicate balance exists between physisorption and reaction.

In this paper, we demonstrate that O_2 interaction with GaAs(110) at 20 K is even more complex than previously thought because the soft x rays ($40 \leq h\nu \leq 90$ eV) used in many of the measurements alter the stability of the physisorbed O_2 layer and produce novel bonding configurations for Ga and As. We demonstrate this dependence on photon exposure by condensing molecular O_2 on cleaved GaAs(110) at 20 K and then measuring with photoemission the changes in core-level and valence-band spectra. Such exposure-dependent data show that As^{1+}- and As^{3+}-like bonding configurations form in a stepwise fashion with approximately equal reaction probabilities for the two steps. The ability to adsorb multiple O_2 layers provides conditions where several novel exposure-dependent effects can be observed. Indeed, the high-sticking coefficient of O_2 at 20 K makes it possible to locally oxidize the surface $\sim 10^{10}$ times more efficiently than in equivalent experiments conducted at 300 K.[1-4] Furthermore, As_2O_5-like oxides are readily formed. The present results also provide evidence for competition between continued reaction and photon-induced oxygen desorption, where desorption occurs via a first-order process.

The second major topic in this paper involves the GaAs(110) band bending induced by O_2 adsorption and reaction at 20 K. As we will show, the position of the surface Fermi level, E_F, in the band gap is strongly dependent on the bulk dopant concentration for *n*-type GaAs, indicative of significant surface photovoltage effects. In contrast, E_F remains near the band edge for *p*-type GaAs, independent of dopant concentration. These results are consistent with the formation of acceptorlike states near the surface. In contrast to investigations that correlated E_F movement into the gap at 300 K with the extent of reaction for *p*-type GaAs, we find that E_F remains near the valence-band maximum, even when the surface is heavily oxidized at 20 K.

EXPERIMENT

Synchrotron radiation photoemission experiments were carried out using the Minnesota–Argonne–Los Alamos extended-range grasshopper monochromator and beamline at the University of Wisconsin Synchrotron Radiation Center (Stoughton, WI). High-resolution core-level and valence-band energy-distribution curves (EDC's) were acquired with a double-pass cylindrical mirror analyzer. The photon energies were selected to emphasize surface features ($h\nu=65$ and 90 eV for Ga 3*d* and As 3*d*, respectively), but tests with lower photon energies (with longer photoelectron mean free paths) were conducted to investigate heterogeneities in oxide formation. Valence-band EDC's were acquired with $h\nu=40$ or 65 eV. The combined resolution (electrons and photons) was ~200, 250, and 400 meV for the Ga 3*d*, As 3*d*, and valence-band spectra.

Clean GaAs(110) surfaces were created by cleaving $\sim 4\times4\times20$ mm^3 single crystals at 300 K and $\sim 5\times10^{-11}$ Torr. Surfaces for which E_F was more than 60 meV from the band edge [conduction-band minimum (CBM) for *n*-type or valence-band maximum (VBM) for *p* type] were considered pinned and discarded. The *n*-type (*p*-type) single crystals were Si doped (Zn doped), with dopant concentrations of 1×10^{17} cm^{-3} [low doping (LD)] and 2×10^{18} cm^{-3} [high doping (HD)]. The LD samples were used in the photon-exposure studies, but surface modifications were not affected by the dopant concentration or type.

Photoemission experiments were conducted at 20 K, a temperature at which the condensation of multiple layers of oxygen was possible.[12] The sample and sample holder were Ga-soldered into a Cu tank attached to a closed-cycle He refrigerator that was mounted on an *x*-*y*-*z* manipulator.[13] The temperature was measured with a Au-Fe/Chromel thermocouple rigidly attached to the tank (accuracy ±5 K). A heater adjacent to the sample holder made it possible to raise the temperature to melt the Ga solder while operating the cold head. This provided rapid sample interchange, controlled thermal stability, and minimal pressure variations. No temperature changes were observed when the sample was exposed to synchrotron radiation.

Clean GaAs(110) surfaces were dosed with small amounts of molecular O_2 via a calibrated leak valve (estimated accuracy ±20%). Exposures are given here in Langmuir units ($1\ \mathrm{L}\equiv1\times10^{-6}$ Torr sec), where 1 L corresponds to a molecular-impact density of 3.57×10^{14} cm^{-2} (Ref. 14) or 0.40 monolayer of O_2 (0.8 monolayer of O) relative to the surface atom density of GaAs(110), namely 8.86×10^{14} atoms/cm^2. At 20 K, the sticking coefficient of O_2 is nearly unity.[12] During O_2 dosing, the ion pumps were turned off to avoid gas excitation, but the cryohead provided continuous pumping. The ion pumps were not restarted until the pressure returned to $\sim 5\times10^{-10}$ Torr (within ~1 min of closing the leak valve). No spectral features were observed that could be related to the condensation of residual gases. Quadrupole mass spectrometer analysis of O_2 at inlet pressures of $(2-5)\times10^{-8}$ Torr showed that the $[O_2]/[CO]$ ratio was ~20, with other active gases present in much lower concentrations. Results obtained with the ion gauge on were identical to those with the gauge off, although use of the ion gauge resulted in more reproducible O_2 exposures.[15] Experiments were conducted in the dark, except during exposure to synchrotron radiation during periods of data acquisition, and these exposures will be explicitly stated.

The core-level EDC's were decomposed with a nonlinear least-squares fitting routine operating on an IBM PC/RT microcomputer, as described in detail elsewhere.[16] The EDC's were modeled by simultaneously varying the intensities and positions of physically realistic spectral features and a cubic polynomial to achieve the best fit to the data, as judged by statistically neutral residuals. Each Ga 3*d* or As 3*d* component was composed of a pair of Voigt functions (the convolution of Lorentzian and Gaussian functions) where the spin-orbit splitting and branching ratio were determined from the clean surface spectra and fixed thereafter. The Gaussian contributions were allowed to vary to account for inhomogeneous band bending and inequivalent interfacial bonding sites. The Lorentzian widths for bulk, surface, and reacted components were assumed to be equal to those determined from the clean surface to minimize the number of free-fitting parameters.

SURFACE REACTIONS

In Fig. 1 we show representative valence-band EDC's for O_2/*n*-type GaAs(110) to demonstrate the flux-dependent evolution of the surface region at 20 K. The clean surface GaAs spectrum is shown at the bottom, and EDC's offset upward (normalized to constant height) correspond to different O_2 exposures (Θ, in langmuirs) and photon exposures (E, in units of 10^{14} photons/cm^{-2}). After dosing with 1 L O_2, the photoemission spectra revealed features related to $1\pi_g$, $1\pi_u$, and $3\sigma_g$ orbitals due to molecular oxygen, as labeled.[17] This 1 L O_2 spectrum is nearly identical to that reported by Frankel *et al.*[10,18] for O_2 exposure at ~45 K, where only ~1 monolayer of O_2 could be condensed.

The results of Fig. 1 show changes in the O_2-derived levels that are directly related to photon irradiation. In particular, the molecular orbital features shift ~0.5 eV to lower binding energy when the total photon exposure is increased to $E=2\times10^{14}$ cm^{-2}. Further exposure results in line-shape changes as broad structures located ~1, 3.5, 5.5, 7, and 9.5 eV from the VBM appear, and as the emission from molecular O_2 is reduced. These structures have been reported previously.[2,4,10] (Energy differences between the present results and those in the literature probably reflect different stages in the photon-mediated oxidation process.) Unfortunately, the peak as-

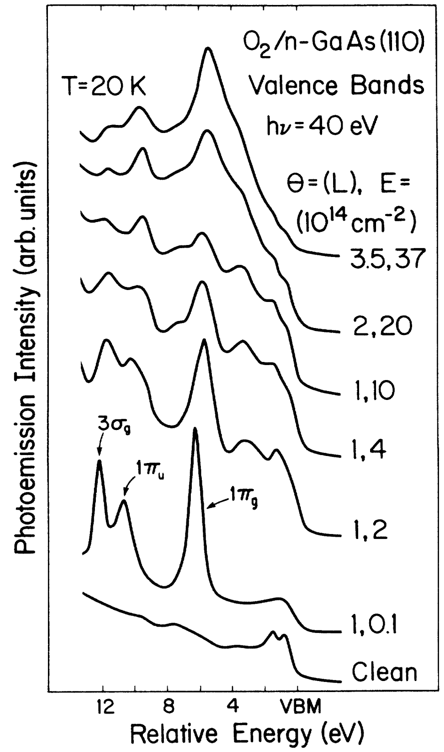

FIG. 1. Valence band results for O_2/GaAs(110) at 20 K as a function of oxygen exposure (Θ) and photon exposure (E). The clean surface spectrum is shown at the bottom. The EDC for 1 L O_2 reveals emission from the $1\pi_g$, $1\pi_u$, and $3\sigma_g$ orbitals of condensed O_2. These features shift toward the VBM with greater photon exposure and line-shape changes indicate reaction with the substrate. Reaction continues upon further O_2 and $h\nu$ exposure.

signments of these features have been controversial. For example, Landgren *et al.*[4] reported that the peak at ~2 eV was due to substrate emission (O_2 exposures and measurements at 300 K). Frankel *et al.*[10] observed the features of molecular O_2 at ~45 K but there was enhanced emission at ~2 and ~7 eV upon warming to 60 K. They attributed the dominant structures that resulted from this warming to a reaction intermediate because those features disappeared between 150 and 170 K as a component due to chemisorbed oxygen formed at ~5 eV. Su *et al.*[2] observed GaAs substrate emission at 6.9 eV for O_2 exposure and measurement at 300 K, but Landgren *et al.* reported that structure 6–8 eV below the VBM was due to Ga—O bonding. Landgren *et al.* also assigned the peak near 10 eV to substrate emission, while Su *et al.* attributed it to Ga—O. The bonding configurations reflected by the broad feature at ~5 eV have also been debated.[2,4]

From Fig. 1, it is clear that the reaction-induced components increase in relative intensity during photon exposure as the molecular O_2 emission decreases (compare results for 1 L for $2 \le E \le 10 \times 10^{14}$ cm^{-2}). Additional O_2 exposure of this reacted surface results in the reappearance of O_2 emission, and further illumination produces continued conversion to surface oxides (compare the top three EDC's in Fig. 1). As will be discussed below, transport through the evolving oxides is reduced as the thickness increases, slowing surface oxidation.

The results presented in Fig. 1 demonstrate that O_2/GaAs(110) interactions are modified by the probe beam at low temperatures. This has not been observed previously on this system because previous investigations did not examine the dependencies on photon exposure (calculations of the energy barrier for reaction have indicated that surface oxidation should be suppressed at low temperature).[19] It is, however, instructive to compare the exposure-dependent trends of Fig. 1 to the temperature-dependent changes observed by Frankel *et al.*[10] They reported that physisorbed O_2 converted to an intermediate state upon warming from ~45 to 60 K that was characterized by structure ~7 eV below the VBM on the high-binding energy side of the $1\pi_g$ peak. The large ~7 eV feature was then lost as continued warming produced a broad chemisorbed oxygen feature at ~5 eV. In contrast, Fig. 1 indicates that the small ~7 eV feature that forms is dominated by emission from molecular O_2 during early stages of reaction and, later, by chemisorbed oxygen at ~5 eV. This indicates that the intermediate oxidation state is readily converted by irradiation at 20 K to the ~5 eV oxide feature.

In Fig. 2 we show the changes that occur in the As 3*d* core-level emission during photon exposure for (2 L O_2)/GaAs(110) at 20 K. These exposure-dependent spec-

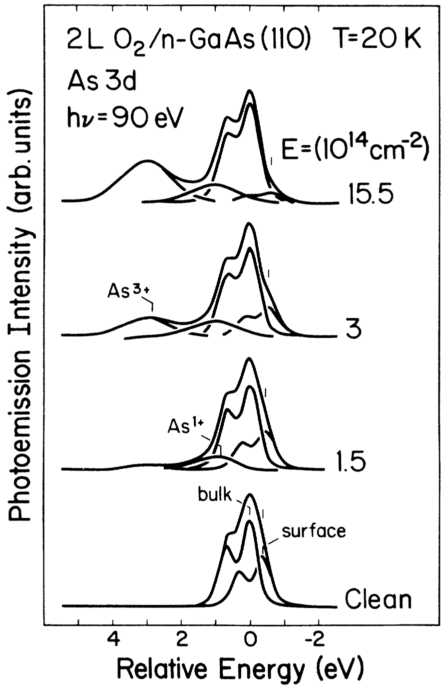

FIG. 2. EDC's for the As 3*d* core level for (2 L O_2)/GaAs(110) at 20 K. Surface-shifted and bulk As features are shown in the decomposition of the clean surface spectra. The surface-shifted component is consumed as reaction produces As^{1+}-like bonding configurations and then As^{3+} bonding.

tra have been shifted in energy to account for band bending (to be discussed) and normalized to emphasize line-shape changes.[20] Analysis of the clean surface spectrum reveals the familiar surface and bulk components, as labeled. During illumination the relative emission from the surface-shifted component decreased and broad structures developed ~0.85 and ~2.8 eV from the As bulk component. The reduction in intensity for the surface-shifted peak was accompanied by a shift of ~200 meV to lower energy. These results show that the surface-shifted peak is lost during surface oxidation, as expected. Moreover, they show that an overlayer of molecular O_2 is not sufficient in itself to produce surface unrelaxation. Hence, condensed O_2 does not significantly oxidize the surface (in the absence of the photon beam), and thermally activated reactions are negligible at 20 K. To confirm this point we exposed a clean GaAs(110) surface to O_2 at 20 K and delayed data acquisition (i.e., illumination) for 1 h. The resulting spectra were identical to those acquired without this delay.

The broad reaction-induced As peaks of Fig. 2 have been observed in previous studies of GaAs oxidation at 300 K (Refs. 1–4 and 6), where they were associated with an intermediate oxide (nominally As^{2+}-like) and an As^{3+}-like bonding configuration. Irradiation of O_2 condensed on GaAs(110) at 20 K makes it possible to induce substrate disruption and produce As-bonding configurations that are generally found at much higher O_2 exposures at 300 K.[1–4,6] [The extent of oxidation for (2 L O_2)/GaAs(110) at total light exposures of $E = 1.5\times10^{14}$, 3×10^{14}, and 15.5×10^{14} cm^{-2} is comparable to that for O_2 doses of $\sim10^8$, 10^{12}, and 10^{14} L at 300 K.[4]] The exposure-dependent results of Fig. 2 show that emission from the intermediate As^{1+}-like component grows faster than the As^{3+}-like feature and is prominent for $E = 1.5\times10^{14}$ photons/cm^{-2}. Upon further illumination, it remains approximately constant relative to the bulk component as the As^{3+}-like component grows.

A quantitative evaluation of the effects of photon irradiation can be obtained from the intensities of the different As 3*d* emission features. In Fig. 3 we show the results by plotting $\ln[I(E)/I(0)]$ versus E where $I(0)$ is the total clean surface emission and $I(E)$ is the intensity of the feature of interest at exposure E. Since the signal from the bulk As peak (solid squares) does not change significantly with irradiation, we conclude that primarily the topmost GaAs layer is involved in reaction for 2 L O_2. At the same time, the total As emission increases relative to that for the surface on which the O_2 had been condensed (solid circles). This reflects incorporation of As into the overlayer as the oxides form (as well as some desorption of oxygen, as will be discussed below). As the photon exposure increases, the surface-shifted As peak of Fig. 2 is lost as As^{1+}-like and As^{3+}-like bonding configurations form.

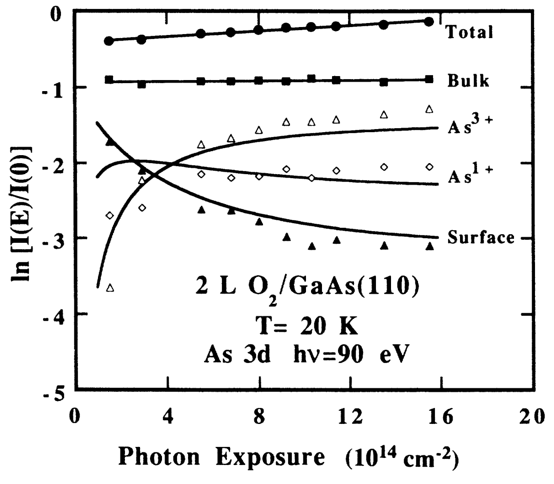

FIG. 3. Normalized intensities for the As features from Fig. 2, plotted as $\ln[I(E)/I(0)]$ vs photon exposure. The flat behavior exhibited by the bulk signal suggests that only the surface-shifted peak is involved in reaction. Photon-induced oxidation leads to changes in the relative intensities of the various As features. The smooth curves through these points represent a fit to two sequential second-order reactions, as described in the text.

KINETICS OF GaAs(110) SURFACE OXIDATION

Low-coverage regime

In this section, we describe a kinetic model of photon-induced surface reactions for O_2/GaAs(110) which is applicable to the low-O_2 regime ($\Theta \leq 2$ L). We find that the predicted behavior of two sequential second-order reactions provides an excellent fit to the results of Fig. 3 (solid lines). While the mathematical details of such a kinetic system are well known, they are more easily understood by first considering the results anticipated for one first-order reaction and for two sequential first-order reactions. These simpler approaches yield useful information about the reaction probabilities (cross sections) and shed light on the importance of both the oxygen and As concentrations prior to irradiation of the surface.

The simplest photon-induced reaction proceeds via a single-step first-order process corresponding to the direct conversion of one bonding configuration into another, $A \rightarrow B$. For example, Wen and Rosenberg[21] modeled the photolysis of physisorbed CH_3F on Si(111)-(7×7) and found that F in CH_3F converts to Si—F bonding configurations via a first-order process. Elementary kinetic theory yields the rate of CH_3F conversion, namely $dC(E)/dE = -\sigma C(E)$, where $C(E)$ is the concentration of CH_3F present on the surface (molecules/cm^2) at exposures E (photons/cm^2). The reaction probability or cross section σ has units of cm^2/photon. Hence, $C(E) = C(0)\exp(-\sigma E)$, where $C(0)$ is the initial amount of reactant on the surface, assuming that the photons induce the reaction. Conversely, the amount of reaction product after exposure is $C(0)[1-\exp(-\sigma E)]$. Since the emission intensity from a monolayer or less of adsorbate is proportional to the surface concentration, a plot of $\ln[I(E)/I(0)]$ versus E would yield a straight line with slope equal to $-\sigma$.

If we assume that the loss of emission from surface-shifted As atoms (Fig. 2) proceeds via a first-order process for low-photon exposures, then a straight line drawn using the first two data points of Fig. 3 (solid triangles) would yield a value for σ of $\sim 6\times10^{-15}$ cm^2/photon. This would correspond to direct conversion of the surface As atoms to As^{1+}-like states. Since the formation of these new states requires oxygen, the probability of dissociating O_2 must be comparable to that for consumption of surface As. The large value of σ indicates a high probability for photon-mediated O_2 decomposition and reaction, and this is consistent with Refs. 7, 8, and 21–23 which suggest that dissociation of O_2 occurs via capture of a secondary electron.[24,25]

The results of Fig. 2 clearly show that two reaction-induced As features are produced by photon exposure, and this surface condition indicates that the results cannot be described by a single one-step reaction. Instead, a model where the surface As is transformed sequentially to As^{1+}-like and then As^{3+}-like bonding configurations can be written as $As\rightarrow As^{1+}\rightarrow As^{3+}$, where a reaction probability for each first-order reaction can be determined by fitting the experimental data. This has the advantage of predicting that As^{1+} forms before As^{3+}-like states (as observed in Fig. 2), but there are two severe drawbacks. First, the two-step model predicts that surface As emission would decay exponentially with photon exposure, but straight-line behavior is not observed in Fig. 3. Second, the As^{1+}-like oxide must convert to the As^{3+}-like form as complete oxidation occurs. This is not observed because the two-step model neglects the presence of oxygen, which is necessary for reaction to proceed.

While the two models considered above provide insight into the mechanism(s) for reaction and explain the sequential appearance of two reacted As features, neither considers the presence of O_2 and neither can reproduce the bowed attenuation of the surface-shifted As emission revealed in Fig. 3. To address these two problems, we must consider that O_2 interacts with GaAs as

$$As+O\rightarrow As^{1+} \;, \tag{1a}$$

$$As^{1+}+O\rightarrow As^{3+} \;. \tag{1b}$$

Equation (1) is able to adequately describe the low-coverage As 3*d* core evolution while introducing a minimum number of fitting parameters (three). While offering a conceptual guide to surface oxidation, it still neglects interactions with Ga (which will be discussed below). A more sophisticated reaction sequence would incorporate O-Ga interactions, would involve the formation of other (additional) oxides, and would specify the bonding configurations. Such a sequence seems unjustified because of the growing number of fitting parameters.

Equation (1) yields a set of coupled differential equations which can be numerically integrated,[26] namely

$$\frac{d[As]}{dE}=-\kappa_1[As][O] \;, \tag{2a}$$

$$\frac{d[O]}{dE}=-\kappa_1[As][O]-\kappa_2[As^{1+}][O] \;, \tag{2b}$$

$$\frac{d[As^{1+}]}{dE}=\kappa_1[As][O]-\kappa_2[As^{1+}][O] \;, \tag{2c}$$

$$\frac{d[As^{3+}]}{dE}=\kappa_2[As^{1+}][O] \;. \tag{2d}$$

The square brackets represent the surface concentration of each species, and the terms κ_1 and κ_2 correspond to reaction probabilities with units of cm^4/photon, as per convention for a second-order reaction where the surface concentrations are given in atoms/cm^2. The initial conditions are that $[As]=[As]_0$, $[O]=[O]_0$, $[As^{1+}]=0$, and $[As^{3+}]=0$ at $E=0$. The initial concentration of surface As has been taken to be the value obtained for the GaAs(110) surface. The fitting parameters are then the initial concentration of O_2 on the surface and the reaction probabilities κ_1 and κ_2. Assuming a unity sticking coefficient, 2 L corresponds to $\sim 7.1\times10^{14}$ molecules/cm^2. Since the atom density of the GaAs(110) surface is 8.86×10^{14} cm^{-2}, there are ~ 1.5 times as many oxygen atoms as surface Ga or As. If oxygen interacted equally with Ga and As, a 2 L O_2 dose would yield $[O]_0\sim 1.5[As]_0$. Letting $\kappa_1=\kappa_2$ results in only one free variable, and it can be determined by comparing the predicted behavior to the experimental results.

In Fig. 3, the smooth curves passing through the experimental points for surface-shifted As, As^{1+}, and As^{3+} emission demonstrate that a two-step reaction adequately describes the experimental results. In obtaining these fits, the probabilities κ_1 and κ_2 were determined to be $6\pm2\times10^{-29}$ cm^4/photon. Insight into the sensitivity of the model equations to $[As]_0$, $[O]_0$, and the constants κ_1 and κ_2 is gained by observing the predicted behavior when the ratios $[O]_0/[As]_0$ and κ_1/κ_2 are varied. For example, if $[O]_0/[As]_0=1.5$ and $\kappa_1/\kappa_2=10$, then As^{1+} formation dominates and As^{3+} is not detectable; the reverse is true if $\kappa_1/\kappa_2=0.1$. In contrast, when $\kappa_1/\kappa_2=1$ and the $[O]_0/[As]_0$ ratio changes from 1 to 4, the surface-shifted As that is still present after 95% of the oxygen has been consumed ranges from much larger to much smaller than observed experimentally. The value of $[O]_0/[As]_0=1.5$ provides the best fit and it also serves as an independent check of the O_2 exposure.

As noted above, this kinetic model neglects reactions with bulk GaAs and the possibility of forming additional distinct bonding configurations. The surface processes are further complicated because photoelectrons emitted from the sample possess sufficient energy to perturb the surface oxides of GaAs via decomposition and desorption.[27,28] Since both photons and electrons can induce these effects,[29,30] the reactions observed here probably reflect a detailed balance between oxide creation and degradation. A more involved approach would be required to describe what happens when O_2 is added to an already oxidized surface and is irradiated.

High-coverage regime

The previous section focused on oxidation kinetics in the low-coverage regime. We now consider the competition between continued reaction and oxygen desorption during irradiation as the amount of O_2 is increased. Figure 4 summarizes the effects of repeated cycles of O_2 condensation and photon irradiation on the As 3*d* core-level emission. The spectrum at the bottom is similar to that at the top of Fig. 2. Two exposures of 1.5 L O_2 each followed by extensive irradiation yields the spectrum labeled 5 L. Line-shape analysis shows that the As^{1+} intensity remains relatively constant while the As^{3+} signal grows to constitute ~50% of the total emission. In addition, the As surface component has been completely consumed, and a new feature appears ~4.3 eV from the bulk As peak. This 4.3-eV feature has previously been attributed to As^{5+}-like bonding configurations.[1,4] It grows when another 5 L O_2 are condensed and the surface is irradiated during data acquisition (10 L EDC). After the addition of another 10 L O_2 (giving 20 L total), the As^{5-}-like oxide dominates. It also shifts ~0.2 eV to higher binding energy as the bonding configurations evolve. We note that all of these O-induced features in Fig. 4 are very broad and the spin-orbit splitting cannot be resolved visually. This reflects the formation of slightly inequivalent bonding configurations that can be characterized as nominally 1+, 3+, and 5+ states. We find no evidence for other oxidation states.

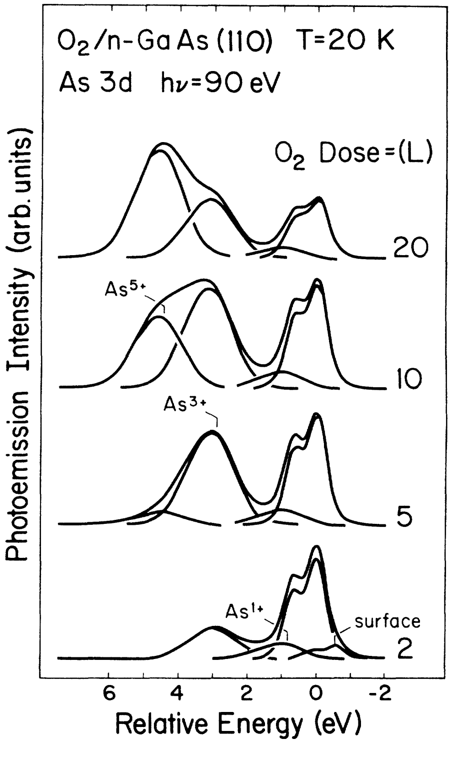

FIG. 4. Repetitive O_2 condensation and photon exposures showing changes in the As 3*d* core level indicative of additional oxidation and the formation of As^{5+}-like bonding configurations. The As^{5+} signal dominates the total As emission after the surface has been dosed with a total of 20 L O_2 and irradiated. These results demonstrate that unprecedented amounts of highly oxidized As can be produced by molecular O_2 at 20 K.

The results of Fig. 4 are particularly important because they show that large amounts of As^{5+} can be produced by low-temperature O_2 condensation and photon irradiation. In contrast, the As^{5+}-like feature is generally observed in significant quantities at 300 K (> 5% of the total emission) only when the GaAs surface is exposed to excited oxygen.[1] Moreover, molecular O_2 usually does not produce pentavalent As unless oxidation occurs under a high partial pressure of As_2O_3.[31] This reflects the high volatility of As_2O_3 and the greater thermodynamic stability of the Ga oxides. We suggest that the present results are unique because of quite different kinetic processes at low temperature with thick oxygen layers. The 20-K oxidation quenches volatilization of As_2O_3, alters the transport kinetics through the evolving layers, and facilitates the formation of As^{5+}-like states. While the formation of Ga oxides via reduction of As oxides is thermodynamically favorable, kinetic constraints apparently favor the formation of the As^{5+}-like species.

Additional insight into surface oxidation of GaAs can be gained by examining the Ga 3*d* EDC's. These are shown in Fig. 5 for the same O_2 coverages and nearly the same photon exposures as in Fig. 4. The spectrum for the clean GaAs(110) surface illustrates the decomposition into bulk and surface-shifted components. Upon exposure to O_2 and the photon beam, the surface component is replaced by a broad (~1 eV) reacted feature. This feature grows in relative intensity and shifts to ~1 eV higher binding energy. As noted before for As, the O-induced Ga 3*d* features are broad, and decomposition into more than a single feature to account for multiple-bonding configurations is not warranted.[6] Nonetheless, others have introduced two peaks which change in intensity but do not move with O_2 exposure.[3,4] This latter approach might be suggested by the As 3*d* features of Fig. 4, because the energy shifts were much larger and the decompositions were obvious. We note that investigations with different photon energies should facilitate identification of distinct Ga bonding configurations if one oxide formed closer to the surface than the others. Analysis of our spectra acquired in this manner suggested that the different bonding configurations are distributed throughout the overlayer. Those same $h\nu$-dependent studies of As emission led to the same conclusion for the As oxides. Finally, the absolute intensities of the reacted Ga and As peaks (relative to the clean surface values) are approximately the same because both are involved in reactions to about the same extent at 20 K and the resultant atom distributions are mixed.

The results of Figs. 4 and 5 show that emission from the GaAs substrate can still be observed after 20 L O_2 and irradiation. This suggests that the process of oxidation induced by the almost-complete consumption of oxygen for (2 L O_2)/GaAs (Figs. 2 and 3) changes as the oxide thickens. In particular, irradiation of a surface exposed to a total of 20 L O_2 would result in the formation of oxides thicker than the probe depth (assuming laterally

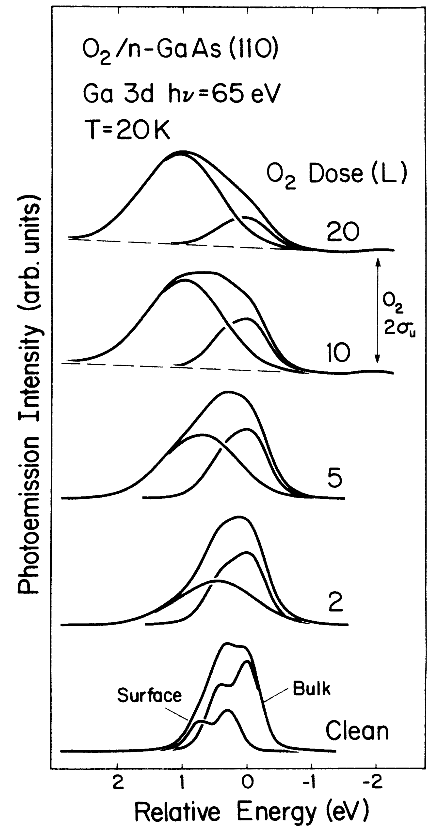

FIG. 5. Ga $3d$ core-level spectra showing perturbation of the Ga atoms by photon-induced reactions. A broad reaction-induced component grows on the low-binding-energy side of the main peak, and its centroid shifts ~0.7 eV for $2 \leq \Theta \leq 20$ L O_2 indicating that it is composed of two or more unresolved components. Core-level decomposition is not possible for thick O_2 layers because O_2 orbitals straddle the Ga peaks.

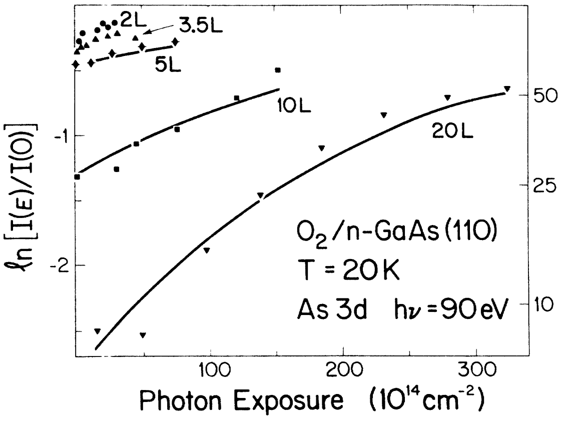

FIG. 6. Total As $3d$ emission normalized to the clean surface signal plotted as a function of relative photon exposure for several O_2 doses. These results indicate that photons induce oxygen desorption as well as reaction. For each O_2 coverage, the As intensity increases with photon exposure, reflecting both oxygen desorption and redistribution through the surface oxides. The smooth curves passing through the 5, 10, and 20 L points represent a simple model of oxygen desorption via a first-order process, as discussed in the text.

uniform oxide growth and a photoelectron mean free path of ~4 Å). This suggests that the reaction rate is reduced as the overlayer thickens, and it indicates that some of the oxygen is desorbed from the surface.

Figure 6 summarizes the results of a detailed study of the As $3d$ emission (bulk, surface, and oxide components) as a function of photon exposure. The As $3d$ signal has been plotted as $\ln[I(E)/I(0)]$ and the exposure has been reset to zero after each O_2 dose. (The rightmost point of each curve corresponds to the Ga and As EDC's of Figs. 4 and 5.) Condensation of 5 L (total 10) and 10 L (total 20) of O_2 initially attenuates the As emission by $\sim 1/e$ and $\sim 1/e^2$, respectively, showing that multiple O_2 layers can be adsorbed and establishing that the photoelectron mean free path through O_2 is ~5 L or 4 monolayers. Each curve shows an increase in total As emission with continued irradiation, indicating that either As moves into the overlayer as an oxide or that the O_2 thickness itself decreases. The reappearance of As at low O_2 doses can be explained in large part by atomic redistribution as oxygen is incorporated into Ga and As oxides as Ga and As are released from the surface layer. However, the reappearance of As emission for O_2 doses above 5 L is more complex.

In order to investigate the possibility that As diffuses into the condensed overlayer for O_2 exposures above 5 L, the photon exposure-dependent trends in Ga and As emission were compared to that for the O_2 $1\pi_g$ orbital in the valence band. Both Ga and As signals increased with irradiation, while that for O_2 decreased, indicating thinning of the condensed overlayer. This conclusion is supported by the results of a separate investigation where an oxidized GaAs surface was repeatedly dosed with O_2 and then quickly examined to minimize photon-induced effects. Both substrate and oxide features were attenuated to the same extent, demonstrating that oxide diffusion through the overlayer (surface segregation) was insignificant.

Analysis of the 10 and 20 L O_2 curves of Fig. 6 suggest that photons induce desorption of O_2 at 20 K. Since the photon energies used in this study, $h\nu = 65$ and 90 eV, and the energies of the resultant photoelectrons and secondaries are above those necessary for photon-stimulated desorption,[21,29,30] it is useful to consider a simple model of desorption. The utility of such an approach is that the effective probability (or cross section) for O_2 desorption can be determined from the rate at which the As emission recovers. If we assume that oxygen desorption involves O_2 overlying the As-containing region, then the emission from a component below the (uniform) overlayer is attenuated as $\ln[I(E)/I(0)] = -x(E)/\lambda$, where $x(E)$ is the overlayer thickness after exposure E and λ is the effective photoelectron mean free path. By assuming that oxygen desorbs via a first-order process, the amount of O_2 remaining on the surface after exposure E is given by $N(E) = N_0 \exp(-\beta E)$, where β is the cross section and N_0 is the initial number of molecules on the surface per cm^2. Since N is proportional to the thickness, $x(E)$, we can obtain an expression for recovery of the substrate signal as a function of the total photon exposure, i.e.,

$$\ln[I(E)/I(0)] = -A_0 \exp(-\beta E) . \tag{3}$$

The experimentally determined constant A_0 relates the thickness, initial amount of O_2, and the mean free path at $E=0$. This simple behavior produces the smooth curves shown in Fig. 6 for the 5, 10, and 20 L O_2 surfaces for $\beta = 4.5 \times 10^{-17}$ cm^2/photon. The agreement between the experimental data and the model curves supports our interpretation of photon-induced desorption. Some deviation might be expected since reactions continue slowly beneath the O_2 layer as the overlayer is desorbed.

Comparison of the rates at which the Ga and As emission recovered was not possible because the O_2 $2\sigma_u$ feature (Fig. 5) partially overlaps, and is larger than, the Ga emission for thick O_2 layers. This prevented the determination of a realistic background and, consequently, a useful measure of the photon exposure-dependent Ga 3*d* intensities. However, as discussed above, after most of the condensate had been desorbed, Ga and As were oxidized to about the same extent and both exhibit a distribution of oxidation states. No evidence for a preferred Ga or As oxide formation or a distribution of oxides was observed at 20 K.

It is not possible to draw a conclusion about what causes the desorption based on the cross section given above because the desorbing oxygen is likely to be composed of positively and negatively charged atoms and molecules.[22,25] The species most likely to desorb is neutral O_2, but since neutral species are hard to detect, very few numbers are available for comparison. In addition, both photons and secondary electrons are incident upon the condensed gas and both can produce desorption. Hence, the probability of desorption in each case is energy dependent.[23,29,30]

Finally, it is instructive to compare the probabilities determined above for reaction to that for desorption. In the discussion of Fig. 3, we estimated that the probability of reaction at low coverage was $\sim 6 \times 10^{-15}$ cm^2, and the results of Fig. 6 give an effective desorption cross section of $\sim 4.5 \times 10^{-17}$ cm^2. Assuming that the ratio of these two probabilities was independent of the formation of surface oxides, one could conclude that 0.15 L O_2 would be desorbed while 19.85 L O_2 would be consumed via substrate reactions for every 20 L O_2 condensed on the surface. That this does not occur indicates that the oxidation rate slows considerably as the oxides thicken. Hence, a more complex model of surface reactions should be considered to combine the desorption phenomena with oxygen transport through the evolving Ga and As oxides. While the role of such complicating factors can be speculated upon, modeling does not appear warranted at this time.

BAND BENDING

The above discussion has shown that the surface evolution for O_2/GaAs is quite complex. Hence, one might expect an equally involved dependence of surface band bending on the extent of surface oxidation. In the following, we examine band bending as a function of dopant type, dopant concentration, oxygen exposure, photon exposure, and temperature. Motivation for considering these effects has been prompted by several low-temperature and room-temperature oxidation investigations and by recent results for metal/GaAs interfaces. The critical issues are reviewed prior to discussing the new band-bending results.

Photoemission,[4,9,10,32,33] scanning tunneling microscopy,[34] Kelvin probe,[35] and other methods[11] have been used to investigate band bending during GaAs(110) oxidation. Most such studies have observed band-bending changes consistent with the formation of donors and acceptors that pin E_F near midgap, with a separation of ~200 meV between the final *n*- and *p*-type pinning positions. During the initial stages of formation, Spicer *et al.*, Landgren *et al.*, Berkovits *et al.*, and Stiles *et al.*, observed pinning to occur faster on *n*- than *p*-type GaAs for $T \leq 300$ K. The latter two groups concluded that the levels formed initially are acceptors and that additional reaction for higher O_2 doses produce donor states as well. Scanning tunneling microscopy (STM) investigations of the low-exposure regime have supported these conclusions.[34] The results of each low-temperature study have suggested that cooling reduces reaction and suppresses the formation of the donorlike states.[9-11] Warming O_2-exposed surfaces from low temperature to 300 K causes changes in the Ga 3*d* core-level line shape, and E_F moves toward midgap, suggesting that states are produced that are necessary for pinning *p*-type surfaces.[9,10]

This description of E_F evolution has enjoyed widespread acceptance. It received additional support recently from tight-binding calculations which predicted that electronegative species would act as acceptors in the submonolayer regime, while electropositive adatoms (metals) would produce donorlike states in the gap.[36-38] Indeed, electropositive metal atoms had been observed to induce rapid band bending on *p*-type GaAs(110) surfaces, while E_F evolved more slowly on *n*-type GaAs, and this was thought to indicate that metals produced donor states in the gap.[39-41] For metal overlayers, this interpretation was shown to be incorrect when it was demonstrated that the low-temperature asymmetric band bending was a consequence of the substrate temperature and bulk dopant concentration.[42-45] Experiments with *n*- and *p*-type GaAs(110) and InP(110) showed that E_F moved symmetrically into the gap for lightly doped samples and that E_F movement occurred faster for more heavily doped samples. This indicated that the adatom-induced states possessed both donorlike and acceptorlike character. Moreover, the rate of E_F movement was opposite to that predicted for a charged defect model. Hecht very recently pointed out that the band-bending differences for LD and HD GaAs(110) at low temperature can be related to surface-photovoltage (SPV) effects.[46] For this situation, an open circuit voltage induced by separation of electron-hole pairs within the depletion region opposes the defect-induced built-in voltage, flattening the semiconductor bands. The restoring current which counters the open circuit voltage is lower for the LD samples than for HD GaAs, resulting in the observation of less band bending for LD surfaces. The significance of these effects has recently been demonstrated for several metal/GaAs(110) interfaces.[47] The question to address here is whether the E_F evolution for oxygen (thought to be a donor) on GaAs(110) would exhibit any dopant concentration dependences.

In Fig. 7, we show the E_F evolution for LD and HD GaAs(110) surfaces induced by O_2 exposures of $0.1 \leq \Theta \leq 20$ L at 20 K. From the discussion above, it should be clear that the amount of reaction depends on the amount of O_2 on the surface and the extent to which that surface has been irradiated. At the same time, band-bending measurements made immediately after O_2 dosing (low-photon exposure limit) and after extensive irradiation exhibited little change. For LD *n*-type GaAs, E_F moves to ~100 meV below the CBM after 0.1 L exposure and then gradually shifts another ~60 meV as the exposure increases to 20 L O_2. In contrast, the *n*-type HD GaAs surface Fermi level moves deeper into the gap for the same O_2 dose, leveling out ~450 meV below the CBM. Intriguingly, the E_F movement for *p*-type GaAs surfaces at 20 K is almost independent of dopant concentration, and E_F remains within ~100 meV of the VBM for all O_2 doses. The lack of movement into the gap is consistent with the formation of acceptor states on the surface.[9,11,34] In addition, since acceptorlike states will not induce band bending on *p*-type surfaces, photovoltage effects that would produce differences in the observed band bending for LD and HD samples are negligible. Consequently, the nearly identical band-bending behavior exhibited by the differently doped *p*-type GaAs surfaces supports the interpretation that oxygen produces acceptorlike states.

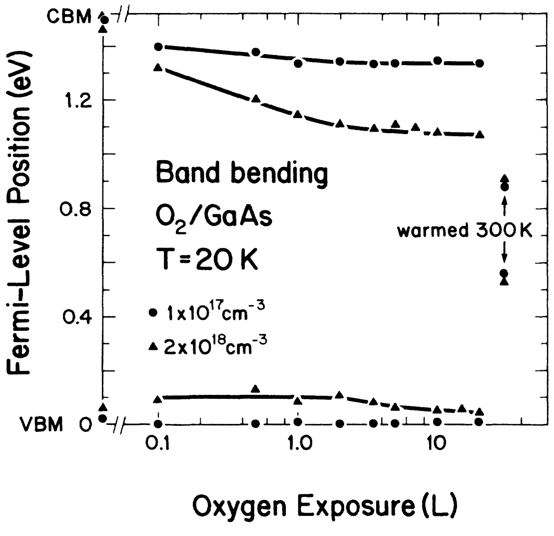

FIG. 7. Band bending for *n*- and *p*-type GaAs(110) surfaces with increasing O_2 exposure. Triangles represent E_F movement for highly doped samples (2×10^{18} cm^3), while the circles represent lightly doped crystals (1×10^{17} cm^{-3}). The O_2 exposure is not directly proportional to the surface oxide concentration because of sample-to-sample differences in photon irradiation which causes reaction and desorption of the overlayer. Strong dopant dependences exhibited by *n*-type GaAs are due to surface photovoltage effects. These effects are not observed for *p*-type GaAs, and the behavior is consistent with the formation of acceptorlike states. The positions of E_F for *n*- and *p*-type GaAs surfaces which were oxidized at 20 K and then warmed to 300 K are in good agreement with previous measurements.

Both Landgren *et al.*[4] and Stiles *et al.*[9] have reported that E_F moves into the gap of *p*-type samples when the surface is sufficiently oxidized because donorlike states are formed in the gap. As shown in Fig. 7, E_F remains near the VBM at 20 K despite the results of Figs. 2, 4, and 5, which demonstrate that these surfaces are heavily oxidized. Consequently, the correlation between band bending and surface chemistry observed by others at both low temperature and 300 K may be coincidental. This conclusion must be tempered by noting that the relative binding energies (and hence the electronic structure) of the photon-induced oxides differ somewhat from those formed in the absence of light. Indeed, the As^{3+}, As^{5+}, and reacted-Ga core-level features gradually shift 200–400 meV to higher binding energy relative to the bulk Ga and As peaks when annealed. Each reacted peak also sharpens upon warming to 300 K, indicating that the surface bonding configurations become more uniform.

The positions of E_F for *n*- and *p*-type LD and HD GaAs surfaces oxidized at 20 K and then warmed to 300 K are shown in Fig. 7. The *n*-type surfaces are pinned ~620 meV below the CBM while E_F is ~550 meV above the VBM for *p*-type surfaces. We conclude that annealing appears to produce donorlike states on *p*-type GaAs, as has been reported previously.[9,10] These band-bending values are nearly independent of dopant concentration, and they are in good agreement with earlier results.[4,9,32,35]

To test the importance of annealing-induced chemical changes on E_F position, EDC's were acquired as each of the samples in Fig. 7 was recooled to 20–100 K. In each case, E_F returned to the position in the gap observed prior to warming, indicating that SPV effects again became significant at low temperature. This observation is particularly interesting for the *p*-type GaAs surfaces, where the SPV counters the effects of the donorlike states formed with heating. The Fermi level for both LD and HD *p*-type surfaces shifts to ~125 meV above the VBM. We note that no dopant concentration dependence was observed, as was seen for *n*-type GaAs, and this is probably due to differences in the extent of surface oxidation for each sample.

In summary, we have shown that O_2 initially physisorbs on GaAs(110) at 20 K, but that photons induce the formation of Ga and As oxides. Models which describe the competition between photoinduced reaction and desorption indicate that initially oxidation rapidly occurs, but that desorption dominates as the oxides thicken. Band-bending studies support previous interpretations that oxygen initially creates acceptorlike states in the gap. Trends in the doping concentration-dependent

E_F evolution for oxidized *n*-type GaAs surfaces suggest that surface photovoltage effects are significant at 20 K.

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[19] After these data were acquired, we learned of a paper by Bermudez *et al.* which investigated the sensitivity of the NO/GaAs(110) interface to photons for $40 < T < 140$ K. V. Bermudez, R. T. Williams, G. P. Willams, Jr., M. W. Rowe, H. Liu, A. Wu, H. R. Sadeghi, and J. C. Rife, J. Vac. Sci. Technol. A **8**, 1878 (1990).

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