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Dynamic photoinduced low-temperature oxidation of GaAs(110)

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Studies of O_2 interaction with GaAs(110) at 20 K show dynamic conversion of multilayers of physisorbed O_2 into As_2O_3-like and Ga_2O_3-like oxides due to the synchrotron radiation beam used to acquire photoemission data ($h\nu = 90$ eV, photon flux $\sim 2 \times 10^{13}$ $cm^{-2}s^{-1}$). A lower coordination of As and O is observed and is the precursor to As_2O_3 at the GaAs surface. As_2O_5-like bonding configurations are also produced when the amount of condensed O_2 is increased but this As_2O_5 is metastable with respect to high-energy photon irradiation. These low-temperature results show the interplay between photoinduced surface chemistry and kinetic constraints on oxygen diffusion over very short distances.

O_2/GaAs(110) surface interactions and GaAs oxidation have been studied for many years, and the complexities of the evolving surface are well known.[1-11] Studies at room temperature have shown that very high oxygen exposures are required for oxidation to occur[4-6] because of the low O_2 sticking coefficient. Studies at low temperature, which take advantage of enhanced O_2 adsorption, have sought to clarify the initial steps of oxidation.[7,8] Multiple reacted species have been reported to exist during the initial steps of oxidation, but the bonding configurations and stoichiometries of the intermediate surface oxides remain controversial. Intriguingly, while photoillumination enhances oxidation,[9-11] the effects of the beam used in photoemission studies of surface oxidation have not been examined.

In this paper, we focus on the oxidation of GaAs(110) at 20 K with ≤ 20 L O_2 exposures (1 L $= 10^{-6}$ Torr s) to examine photoenhanced reactivity at temperatures where thermally activated processes are suppressed. High-resolution synchrotron-radiation photoemission results show flux-dependent conversion of multiple layers of physisorbed O_2 to oxide species during photon irradiation ($h\nu = 90$ eV, photon flux 2×10^{13} $cm^{-2}s^{-1}$). This novel oxidation procedure requires $\sim 10^{10}$ times less O_2 exposure to produce the same amount of surface oxide compared to 300-K oxidation. Both As_2O_3-like and As_2O_5-like oxides can be formed at 20 K (in contrast to primarily As_2O_3 at 300 K) because oxygen transport to the GaAs surface is more kinetically limited at low temperature. Ligand shift calculations demonstrate that the intermediate AsO_x configuration that forms in contact with the GaAs substrate involves O atoms bonded to As with three Ga back bonds.

The photoemission experiments were conducted with the Minnesota-Argonne-Los Alamos extended-range grasshopper monochromator and beamline at the Wisconsin Synchrotron Radiation Center. Photoelectrons were collected with an angle-integrated double-pass cylindrical mirror analyzer. All spectra were obtained with a computer-interfaced data acquisition system, and core-level spectra could be fitted with a least-squares minimization routine. Si-doped GaAs(110) posts doped at 1×10^{17} cm^{-3} were cleaved at 300 K at 5×10^{-11} Torr. The quality of the cleaved surface was checked using core-level spectra, and the sample was cooled to 20 K (± 5 K) using a closed-cycle helium refrigerator. Core-level and valence-band spectra remeasured at 20 K were used as standard spectra during O_2 exposure and reaction. The O_2 exposures ranged from 2 to 20 L (using a precalibrated leak valve at O_2 pressures $1-5 \times 10^{-8}$ Torr). During exposure, the ion gauge was on but tests indicated that there was no dependence on gauge condition.

In Fig. 1 we show As $3d$ core-level spectra for GaAs(110) exposed to 2 L at 20 K. Clean surface results (not shown) reveal only the usual bulk and surface-shifted As components. The difference between the spectra in the upper and lower panels is the total photon irradiation at $h\nu = 90$ eV, namely 4.4×10^{14} and 3×10^{15} photons cm^{-2}. The initial spectrum shows two broad oxygen-induced species at ~ 0.9 and ~ 3 eV relative to the substrate component. The valence-band spectrum obtained immediately after core-level acquisition shows residual molecular oxygen (inset of lower panel with four structures from ~ 46- to ~ 54-eV kinetic energy corresponding to $3\sigma_g$, $3\sigma_g$, $1\pi_u$, and $1\pi_g$ molecular orbitals[8]). Repetitive acquisition of As $3d$ spectra for 2 L O_2/GaAs at 20 K showed that the intensity of ~ 3-eV peak increased with photon flux, as can be seen in the top panel, while emission from molecular O_2 decreased (top inset). The ~ 3-eV structure that has been observed by many authors[4-6,9,10] can be attributed to As_2O_3-like bonding configurations, i.e., to As atoms with three single bonds to oxygen, with a range of inequivalent bonding configurations in the reacted region to account for its width. Note also that the spectra of Fig. 1 for 2 L O_2/GaAs show a large surface-shifted As $3d$ component that diminishes during beam irradiation and surface oxidation. We conclude that physisorbed O_2 does little to induce GaAs(110) surface unrelaxation.

To demonstrate that the conversion from molecular to reacted oxygen is due to photon beam excitation rather than a thermally activated process, we repeated the experiment under identical conditions but delayed data acquisition (i.e., photon-beam irradiation) for 1 h after O_2 exposure. The initial scan produced the same spectrum as in Fig. 1. This dynamic beam-induced conversion from physisorbed molecular oxygen to an As_2O_3-like oxide has not

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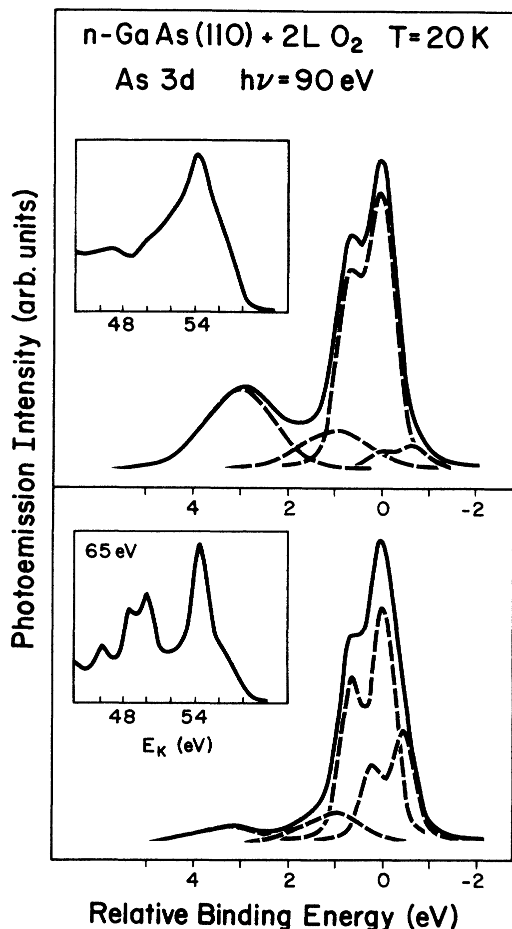

FIG. 1. As 3*d* core-level and valence-band photoemission spectra for *n*-type GaAs at 20 K after exposure to 2 L of molecular oxygen. The spectra at the bottom were acquired with effective photoillumination of 4.4×10^{13} photons cm^{-2}, while those at the top were acquired with 3.0×10^{14} photons cm^{-2}. Beam exposure induces O_2 dissociation, the loss of emission from the $3\sigma_g$, $3\sigma_g$, $1\pi_u$, and $1\pi_g$ molecular orbitals (see insets), the loss of the surface shifted As component, and an increase in the As_2O_3-like oxide emission.

been reported previously but it clearly plays a critical role in studies of surface reaction. Indeed, recognition that the incident beam alters the system under examination makes it possible to resolve many of the controversies in the literature regarding oxidation of GaAs.

The reacted peak at ~0.9 eV appears during the initial steps of oxidation and persists thereafter regardless of the extent of oxidation. Analysis of its relative intensity shows that it is attenuated at the same rate as the bulk As 3*d* emission during oxygen exposure up to 20 L. The chemical shift of this intermediate oxide relative to As_2O_3-like bonding indicates oxygen deficiency, namely AsO_x which $x \leq 1.5$. We conclude that O atoms responsible for the 0.9-eV feature exist at the interface where the As-O coordination is reduced and the structure is neither GaAs-like nor As_2O_3-like.

Intermediate oxide bonding configurations that give rise to the 0.9 eV shifted feature have been observed previously[6,12] and have been attributed to structure of the form AsO_x. However, the local bonding configuration for these atoms is not well known. The binding energies of the As_2O_3-like and As_2O_5-like oxides can be used to identify the local configuration of this precursor or intermediate oxide. The local configuration of the As_2O_5-like oxide can be estimated by assuming one double bond between O and As (As=O) and the rest single bonds (As—O).[13] For As_2O_3 configurations, As has three single O bonds and no double bonds. The chemical shift for one single O bond to elemental As (As—O) and one Ga bond to elemental As (As—Ga) can be calculated using the binding energies of As_2O_3 and As_2O_5, assuming that ligands of a given type shift the core energies of the central atom by the same amount.[4,14] For As_2O_3 and As_2O_5, the binding-energy relations relative to elemental bulk As are

$$\Delta E_{As_2O_3}\,(\text{eV}) = 3\,\Delta E_1 - 4\,\Delta E_2\,, \quad (1)$$

$$\Delta E_{As_2O_5}\,(\text{eV}) = 5\,\Delta E_1 - 4\,\Delta E_2\,, \quad (2)$$

where ΔE_1 is the ligand shift of As-O relative to elemental As and ΔE_2 is the ligand shift of bulk As in Ga-As relative to elemental As. Here we assume that As=O will have twice the ligand shift of As—O.[4] From Eqs. (1) and (2), the ligand shift of As-O (ΔE_1) is 0.73 eV and that of As-Ga (ΔE_2) is -0.17 eV, using the average values for As_2O_3 and As_2O_5 from Figs. 1-3. We can easily determine the local configuration of the intermediate oxide AsO_x ($x < 1.5$) from these two results. One oxygen single bond and three Ga bond configurations give 0.9-eV higher binding energy relative to the As in GaAs. If two oxygen single bonds or one oxygen double bond were to exist, then the binding energy relative to the bulk would be 1.7-1.8 eV, but no such feature was detected experimentally. Therefore, we conclude that the 0.9-eV As feature corresponds to bonding at the GaAs surface to form AsO_x ($x < 1.5$) with only one oxygen single bond and three Ga bonds.

Studies of interactions of this reacted 2 L O_2/GaAs(110) surface when thicker layers of O_2 are condensed show continued reaction and allow flux-dependent characterization of the evolving species. For 3.5-L exposures at 20 K, O_2 initially covers the surface, and subsequent irradiation leads to the disappearance of the surface-shifted As emission of GaAs(110). As for the 2-L results, exposure to the photon beam increases As_2O_3-like emission while reducing valence-band features associated with O_2. For 5 L O_2 exposures, the As_2O_3 intensity amounts to ~50% of the total As emission, and measurements during photon irradiation to 1.6×10^{15} photons cm^{-2} show that the amount of O_2 diminishes. The growth of another oxide with ~4.3 eV relative binding energy and higher oxygen coordination is clear at this exposure. This species can be ascribed to As_2O_5-like bonding where one more oxygen atom with a double bond has been added relative to As_2O_3.[2,4]

The results for 10-L exposure summarized in Fig. 2 demonstrate that the As_2O_3-like bonding at ~3 eV does not change significantly relative to As in GaAs during illumination but that the As_2O_5-like oxide (at ~4.3 eV) increases at the expense of molecular oxygen. The valence-

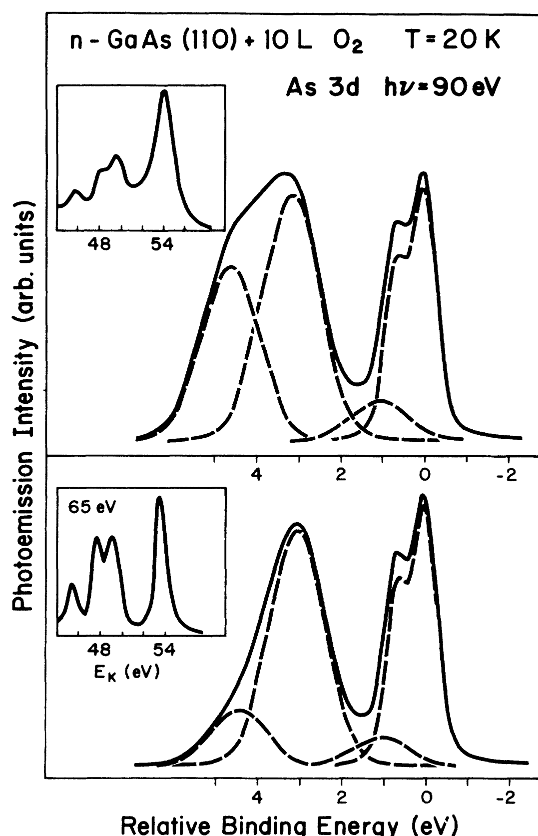

FIG. 2. As $3d$ core-level and valence-band spectra for 10 L O_2 GaAs(110) formed by condensing 5 L O_2 following 5 L O_2 exposure and reaction induced by 1.6×10^{16} photons cm^{-2}. With illumination, the O_2 molecular features shown in the insets are diminished and the As_2O_5-like components at ~4.3 eV grow but there is little change in the As_2O_3 or AsO_x features at ~3 and ~0.9 eV. The appearance of As_2O_5 reflects kinetic limitations that hinder O transport to the GaAs surface and favor formation of the higher oxide at the surface. Effective photoilluminations were 2.0×10^{16} photons cm^{-2} (lower panel) and 3.2×10^{16} photons cm^{-2} (upper panel).

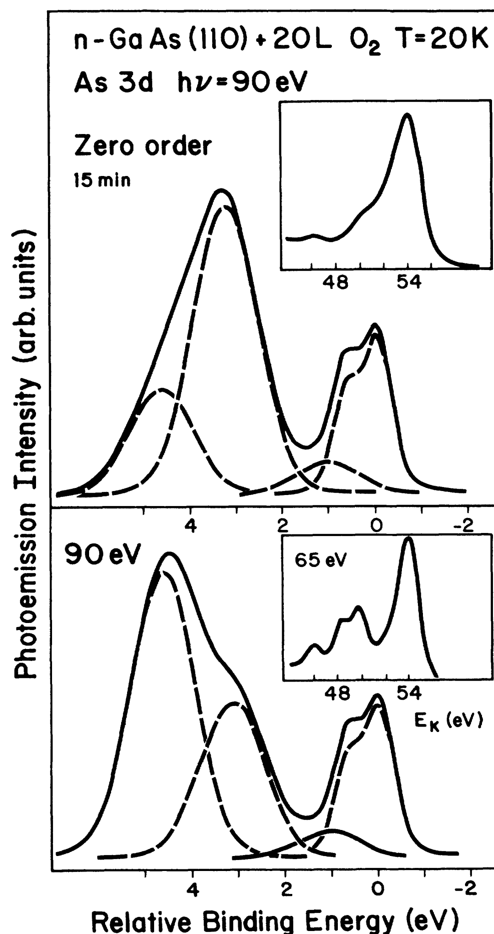

FIG. 3. As $3d$ core-level and valence-band spectra for 20 L O_2 GaAs(110) formed by condensing 10 L O_2 onto the reacted surface shown at the top of Fig. 2. Comparison to Fig. 2 shows that photoillumination (6.4×10^{16} photons cm^{-2}) enhances As_2O_5 growth, again with little relative change of the As_2O_3 and AsO_x components, but the inset shows the persistence of molecular O_2. Exposure to 15 min of nonmonochromatized illumination (~0.1 w/cm^2 and $h\nu$=2–1200 eV) shows that molecular O_2 is no longer present (insets) and that As_2O_5 is degraded as changes occur in the reacted region.

band results show conversion of molecular O_2 to these species, and core-level results demonstrate that it is the As_2O_5-like oxide that increases. The results summarized in the lower panel of Fig. 3 obtained after 20 L O_2 exposure at 20 K confirm that the As_2O_5-like oxide continues to form but also that emission from the other As oxides persist. This means that, on average, the As_2O_5-like oxide is located above the other As oxides (closer to the vacuum surface); lateral homogeneity is not implied.

The Ga $3d$ core-level spectra obtained in conjunction with those for As $3d$ at each exposure show a broad oxide peak at higher energy than the bulk Ga component in GaAs which evolves with O_2 and beam exposure. This oxygen-induced Ga structure has been observed by many authors,[4–6,9,10] and it can be attributed to Ga_2O_3-like bonding. The intensities of the oxidized Ga and As peaks relative to the clean surface emission suggests that the Ga_2O_3-like species are distributed in a fashion that is approximately homogeneous in the composite layer.

These line shape and intensity analyses make it possible to describe low-temperature, photon-induced oxidation of GaAs(110). At 20 K, O_2 physisorbs without dissociation because thermally activated dissociation is negligible.[15] While photons can excite the O_2/GaAs system in a variety of ways, the most likely source of reactive species is due to low-energy secondary electrons which can produce O_2^- (Ref. 16). These molecules can then dissociate into atomic oxygen and form As–O and Ga–O bonding configurations. For O bonded to As, the electronegativity of oxygen alters the charge distribution of As in GaAs surface bonds, i.e., in the GaAs back bonds. Substrate surface disruption then occurs and As_2O_3-like and Ga_2O_3-like configurations form as surface atoms redistribute to form new structures. (In principle, oxygen atoms could also form bridges between Ga and As surface atoms when two oxygen atoms bond to surface As atoms, but

there is no evidence for such bonding in the spectra.) As the oxide layer thickens, the probability that atomic oxygen can be trapped by As_2O_3 increases relative to thermally mediated kinetic processes that involve diffusion to the unreacted GaAs substrate. The former gives rise to As_2O_5-like bonding while the latter accounts for the transport of oxygen atoms to the GaAs surface where AsO_x-like bonding occurs and disruption produces As_2O_3-like structures. In general, As_2O_5 is difficult to create because O transport to the GaAs surface where As_2O_3 production occurs dominates over O trapping in the oxide (As_2O_5 formation). This balance between competing pathways is altered when substantial amounts of O are present, as has been accomplished here by O_2 physisorption at low temperature.

In order to further investigate photoinduced reactions, we first exposed GaAs(110) to 20 L of O_2 and irradiated it with 90-eV photons to produce a reacted surface characterized by strong As_2O_5-like emission (Fig. 3, bottom, exposure to 6.4×10^{16} photons cm^{-2}). These results show that As_2O_5-like bonding is likely to be established if there is O_2 on the surface. This surface was then exposed to the nonmonochromatized light transmitted through the beamline from Aladdin to maximize photon flux and energy distribution (energies $\sim$2–1200 eV). The spectra shown at the top of Fig. 3 were produced by 15 min irradiation. Comparison to the results for less extreme irradiation shows the growth of the As_2O_3-like bonding and the decrease of As_2O_5-like oxide. The valence-band results show that no molecular oxygen remains. These results demonstrate that As_2O_5-like bonding configurations at the surface are metastable with respect to intense, broadband illumination. For processes such as these with higher-energy illumination (or higher flux), it is likely that an Auger transition mechanism contributes to the release of a double-bonded oxygen atom from As_2O_5.[17] Perhaps most importantly, these results suggest that photoemission studies conducted with different photon energies may produce different surface oxides, complicating comparisons of results from different experiments.

In this paper, we have shown that the beam used in photoemission studies of O_2/GaAs(110) induces surface oxidation at low temperature. From the analysis of relative intensities of various oxides, the oxide phases were found to vary in amount according to the availability of physisorbed O_2 and the presence of secondary electrons. While the Ga_2O_3-like oxide appears to be mixed through the overlayer, As_2O_5-like oxides were dominant at the surface when there was sufficient O_2. As_2O_3-like bonding configurations were more pronounced closer to the substate and AsO_x-like bonds formed at the substrate itself. These profiles are a consequence of kinetic limitation. The present results show that they can be altered by intense, broadband photon irradiation. We expect similar radiation-induced oxidation mechanisms for other oxidizing gases in this low-temperature regime. From these results, it is clear that novel surface profiles can be produced at low temperature and that the effect of the incident photon beam (or electron beam) is of great importance.

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