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Oxidation of GaAs(110): New results and models

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The oxidation of ultrahigh-vacuum–cleaved GaAs(110) surfaces has been studied with high-resolution, core-level photoemission excited with synchrotron radiation. The oxidation is spatially and chemically inhomogeneous, and both subsurface oxidation and multibonding geometries occur already at submonolayer coverages.

Despite the large number of studies devoted to the oxidation of clean GaAs(110) surfaces[1-11] there has not been any direct and conclusive evidence in support of a particular oxidation mechanism. Models in which the oxygen binds predominantly to As,[1] to Ga,[3] or sits in a bridge-bond position[4] have been proposed. It has also been suggested that the oxidation proceeds in two consecutive steps, presumably with different reaction paths dominating in each step.[10] The reason for the difficulty in reconciling all the available data into one model can be attributed to certain assumptions common to the previous proposals. Most striking of these is that of homogeneous oxidation across the surface. Such an *a priori* assumption does not seem to be justified, particularly in view of other recent adsorbate studies involving metals,[12-14] which show that nucleated, three-dimensional (3D) processes dominate the interface formation.

In this paper we present the first results of a high-resolution photoelectron spectroscopy study of cleaved GaAs(110) surfaces exposed to molecular, unexcited oxygen. We have utilized the tunability of a synchrotron radiation source to obtain Ga and As core-level spectra which exhibit either predominantly surface or bulk features. The good overall resolution of less than 0.2 eV, in combination with the excellent fits produced using simple line-shape analysis has made possible the identification of a number of chemically shifted components not previously resolved. The movement of the Fermi level at the surface has also been monitored. The results necessitate a major revision of current ideas about the oxidation mechanism for this surface.

Both n- and p-type samples were studied and all surfaces exhibited negligible (≤ 0.1 eV) band bending prior to oxygen exposure. The exposures were carried out in the dark with all ion sources turned off. After exposure the oxygen was pumped away with a turbopump before starting the ionpump. Exposures ranged from 10^1 to 10^{14} L ($1\ \mathrm{L} = 10^{-6}$ Torr sec). The photoemission spectra were obtained with the IBM 2D electron spectrometer[15] located at the National Synchrotron Light Source, Brookhaven National Laboratory. The spectra were smoothed by a three-point averaging routine and, after background subtractions, were compared to spectra synthesized from suitable components consisting of a Lorentzian line shape convoluted with a Gaussian broadening function. The spin-orbit splitting and branching ratio were assumed to be the same for all components of a given core level and were determined by fitting the bulk and shifted surface core levels to the clean surface spectra.[16,17] All other fitting parameters, including the number of components, their spectral shifts, widths, and intensities were freely adjustable and uniquely determined for each spectrum with an iterative, least-square-fitting routine. Fits were always attempted with a minimum number of components, and their number increased only if the results were unsatisfactory and inconsistent with values and trends obtained from other decompositions. The widths of the oxidized peaks within a given spectrum were constrained to a common but freely adjustable value. The overall decomposition picture was not affected by this assumption unless variations in peak widths as large as a factor of 2–3 were allowed. However, such large variations are both physically unreasonable[18-20] and inconsistent with the oxygen-dependent spectral evolution, which indicates a sequential appearance of shifted features in the core-level spectra. The fitted widths of the oxidized peaks were generally 0.2–0.3 eV larger than those in GaAs [full width at half maximum (FWHM) ~ 0.5 eV]. This difference is attributed to inhomogeneities in the bonding environment of the oxides. The increased broadening of the GaAs bulk peaks with oxygen exposure is due to inhomogeneous band bending across the surface (see, for example, Fig. 2).

The decomposition of the surface-sensitive Ga $3d$ spectrum after an exposure to 10^8 L of oxygen is shown in Fig. 1(a). Both oxide components are clearly observable for exposures down to 10^6 L, which corresponds to an estimated oxygen adsorption of the equivalent of ~ 0.3 monolayer (ML).[10] For lower coverages the unambiguous identification of the oxide contribution became difficult due to the overlapping surface core-level peak. However, from the change in the surface core-level contribution (not shown here) it became clear that the oxygen adsorption affected the Ga $3d$ spectrum already at 10^4 L (< 0.1 ML). This observation is consistent with electron energy loss data,[4,10] which indicate a cleavage-dependent and saturable low coverage oxidation phase involving only the Ga.[10] Surface-sensitive As $3d$ spectra for various exposures are shown in Fig. 2. Their development differs from that of Ga in that the first oxide component was not clearly discernible until 10^6 L [Fig. 2(b)], with others successively appearing for larger exposures. The experimental data in both figures already suggest that oxide components underlie the main peak because of the substantial deviation in the apparent branching ratios from the expected value $\sim \frac{2}{3}$. It should be noted that a reduced surface component of the clean surface is still observable in Fig. 2(b). The successive appearance of additional and distinct oxide components increased both the ease of spectral decompositions and the confidence in their uniqueness. For exposures exceeding 10^{12} L four shifted components were necessary for a satisfactory fit.[21] The dominant contribution in a fully developed spectrum was always the previously observed peak shifted by 3.1 eV, whose

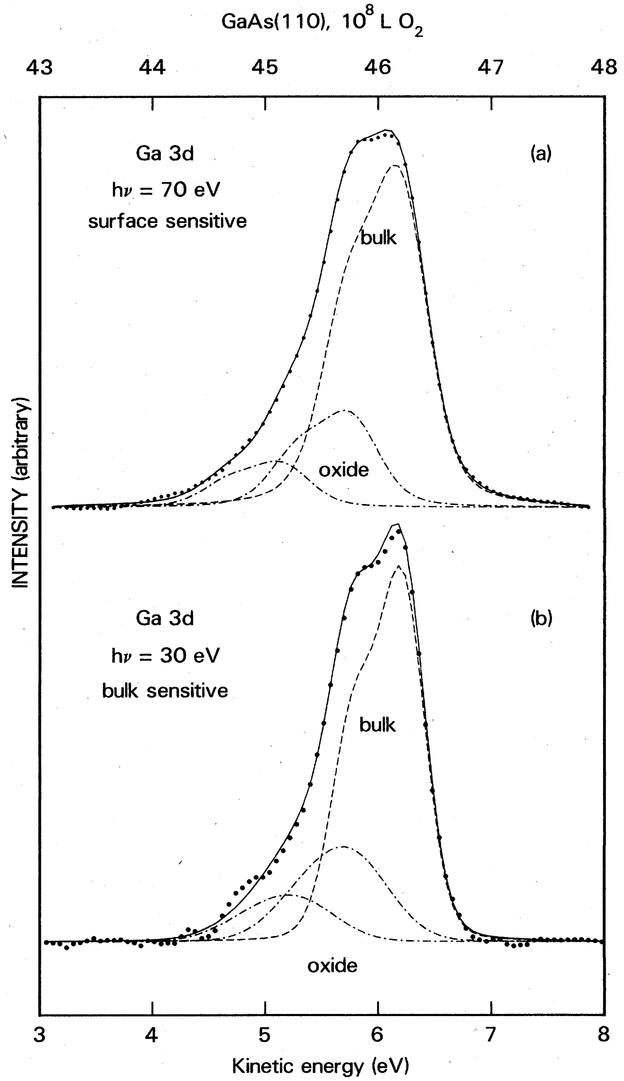

FIG. 1. Ga 3*d* spectra and their decompositions for an exposure of 10^8 L of oxygen, for (a) surface-sensitive and (b) bulk-sensitive conditions. The dots are the experimental data points and the solid line is the fitted curve.

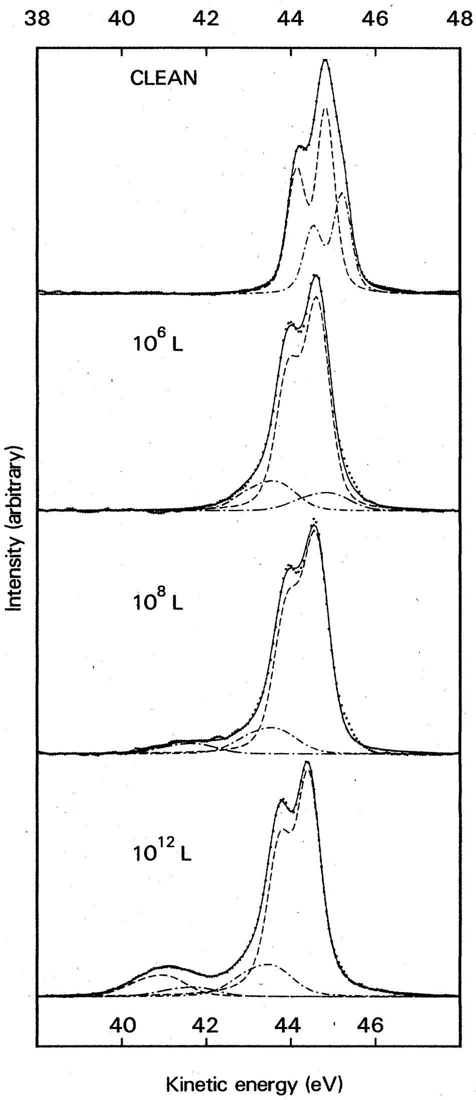

FIG. 2. Surface-sensitive As 3*d* spectra and their decompositions for indicated exposures. The dots are the experimental data points and the solid lines are the fitted curves.

intensity is also cleavage dependent for a given exposure. Table I summarizes the averaged values of energy shifts and intensities derived from several samples, including that of Fig. 2, exposed to 10^{12} L. The four shifted As components most likely correspond to As atoms with one-, two-, three-, and four-fold oxygen coordination. The latter seems to correspond to the configuration of three single and one double bond as in As_2O_5. The assignment of the Ga components is more uncertain. Because of the small shifts involved, we cannot exclude the possibility that the spectrum actually has additional unresolved components. However, we do not observe any shifted peaks around 2 eV as has been found for thick oxides of GaAs (Ref. 22) and Ga.[23]

Similar decompositions have also been carried out for the bulk sensitive spectra ($h\nu = 30$ eV for Ga and $h\nu = 50$ eV for As). Because of the low kinetic energies of the photoelectrons in these cases (around 6 eV) the background subtraction is more difficult. Nevertheless, good fits were obtained for the Ga spectra, as shown in Fig. 1(b) for an exposure of 10^8 L. The relative contribution of the surface core-level component to the total emission intensity for the clean surface spectrum was used to deduce photoelectron escape depths of 5 and 20 Å for our surface and bulk-sensitive conditions, respectively.[16] For the reasonable as-

TABLE I. Average shifts and intensities for the various Ga 3*d* and As 3*d* components after 10^{12}-L oxygen exposure. The shifts are given in eV from the corresponding bulk peak and the intensities give the fraction of the total 3*d* intensity.

	Ga 3*d*		As 3*d*	
	Δ*E* (eV)	*I*	Δ*E* (eV)	*I*
1	0.45 ± 0.05	0.22 ± 0.03	0.8 ± 0.1	0.09 ± 0.03
2	1.00 ± 0.05	0.14 ± 0.03	2.3 ± 0.2	0.07 ± 0.03
3			3.2 ± 0.1	0.14 ± 0.05
4			4.2 ± 0.2	0.02 ± 0.02

sumption that the escape depth does not change drastically with the oxygen adsorption,[24] we expect the ratio of the total oxide intensity in the surface sensitive spectrum to that in the bulk to be about three if the oxide was strictly confined to a surface layer. In sharp contrast, only ratios between 1.2 and 1.5 are observed for exposures of 10^8 and 10^{12} L, respectively. Qualitatively similar results were observed for the As core levels. The obvious conclusion is that contrary to all previous notions of the oxide growth, a subsurface oxide already forms for submonolayer coverages. A further consequence is that the oxide is distributed inhomogeneously across the surface even for exposures exceeding 10^8 L. This conclusion is also consistent with the broadening of spectral features due to inhomogeneous band bending.[21]

The results presented above clearly require a different model of the oxidation mechanism than those previously presented. Basically, a local, atomistic point of view is needed, which easily can accommodate mixed bonding configurations in order to account for the many chemical shifts observed. The model cannot adopt a layer-by-layer approach but must instead allow immediate and progressive breakage of backbonds. Presumably this occurs first at some cleavage-induced defect or step site, resulting in three-dimensional growth down and out from these nucleation sites. The nature of these defects is not known; however, the deep penetration of the oxidation (which exceeds 15 Å even at 10^8 L)[21] suggests microfissures or dislocations as plausible defects. Furthermore, the inhomogeneous oxide growth should cause a nonuniform position of the Fermi level in the band gap across the surface. This is indeed observed as a general broadening of the linewidths (both Ga and As) by about 0.2 eV when going from the clean, unpinned surface to one exposed to $\geqslant 10^8$ L of oxygen. As a consequence the idea of Fermi-level pinning as presented in the so-called unified defect model[25] may not be applicable to the case of oxygen on GaAs. In fact, we have not been able to establish a definite pinning level on any of our samples. The Fermi-level position continues to move by 0.1–0.2 eV even after a "quasipinning" has been reached at about 10^6 L.[21]

Another interesting point, which has been much debated in the past,[1-4,10] is the occurrence of changes in the electron-energy-loss spectum of Ga before that in As. It is now clear that similar observations by photoemission eluded Pianetta and co-workers[1,2] because of the lower resolution in their experiment. Bartels, Surkamp, Clemens, and Mönch[10] have suggested that beyond the previously mentioned low coverage (< 0.1 ML) adsorption phase involving only the Ga, the oxidation proceeds in two distinct steps, with the Ga involvement ($\sim 10^6$ L) preceding that of As ($\sim 10^7$ L). We do not concur with this separate picture. Instead, we observe the simultaneous oxidation of both components beyond 10^5–10^6 L. However, the rate of oxidation, as determined from the exposure-dependent ratios of intensities of the shifted and bulk core-level contributions, is greater for Ga than for As, which indicates the formation of separate oxide phases. Thus, all phases of the oxidation of the GaAs(110) surface are chemically inhomogeneous, a notion also supported by the emission spectra of the valence bands.[21]

In summary, we have presented a conceptually simple model for the GaAs(110) surface oxidation, which qualitatively describes the whole range of coverages from submonolayer to a fully oxidized surface. The stipulation that the oxidation nucleates and proceeds at extended, cleavage-induced defect sites has strong potential implications on the interface reactivity of other adsorbate systems on cleaved surfaces and on previous conclusions deduced under precarious assumptions of surface ideality.

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