

Site of Oxygen Chemisorption on the GaAs(110) Surface

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We reconcile energy-loss spectroscopy and chemical-shift studies of the oxidation of the GaAs(110) surface, which previously have led to contradictory conclusions about the oxygen bonding site. We have calculated densities of states and 100-eV ultraviolet-photoelectron-spectroscopy (UPS) valence-band spectra to examine the site and molecular species of the chemisorbed oxygen. We conclude that for low coverages oxygen prefers to chemisorb to the surface arsenic atoms and chemisorbs as an O_2 molecule.

Currently the most detailed information about oxygen chemisorption on the (110) surface of GaAs is provided by experiment.¹⁻³ This is unfortunate, since electron-energy-loss spectroscopy⁴ (ELS) and photoemission chemical-shift studies² have not yielded a consistent picture of one of the most fundamental aspects of this phenomenon, the site of oxygen chemisorption on this surface. While the observation of a large chemical shift of the arsenic $3d$ state upon exposure to oxygen² indicates that the oxygen is preferentially bonding to the surface arsenic atoms, the movement of cation-derived features in the energy-loss spectra has led to the conclusions that the surface gallium atoms are the preferred bonding targets.⁴ Our work shows that the analyses which have led to these experimental conclusions may be too simplified. Oxygen chemisorption changes the surface chemistry in a complicated manner. We find that adsorbing oxygen on either site may redistribute charge on both species of surface atoms and in some cases shifts both anion- and cation-derived features in the valence band and in the bottom of the conduction band. While this theoretical observation would indicate that neither experiment has provided conclusive evidence about this question, we find that the magnitude of the observed As $3d$ core shift tends to indicate that the surface arsenic atoms are primarily involved in the oxidation process. Moreover, our calculation shows that specific features in the valence band indicate quite clearly which surface species is bonded to the oxygen and also which molecular species of oxygen (i.e., O or O_2) is chemisorbed.

In this Letter we will discuss these two most fundamental aspects of our calculations for oxygen adsorbed on the GaAs(110) surface. Namely, we will present a criterion for distinguishing between the adsorption of atomic and molecular oxygen on either the surface anions or the surface

cations. A lengthier discussion of our methods and results will be reserved for a later publication. Here, we will briefly describe our model and the formalism which makes the calculation of a large number of oxidation configurations feasible. Then we will present a single model which is compatible with both the ELS and photoemission experiments. We will then examine the theoretical UPS (ultraviolet photoelectron spectroscopy) spectra from four representative oxidation models which provide some insight into the surface chemistry of oxygen on GaAs(110).

To perform these calculations we have generalized the effective-field or transfer-matrix technique to a real surface, using a realistic empirical tight-binding model. The details of this extension are discussed elsewhere.⁵ Here we merely emphasize that the transfer-matrix technique provides an exact and convenient mathematical representation for the interaction of a surface atom with a crystalline array of atoms extending infinitely deep into the bulk. The empirical model for GaAs is obtained by fitting critical points in the bulk photoemission spectrum.^{5,6} We have shown that this particular model yields results for the ideal and relaxed surfaces which are in good agreement with self-consistent pseudopotential results.⁵ We have constructed empirical tight-binding parameters which model the As-O, Ga-O, and O-O bonds. These parameters are fitted to photoemission data for AsO_4^{3-} ,⁷ a Roothan-Hartree-Fock calculation for GaO_4^{5-} ,⁸ and photoemission from O_2 ,⁹ respectively.

One further novel feature of this work is worthy of note. The chemisorption of oxygen on a semiconducting surface falls in an intermediate theoretical regime to which neither one-electron band theory nor a formalism which treats atomiclike correlations is strictly applicable alone. We find in chemisorbed oxygen, for instance, both valence states which are bandlike (i.e., strongly

dispersed and mixed with the semiconductor states) and states which are atomiclike (i.e., nearly dispersionless, with very weak mixing from the substrate). We have found that we can sensibly deal with the charge transfer in this problem if we restrict the population of the latter atomiclike adsorbate states to equal the population of the same states in the free atom or molecule, and treat the bandlike states in the usual one-electron band theory. This is conveniently accomplished by projecting out states which are weakly mixed with the substrate.

We now turn to some of the results of our calculation for oxygen adsorbed on the GaAs(110) surface layer. In the lower panel of Fig. 1, we show the density of states for the relaxed GaAs(110) surface. This particular relaxation involves a buckling of the surface where the cations move inwards and the anions are pushed outwards.⁵ The significant result is that the dangling-bond surface states are pushed out of the band gap^{5,6} and are evident in the shoulder near -1 eV and the two-peak structure about 2 eV. In the upper panel we have adsorbed molecular oxygen on the relaxed As atom and have projected the density of states onto the substrate surface layer. The geometry is chosen so that oxygen bonds along the $[111]$ direction, perpendicular to the O-O axis, and the azimuthal angle is chosen so that the O₂ molecule points out of the (110) plane roughly perpendicular to the zigzag chains in the (110)

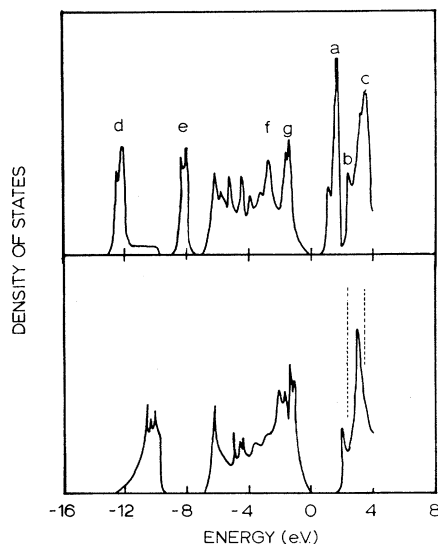


FIG. 1. Lower panel, the local density of states (LDOS) of the clean relaxed surface layer. Upper panel, the LDOS on this layer when O₂ is adsorbed on the arsenic surface.

plane. We draw attention to the labeled features in the figure. Peak *a* is unfilled and is primarily localized on the arsenic surface. About 20% of the strength of this state is due to the surface gallium *p* orbitals (in the bonding plane) and another 30% is projected onto the adsorbed oxygen (not shown in the figure). This peak corresponds to the antibonding As-O state induced by chemisorption.

Secondly, we see two peaks *b* and *c* which correspond to the two peaks found above the conduction-band edge in the relaxed clean structure. These are localized primarily on the unbonded gallium *p* orbital, with state *c* containing a slightly larger *s* admixture than *b*. Note, however, that these states have been shifted when oxygen is adsorbed. Both peaks shift to higher energy by about 0.6 eV as shown by the dotted lines. We emphasize that these orbitals have not been saturated in the chemisorbed configuration; the O₂ is adsorbed on an arsenic site.

Thirdly we focus attention on the feature labeled *d* in the lowest valence band near -12 eV. The lowest valence band is derived strongly from the arsenic *s* states and this peak is due to the strong bonding between the arsenic surface *s* state and the oxygen bonding *p* orbital. The observed shift of the strength of this band from -10 eV for the clean surface to -12 eV for the oxidized surface is the *signature* of chemisorption to the surface arsenic atoms.

Fourthly, we briefly call attention to the states labeled *e*, *f*, and *g*. State *e* represents the As-O bonding state, and most of its strength is actually localized on the oxygen bonding *p* orbital (not shown in the figure). States *f* and *g* indicate strained backbonds directed from the arsenic towards the bulk, *f*, and towards nearest neighbors in the surface plane, *g*.

In addition, we have calculated the charge transfer for this configuration. For an intrinsic substrate we find that the charge localized on the surface cation is preserved with oxidation while the surface anion loses $0.63e^-$ to the adsorbed oxygen. Chemisorption to the surface cations generally requires a transfer of 0.2 electrons from the surface arsenic and gallium atoms. Hence, the observed 3-eV chemical shift in the arsenic $3d$ state with oxidation² is consistent with the large charge transfer characteristic of bonding to the surface anion.

The particular oxidation model of Fig. 1 provides an example in which we have a direct bond to the surface arsenic, with a nonnegligible ef-

fect on the cation dangling-bond state. Clearly this shows that the surface chemistry is sufficiently complex that the surface anion and cation dangling bonds cannot be properly considered as uncoupled. Moreover, this shows that *both* chemical-shift measurements and ELS results are consistent with chemisorption to the surface *anions*.

Finally, to examine more carefully the location and conformational state of oxygen on the GaAs (110) surface at low coverages, we present in Fig. 2 a representative cross section of theoretical UPS (100 eV) spectra for several configurations. The spectra are matrix-element-weighted densities of filled states which include the effects of the finite escape lengths of the photoemitted electrons, and assume a plane-wave final state. We note that this latter assumption spuriously enhances the effective oscillator strength of the lowest 5 eV of the spectrum but the trends, from spectrum to spectrum, are important and noteworthy. All the spectra correspond to the oxidation of an unrelaxed surface, except for the dashed curve which is calculated for the relaxed surface previously discussed. In the interest of brevity we will discuss only the dominant features of the spectra. In the two spectra corresponding to adsorbed *atomic* oxygen, we see large peaks near -6 eV. This peak arises from the oxygen nonbonding states and is the signature of chemisorbed atomic oxygen. When O₂ is adsorbed, we

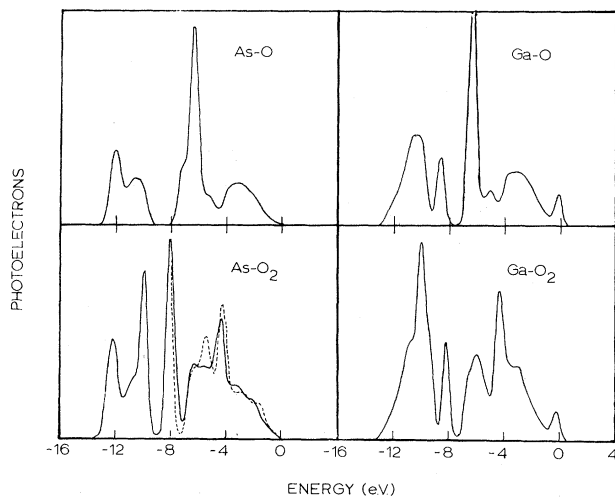


FIG. 2. Theoretical UPS (100 eV) valence-band spectra for four oxidation configurations on unrelaxed GaAs (110) surfaces (solid curves) and a relaxed surface (dashed curves). The chosen matrix elements tend to enhance spuriously the low-energy region of these spectra. Nonetheless, the valence-band structure specific to each configuration is apparent.

see that the oxygen-oxygen interactions strongly split this state into Σ -like and Π -like states at -10, -8, and -4 eV. In fact, the experimental observation¹⁰ shown in Fig. 3 (UPS at 21 eV) of states growing near these energies during oxidation is strong evidence for the chemisorption of molecular oxygen on the surface. Also, we call attention to the lowest valence band between -12 and -10 eV. When oxygen chemisorbs to arsenic we see a shift of states to the low-energy edge of this band. When oxygen chemisorbs to the gallium this band retains the shape characteristic of the clean surface. We feel that a high-resolution study of the effect of oxidation on this region of the valence band will provide very important information about the identity of the bonding sites during chemisorption. In fact, the UPS spectrum in Fig. 3 shows a shift of states to -13 eV with oxidation, further indicating chemisorption on the surface arsenic atoms. The other slight changes from spectrum to spectrum give detailed information about the variations in the bonding in each configuration.

In summary, we have shown that oxygen chemisorption significantly alters the surface chemistry of the GaAs(110) surface. Chemical-shift studies and ELS measurements which have previously led to different conclusions about the principal adsorption sites on this surface can now be reconciled, and the details of the valence-band structure provide very strong evidence about bonding sites on this surface. In addition, we feel that our calculations for the chemisorbed GaAs surfaces represent an important advance

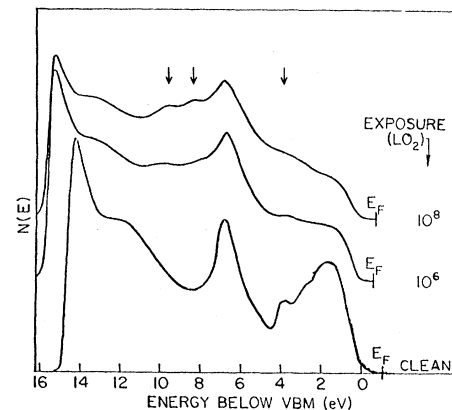


FIG. 3. Experimental UPS (21 eV) valence-band spectra from Ref. 10 for GaAs(110) with various exposures to oxygen. With increasing exposure, peaks are found to develop near 4, 8, 10, and 13 eV below the valence-band maximum.

in the understanding of adsorption on semiconducting surfaces in general. We plan to discuss our methods and findings at length in a forthcoming publication.

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¹R. Dorn, H. Luth, and G. J. Russell, Phys. Rev. B **10**, 5049 (1974).

²P. Pianetta, I. Lindau, C. Garner, and W. E. Spicer, Phys. Rev. Lett. **35**, 1356 (1975).

³W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, J. Vac. Sci. Technol. **13**, 780 (1976).

⁴R. Ludeke, Solid State Commun. **21**, 815 (1977).

⁵E. J. Mele and J. D. Joannopoulos Phys. Rev. B (to be published); D. J. Chadi, Phys. Rev. B **16**, 3572 (1977).

⁶J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **14**, 4724 (1976).

⁷V. I. Nefedov, Y. A. Buslaev, N. P. Sergushin, Y. V. Kokunov, V. V. Kovalev, and L. Bayer, J. Electron Spectrosc. **6**, 221 (1975).

⁸B. F. Shegolev and M. E. Dyatkina, Zh. Strukt. Khim. **15**, 325 (1974).

⁹D. W. Turner, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970).

¹⁰P. Pianetta, I. Lindau, P. E. Gregory, C. M. Garner, and W. E. Spicer, to be published.

Experimental Evidence for the $X_{2\downarrow}$ Hole Pocket in the Fermi Surface of Ni from Magnetic Crystalline Anisotropy

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The anomalous behavior of the magnetic crystalline anisotropy in Ni metal at 4 K can be interpreted by the passage of the top of the $X_{2\downarrow}$ sub-band through the Fermi energy, when the magnetization direction is changed. The number of holes in the corresponding hole pocket varies between 0 and 1.4×10^{-5} holes/atom. Fair agreement between theory and measurements is obtained.

It is known^{1,2} that the magnetic crystalline anisotropy in Ni metal at low temperature cannot be described with only a few anisotropy constants, as is the case with most other magnetic metals and alloys. Aubert *et al.*² recently published very accurate measurements of the torque due to this anisotropy as a function of the crystallographic direction of the magnetization, which show significant Fourier components at least up to degree 34.

On analyzing these results we observed a small anomaly in the torque as a function of the magnetization direction if this direction has an angle of about 18° with the nearest cubical axis. This anomaly has been observed earlier by Franse,¹ who tentatively associated it with the movement of the top of a band through the Fermi level. Furthermore, we found that the Fourier components of degree 12 and higher can be interpreted as due to an anomalous contribution, which is zero unless the magnetization direction lies within 18° of the nearest cubical axis. The measured

torque can be decomposed into a regular torque, which is described with four conventional anisotropy constants, plus a much smaller anomalous contribution, as shown in Fig. 1.

We suggest that the latter contribution is due to a movement through the Fermi-energy level of the top of the $X_{2\downarrow}$ band. Band calculations position this band near the Fermi level; an old semi-empirical calculation by Zornberg³ places it at the Fermi energy within the attained accuracy of 0.002 Ry (30 meV). In more recent self-consistent calculations, Wang and Callaway⁴ find the top of the $X_{2\downarrow}$ band about 0.03 Ry (0.4 eV) above the Fermi level. The partial inclusion of electron correlations reduces⁴ this difference to 0.002 Ry; these authors suggest that, with another correction, the top of this band may be pushed down below the Fermi energy.

Because of spin-orbit coupling, all energy bands shift slightly if the magnetization direction is varied; Wang and Callaway⁵ computed that the top of the $X_{2\downarrow}$ band at the point in reciprocal