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Theory of oxygen chemisorption on GaAs(110)[†]

Eugene J. Mele and J. D. Joannopoulos
Department of Physics, Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Using a localized-orbital representation, we have calculated the electronic structure of oxygen chemisorbed on the GaAs (110) surface in various bonding configurations. Two principal results which emerge are (i) that the effects of chemisorption on the surface species are strongly affected by allowing the surface to relax, and (ii) that molecularlike correlations persist and are important for localized nonbonding orbitals in the adsorbate. Our results provide detailed interpretations of x-ray photoemission spectroscopy, ultraviolet photoemission spectroscopy, and electron-loss spectroscopy studies of the oxidation of GaAs(110), and a comparison with *all* the experimental data strongly indicates that in the initial stages of oxidation O_2 chemisorbs principally on the surface As, with the surface maintaining its relaxed configuration.

I. INTRODUCTION

The development of a theoretical understanding of the chemisorption properties of semiconductor surfaces is a matter of practical importance and is currently being realized through the extension of several techniques previously used to study clean surfaces.[1-5] We have studied the oxidation of the nonpolar GaAs surface, using an effective-field technique discussed in detail elsewhere.[6] This study addresses several questions which pertain to the chemisorption properties of semiconductor surfaces in general, and several problems relating specifically to the nonpolar GaAs surface.

From a general point of view, we are interested in how the chemical reactivity of a bonded atom at a semiconducting surface may differ from the reactivity of the free atom. Similarly, we are interested in how this behavior may be altered by the crystal face involved, or by reconstructions or relaxations at the semiconductor surface. In addition, we must combine the language of a localized-molecular-orbital representation which in general may include correlation effects appropriate to free atoms and molecules and the one-electron band theory which we are accustomed to in discussing solids and solid surfaces.

Focusing specifically on the nonpolar GaAs surface, we are interested in which species is preferentially oxidized, whether chemisorption is dissociative and how the surface weakens in the first stage of the formation of thick oxide layers. We will also discuss the interpretation of spectroscopic investigations[7-10] of the oxidation of GaAs (110) which relate to this question.

The plan of this paper is as follows. In Sec. II, we will briefly present our results for the clean GaAs (110) surface in the ideal and relaxed (buckled 1×1) geometries. In Sec. III we will present our bonding models for the Ga–O, As–O, and O–O bonds. In Sec. IV we will look at the electronic structure of oxidized GaAs(110) in the unrelaxed geometry which illustrates several important features general to all the calculations. In Sec. V we present calculations for oxidized GaAs(110) in the relaxed geometries. In this section we find one chemisorption model consistent with both core shift photoemission studies[9] and electron-loss spectroscopy (ELS)[7] investigations of this system. In Sec. VI we will investigate the effect of various nonideal bonding geometries on the surface electronic spectrum, including geometries in which surface bonds are broken. In Sec. VII we relate this work to the available experimental data and we conclude with a summary in Sec. VIII.

II. CLEAN-SURFACE SPECTRA

All of the surface calculations to be discussed in this paper have been performed using an effective-field or transfer-matrix technique which we have discussed extensively elsewhere.[6] Briefly, given a Hamiltonian of finite range the effective field provides a convenient and exact mathematical representation for the interaction of a surface layer of atoms with a crystalline array of atoms extending infinitely deeply into the bulk. The Hamiltonian which we employ is an empirical tight-binding model[6,11] which treats four orbitals per atom, and parametrizes all the distinct interactions between any two nearest neighbors. The parameters are then chosen to fit the bulk-photoemission spectrum, and are not adjustable at any subsequent point in the calculations.

In Fig. 1(a) we present the density of states obtained using this model for the clean unrelaxed GaAs (110) surface. The energies are given relative to the valence-band maximum. These spectra have been discussed previously[6]; here we merely

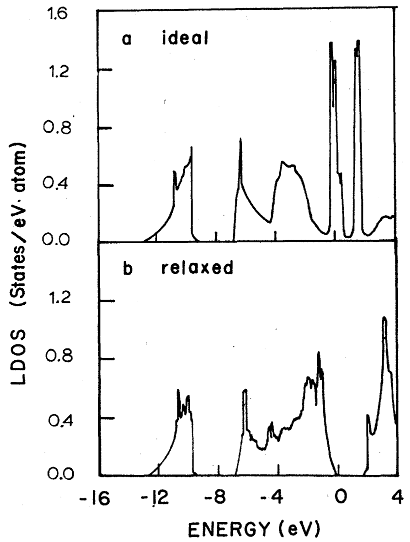

FIG. 1. Tight-binding surface densities of states for the clean unrelaxed or ideal surface (top panel) and for the relaxed surface (lower panel). In the lower spectrum there are no band-gap surface states. LDOS: local density of states.

call attention to the two prominent features in the band gap. The lower of these is filled and corresponds roughly to a dangling As hybrid. The upper feature is unfilled and corresponds to the dangling Ga bond at the surface.

However, both data from elastic low-energy-electron diffraction (ELEED)[12] experiments on this surface and arguments from the elemental chemistry of Ga and As indicate that the three fold coordinated surface Ga and As atoms do not retain this ideal geometry. Rather the surface buckles somewhat with the cations shifting into the surface plane, while the anion moves slightly out of the plane. The exact nature of this buckling as well as the role of subsurface distortion at the surface has been a subject of some recent controversy.[11,12] We have calculated the surface electronic structure which terminates in a surface layer where the cation has rotated into the plane of its three nearest neighbors keeping bond lengths fixed (the 34.8° rotational relaxation model). The results of this calculation are shown in Fig. 1(b). We see that the dangling-bond states have moved out of the gap, the lower As-derived band has merged with the valence band, the upper Ga-like band has moved into the conduction band. These trends are in good agreement with self-consistent pseudopotential calculations[13] for this structure.

However, this pseudopotential calculation[13] provided another very significant result. That is, the Ga-derived surface states which occur near the conduction-band minimum are *different* in character from the dangling cation states found in the gap in the ideal structure. These empty relaxed surface states have charge (virtual charge) localized behind the surface Ga. This has important consequences for the reactivity of the surface Ga with adsorbates in this geometry, as we will see.

Finally, we should note that detailed variations in the surface atomic geometries induce slight changes in the surface electronic spectra. (In fact, comparison of angle resolved UPS data with predictions from this sort of calculations can be used to help established surface geometries.[11]) Nonetheless, these effects are small compared to the effects of oxidation on the surface electronic structure that we will discuss, and our results for oxidation of the relaxed structure are applicable to all of the proposed "buckled" geometries.

III. CHEMISORPTION BOND MODELS

We wish to model the As–O, Ga–O, and O–O bonds which may occur at the surface when GaAs is oxidized in terms of the nearest-neighbor interactions of the localized orbitals on each species. To obtain information about the strengths of these interactions, we refer to experimental (photoemission) results when possible or to very accurate numerical calculations when experimental data are not available.

The interaction parameters for the As–O system are taken from photoemission studies of the AsO_4^{3-}

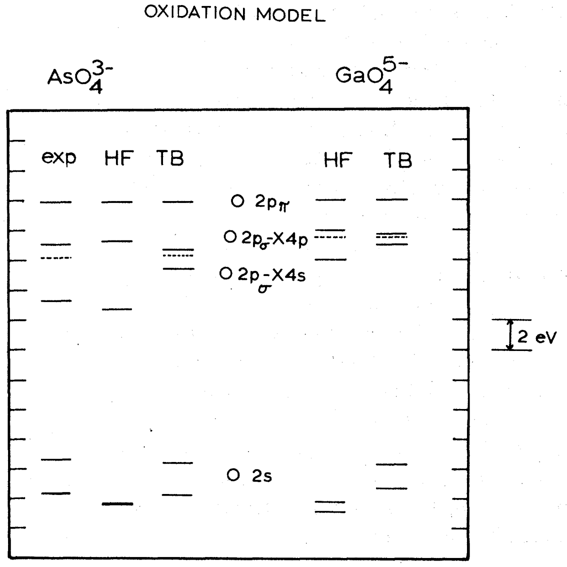

FIG. 2. Comparison of experimental and/or Hartree-Fock energy levels for AsO_4^3 and GaO_4^{5-} with the results from the tight-binding-bond model used in this paper. The central column characterizes the molecular states.

radical. The experimental results[14] are given schematically on the left-hand side of Fig. 2. The upper three lines are relevant for the (GaAs) valence-band calculations which we will discuss. These correspond to the nonbonding oxygen levels (O $2p_\pi$), and the primarily oxygenlike bonding levels (O $2p_\sigma$). The second column shows a Roothan–Hartree-Fock calculation[15] for this radical and the third column presents our tight-binding fit. The tight-binding model is chosen so that the mean O $2p_\sigma$ level (denoted by the dashed line) fits experiment. The error in the splitting of the two O-like levels is due to the absence of a second-nearest-neighbor O-O interaction in the model. The second-neighbor O-O interaction is not included since O-O second-neighbor pairs do not occur in the chemisorption configurations which we will study. In addition, the O-O separation in the AsO_4^{3-} radical is reasonably small, ~2.5 Å, while on the GaAs surface the distance from a chemisorbed oxygen to a second-neighbor substrate atom in the surface plane is large (~3.3 Å). This indicates that second-neighbor interactions in the model will provide insignificant changes in the electronic spectra. Finally, we would ideally extract such a bond model from a neutral molecule. However, the excess charge on this radical lies in nonbonding oxygen *p* orbitals which surround the complex, encasing it in an effective shell of charge which uniformly raises the potential of the molecule. Hence, we approximate the neutral molecule by a static shift of the ion radical levels.

Photoemission data from GaO_4 are unavailable to our knowledge, but a Hartree-Fock calculation[16] for GaO_4^{5-} (similar to that for AsO_4^{3-}) has been reported and was used in a similar way to obtain the Ga-O interaction parameters as shown on the right-hand side of Fig. 2.

Molecular photoelectron spectra for O_2 are available in the literature.[17] We have chosen the O-O interactions to reproduce the splittings at the levels corresponding to transitions from the $^3\Sigma_g$ neutral gound state to the $^2\Pi_g$, $^4\Pi_u$, and $^4\Sigma_g$ states of O_2^+. These final states correspond to photoemission of electrons from the antibonding π orbitals, bonding π orbitals, and bonding σ orbitals of O_2, respectively.

As for the interaction parameters at the clean surface, once these interactions are taken from molecular spectra they are fixed throughout the remainder of the calculation.

IV. OXIDATION OF THE IDEAL GaAs (110) SURFACE

In this section we will study, separately, the effects on the surface electronic spectra of the chemisorption of oxygen (O and O_2) on the surface As and Ga for GaAs crystal terminated on an ideal (110) plane. These spectra illustrate some important features which occur for all these chemisorption models and exhibit certain other characteristics which differ considerably from calculations on the relaxed surface.

A. O adsorption

In Fig. 3 we show local densities of states for the clean ideal GaAs (110) surface (middle panel) and for oxygen-exposed surfaces. The upper two traces are projections on to the GaAs surface layer and on the oxygen adsorbate for a configuration in which atomic oxygen is bonded to the surface arsenic. Similarly, the lower two panels are the same projections when oxygen is chemisorbed on the surface Ga. We call attention to the principal features of the spectra.

Firstly we see that most of the oxygen electrons do *not* participate in the chemisorption process. These form the prominent nonbonding oxygen peak

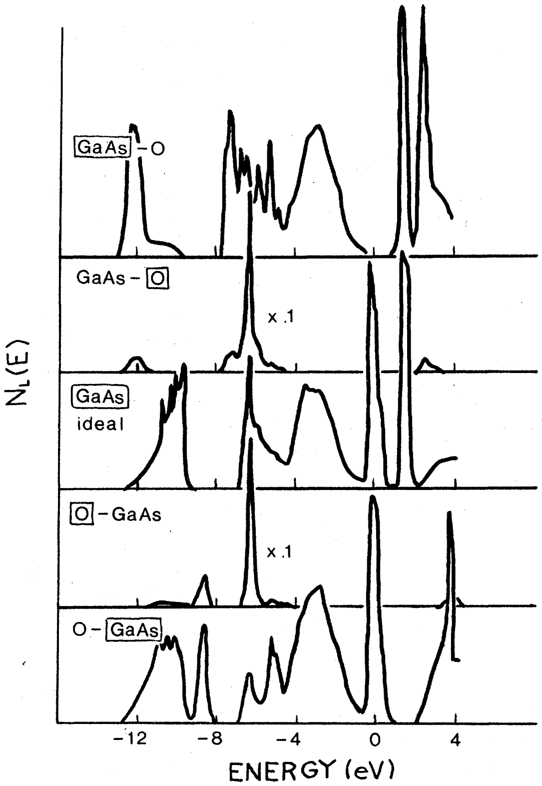

FIG. 3. Local densities of states when oxygen atoms are adsorbed on unrelaxed GaAs(110). The densities of states are projected onto the atoms enclosed in boxes. The middle panel corresponds to the clean unrelaxed surface layer. The upper two and lower two panels correspond to oxygen chemisorption on the surface As and surface Ga atoms, respectively.

at ~6 eV below the valence-band maximum, a feature evident in both spectra. These states are weakly mixed with the substrate, strongly localized on the chemisorbed oxygen, and, in fact, are more representative of localized atomic states than delocalized band states. This has important implications for the filling of these levels, which we will discuss later in this section.

We see two other interesting features when oxygen chemisorbs to the surface arsenics. First, the prominent dangling arsenic state has moved into the conduction band is found near 3 eV. This new state is an antibonding admixture of arsenic hybridlike states and the oxygen p orbital directed along the bond. Secondly, in the lowest valence band we see a shift of states from the lower edge of the heteropolar gap to higher binding energy. These new states near the bottom of the lowest valence band are a bonding admixture of s-like arsenic states and the oxygen bonding p orbital.

The situation is a bit different when oxygen bonds on the surface Ga. As expected, in the lowest panel we see that it is the dangling Ga-derived state which has been shifted into the conduction band. There is also a bonding oxygen-Ga state which has emerged from the central valence band and is found near −9 eV in the heteropolar gap.

Previously, we remarked that certain states which we obtain in these calculations are strongly localized on the chemisorbed oxygen and very weakly dispersed. This situation is shown dramatically in Fig. 4 where we have separately projected the total density of states for atomic oxygen chemisorbed on the surface Ga on to the nonbonding oxygen p orbitals, the oxygen bonding p orbitals, the GaAs surface layer, and the next GaAs layer into the bulk. Note that the nonbonding oxygen p levels are very narrow and strongly localized on the adsorbate. On the contrary, the oxygen bonding p states are more thoroughly mixed with the substrate and are found throughout the bands. While these latter states are sufficiently delocalized to be treated in the usual uncorrelated one-electron band theory, correlations are likely to be quite important in the former atomic-like states. We have found that we can sensibly deal with charge transfers in this problem if we restrict the population of the "localized states" to equal the population of the same states in the free atom or molecule. The excess states and electrons are then filled according to the usual one-electron band theory. In this particular example we assume that oxygen is incident on the GaAs surface with an unpaired electron in a p orbital directed along the Ga-O axis and three electrons reside in the remaining p orbitals. Thus we restrict the population of the states depicted in the top panel in Fig. 4 to be three electrons. This generally results in the apparent "presence" of empty one-electron states in the valence band. This existence of these states if justified as follows. These states are sufficiently localized that we must fill them with an integral number of electrons. The addition of one more full electron in such a level would result in an enormous Coulomb repulsion and move the level well into the conduction band. Thus the state is unfilled and stable below the valence-band maximum.

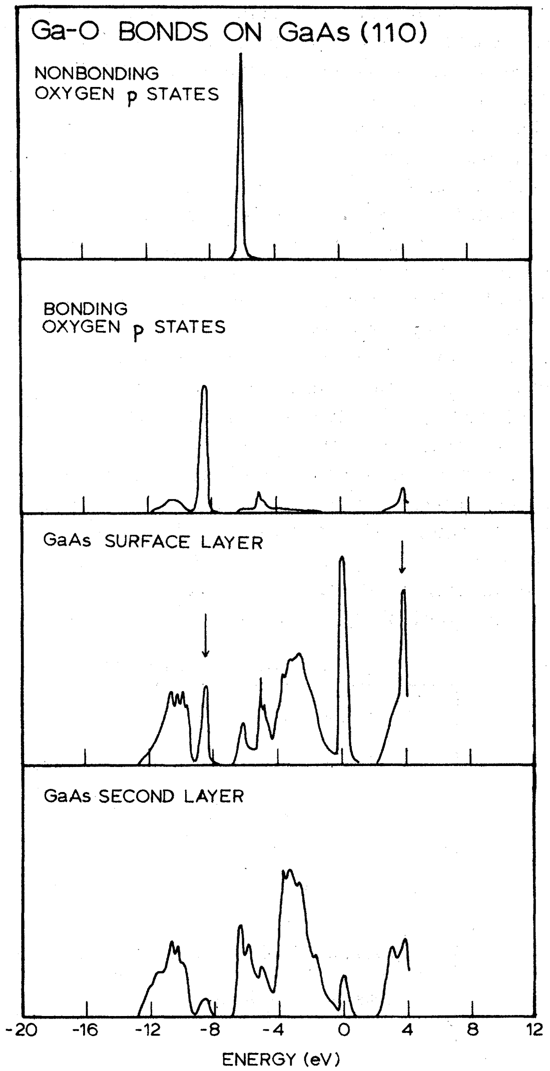

FIG. 4. Total density of states from the lower two panels of Fig. 3 is projected separately onto the oxygen nonbonding levels, the oxygen bonding levels, the GaAs surface layer, and the next layer in the bulk. Note the difference in character and localization of the nonbonding and bonding states in the first two panels. In the third panel arrows denote the principal oxygen-induced features in the spectrum.

Using these rules we have computed the charge transfers in these two configurations. We find first of all for the *clean* unrelaxed surface 5.2 electrons on the surface As and 2.8 on the surface Ga. When oxygen is chemisorbed on the As we find 4.25 e^- on the surface As, 3.10 e^- on the surface Ga, and 4.64 e^- on the chemisorbed oxygen p orbitals. The excess charge on the Ga is distributed partially into the dangling Ga-derived band. This result is understandable from a simple model of the surface in which two electrons initially occupy the dangling As orbital. After chemisorption one electron pairs off with an unpaired oxygen electron forming the chemisorption bond while the second electron finds the next available level. At the real surface the situation is somewhat more complicated and less than one full electron needs to be promoted into the previously empty dangling-bond orbitals. The entire surface, *including* the oxygen overlayer, is neutral.

Similarly, we have computed charge transfer for the configuration in which oxygen bonds to the surface Ga. Here we find that the surface As holds 4.86 e^-, the surface Ga 2.73 e^- and the chemisorbed oxygen 4.41 e^-. It is interesting that Ga–O bond is formed at the expense of some electrons from the surface As. This clearly must be so since the dangling Ga orbital is initially unfilled.

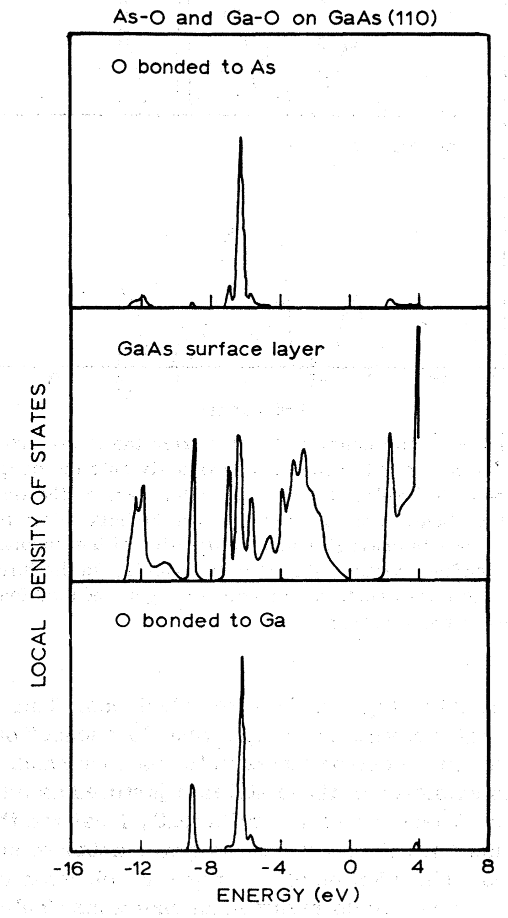

FIG. 5. Local densities of states when all dangling bonds on the unrelaxed GaAs (110) surface are saturated with atomic oxygen.

Finally, in Fig. 5 we show the density of states for a system in which *both* the surface As and Ga are bonded to atomic oxygen. Not surprisingly, we see a superposition of features found in both geometries of the Fig. 3 spectra. The shift of states to −12 eV, states at the upper edge of the heteropolar gap near −7 eV, and the peak at the conduction-band minimum near −2 eV are anion-oxide derived features. The bonding state in the gap near −9 eV and the conduction-band antibonding state near 4 eV are the signatures of the cation-oxygen bonds on the surface. Again, we see from the oxygen projections (in the upper and lower panels) that most of the oxygen states are nonbonding in character. The charge redistribution is similar to that which occurs for the spectra in Fig. 3. The surface As has ~4.2 e^-, the Ga ~2.8 e^-.

However, in this geometry the charge transfer to each oxygen is nearly equal (about 0.5 e^-). An interesting feature of this geometry is that we obtain a very slight charge excess after filling valence states, and this charge should reside in states near the conduction-band minimum. This would presumably leave the surface layer (including the adsorbed oxygen) slightly positively charged with respect to the bulk.

B. O_2 adsorption

We have performed a similar calculation for the nondissociative chemisorption of O_2 on the GaAs surface. The results are presented in Fig. 6. The convention is identical to that of Fig. 3; i.e., the central panel depicts the clean surface, the upper two panels refer to O_2 chemisorption on the surface As, and the lower panels depict bonding to the surface Ga. In these geometries the O-O axis is normal to the O-substrate bond direction. Again, we call attention to the principal features in the spectra.

As is evident from the projections on the oxygen orbitals, most of the electrons are not involved in the chemisorption process. In fact, much of the spectrum can be interpreted directly from the molecular-level assignments for O_2. Hence the narrow peak near −10 eV corresponds to a Σ_g orbital, the band near −8 eV to a Π_u bonding orbital, the peak near −4 eV to a Π_g orbital, and the states near −2 eV to the antibonding Σ_u level.

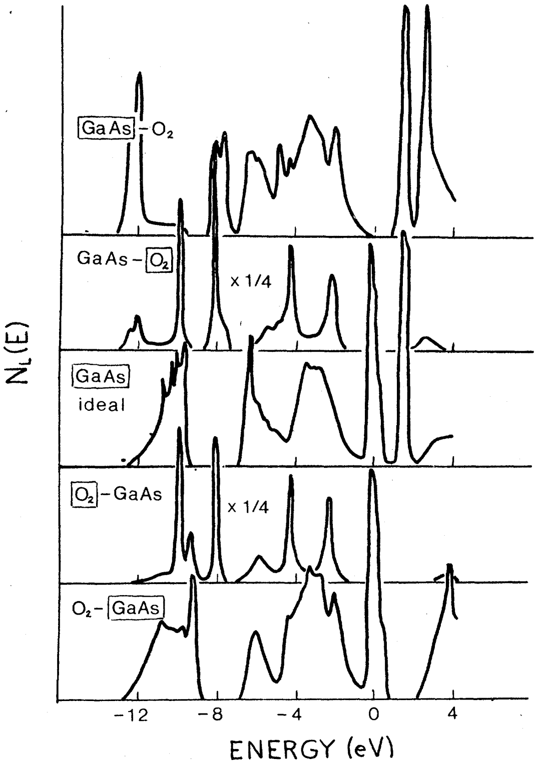

FIG. 6. Local densities of states when O_2 is chemisorbed on unrelaxed GaAs(110). The convention is the same as for Fig. 3.

This last level and part of the Π_u level are unfilled using the filling rules previously discussed. However, we note that it should be possible to *excite* electrons from any of the filled O_2-like states (including the 2*s* and 1*s* core states) into these levels since these processes would not leave the O_2 complex with an anomalous charge excess. Such partial-yield spectroscopy into states *below* the Fermi level would be an interesting test of the filling rules we have employed.

Aside from the presence of these new molecular-like nonbonding orbitals, the spectra show the same bonding trends as we saw for the chemisorption of atomic oxygen. When we bond to the surface As, the anion dangling-bond state slides into the conduction band and contributes to the prominent peak near 3 eV. For this configuration we also see the strength of the lowest valence band shifting to higher bonding energy as the As-*s*-like states bond with the incident oxygen. We also see a second state near −8 eV which is nearly degenerate with the $\Pi_u O_2$ state, but primarily projects onto the As–O_2 bond. (A similar state occurs for the As–O geometry, but is found slightly higher in energy at the edge of the heteropolar gap.) Using our filling rules we see that the suface As has 4.20 e^- and the surface Ga 3.34 e^- and the O_2 p orbitals hold 8.46 e^-. The chemisorption on the surface As involves a large charge transfer from the surface anion with charge transferring into oxygen *p* orbitals and, as for atomic oxygen, into the surface cation orbitals.

The chemisorption of O_2 on the surface cation shows characteristic bonding states similar to those observed for the chemisorption of atomic oxygen. The dangling-cation state moves into the conduction band near 4 eV and we see a bonding state near the upper edge of the lowest valence band. For this geometry, we find the surface anion with 4.74 e^-, the surface cation with 2.74 e^-, and the chemisorbed O_2 with 8.52 *p*-like electrons. This is quite interesting, since we see that chemisorption on the surface cation in this geometry requires *equal* charge transfers from the surface As and Ga. We directly attribute this behavior to the absence of charge in the dangling cation states for the clean surface.

V. OXIDATION OF THE RELAXED GaAs (110) SURFACE

In Sec. II we remarked that it is generally understood that the clean GaAs (110) surface exists in a relaxed, buckled geometry. It is therefore important to investigate the effect of oxygen chemisorption of the surface in this relaxed geometry. The relaxed surface exhibits some chemical properties which are distinctively uncharacteristic of the ideal surface.

A. O adsorption

In Fig. 7 we present densities of states for atomic oxygen chemisorbed separately on to the surface As (top two panels) and on the surface Ga (bottom two panels) as well as the electronic spectrum for the clean surface (middle panel). As for the unrelaxed geometry we see that the oxygen states are predominantly nonbonding in both geometries. When oxygen chemisorbs to the surface As we observe the states in the lowest As-like *s* band shifting to higher binding energy. For chemisorption to the surface Ga, we see the characteristic Ga–O bonding state in the heteropolar gap near −8.5 eV.

However, unlike the spectrum obtained in the unrelaxed geometry, when As-O bonds are formed at the surface, we obtain an antibonding state *in the gap* with threshold about 0.7 eV above the valence-band edge. A second dramatic and unexpected feature of this spectrum is that the two peak structures above the conduction-band minimum, which are primarily cation-derived states, have shifted by about ~0.6 eV when the nearest-neighbor *anion* is saturated. This is an interesting result which is due to several effects. First, as we noted in Sec. II, the virtual charge density associated with cation-derived surface states near the conduction-band minimum is not characteristic of the usual dangling bond. Rather, these states are directed "behind" the surface atoms and hence are probably quite sensitive to perturbations in the back bonds. The perturbations induced by the oxidation of a nearest-neighbor As can then be expected to alter not only As-derived levels but *also* effect such states on neighboring cations. Secondly, it is quite likely that the As–O antibonding state and this cation-derived surface state directly interact somewhat. By comparing the top and middle panels of Fig. 7 we see that the As–O antibonding state is nearly degenerate with the unperturbed cation-derived surface state. Any interaction between these states would tend to repel these levels, and contribute to the movement of the cation-derived features which we observe.

In this geometry we observe a charge transfer of 0.7 e^- from the surface As, 0.05 e^- from the surface Ga, and find 4.75 e^- in the oxygen p manifold. Interestingly, as for the unrelaxed surface, a slight charge excess exists after filling the valence bands. This charge is promoted to the As–O antibonding state in the gap, leaving the surface neutral overall. However, unlike the situation at the unrelaxed surface, this partially filled band-gap state will pin the Fermi level near *midgap* for both p and n-type substrates.

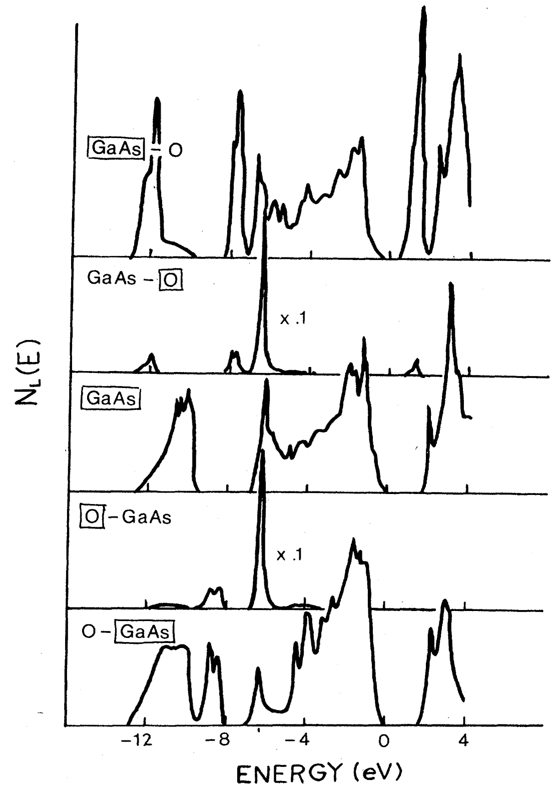

FIG. 7. Local densities of states when oxygen atoms are chemisorbed on the relaxed GaAs (110) surface. The convention is the same as for Fig. 3.

Next, we call attention to the bottom panel of Fig. 7 which depicts the density of states on the GaAs relaxed surface layer when oxygen tries to chemisorb to the surface Ga. An interesting and very surprising feature of the spectrum is that the surface states near the conduction-band minimum are nearly *insensitive* to the oxygen overlayer. Again, we attribute this effect to the back-bonding character of these states; they are shielded from the surface and hence do not readily interact with an adsorbate.

As we populate these states with electrons we find a further interesting feature of this geometry. For cation oxidation on the *unrelaxed* surface, we noted that the chemisorption bond was formed at the expense of electrons from the As dangling-bond state. As the As dangling-bond states occur in the gap this process left the overall surface neutral. In the relaxed geometry, however, the "dangling-bond" states occur at and *below* the valence-band edge. Thus, to satisfy the Ga–O bond on the relaxed surface the least strongly bound bulk-valence electrons would require to rise to the surface, leaving the surface layer charged. Within a self-consistent formulation this would result in a rather large band bending at the surface (~1 eV) which would be independent by the doping of the material. It is more reasonable physically that the formation of the Ga–O bond in this geometry would be an energetically unstable configuration, in which atoms could rearrange, react, and stabilize the Fermi level in some other molecular geometry.

B. O_2 adsorption

Finally, we have also studied the nondissociative chemisorption of O_2 on the relaxed surface. In Fig. 8 we present densities of states for O_2 chemisorbed separately on the surface As and Ga. The convention employed is identical to that in Figs. 3, 6, and 7. The oxygen projections are again dominated by the molecular like O_2 states at −10, −8, −4, and −2 eV. Again, the signature of chemisorption to the surface As is the movement of states to lower energy in the deepest valence band. For chemisorption of the surface Ga we again find a bonding state in the heteropolar gap near −9 eV. As for the adsorption of atomic oxygen on the relaxed surface, we find very interesting behavior in the band gap. When the surface As is saturated,

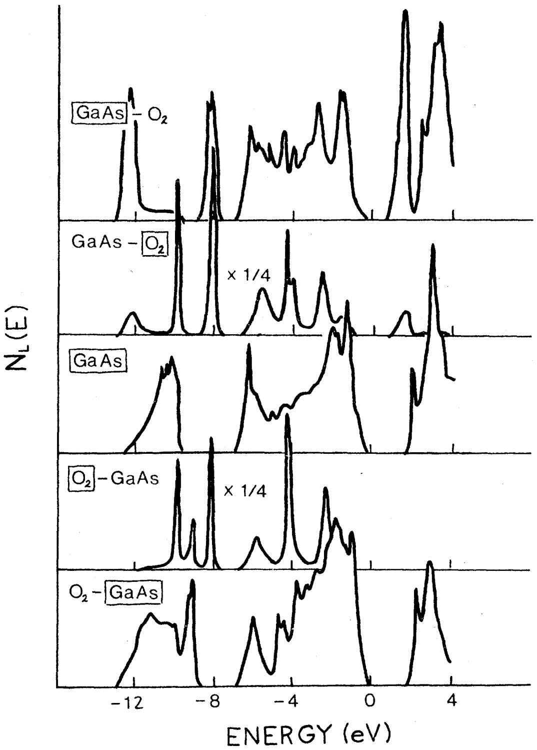

FIG. 8. Local densities of states when oxygen molecules are chemisorbed on the GaAs (110) surface. The convention is the same as that employed in Fig. 3.

we obtain an antibonding state in the gap, partially filled, with threshold near midgap. Above the conduction-band minimum we again observe that cation derived features are sensitive oxidation of the nearest-neighbor As as we have previously discussed. From the bottom panel of Fig. 8 it is again apparent that the rearward-directed Ga-derived surface states near the conduction-band minimum are insensitive to the O_2 overlayer.

In the spectra depicted in the upper two panels of Fig. 8 we obtain 4.36 e^- localized on the surface As, 3.01 e^- on the Ga, and 8.63 on the O_2 chemisorbed molecule. For the Ga-O_2 spectra we find the same sort of charge instability as discussed for the Ga-O complex on the relaxed surface.

VI. MISCELLANEOUS BONDING GEOMETRIES

In this section we will present the electronic spectra characteristic of several oxidation configurations on the surface. We will briefly discuss the electronic structures of (a) a geometry in which a peroxide bridge bonds to second-neighbor Ga and As atoms on the surface, (b) a configuration in which surface bonds are broken, and (c) geometries which vary the As–O–O bond angle for nondissociative chemisorption on the relaxed surface.

A. Bridging oxygen

Bridging geometries on the surface have been previously hypothesized.[7] We find first of all that bond-length constraints argue *against* the existence of atomic oxygen as a bridge between adjacent zig-zag chains in the (110) plane. Similarly, we cannot bridge nearest neighbors in the (110) plane with monatomic oxygen without inducing severe surface strains. Variations of these configurations may indeed occur in an advanced degenerate state of surface oxidation in which all order in the surface plane has been destroyed. However, for the purpose of this paper, we are principally interested in the initial stages of chemisorption on a crystalline substrate. With this

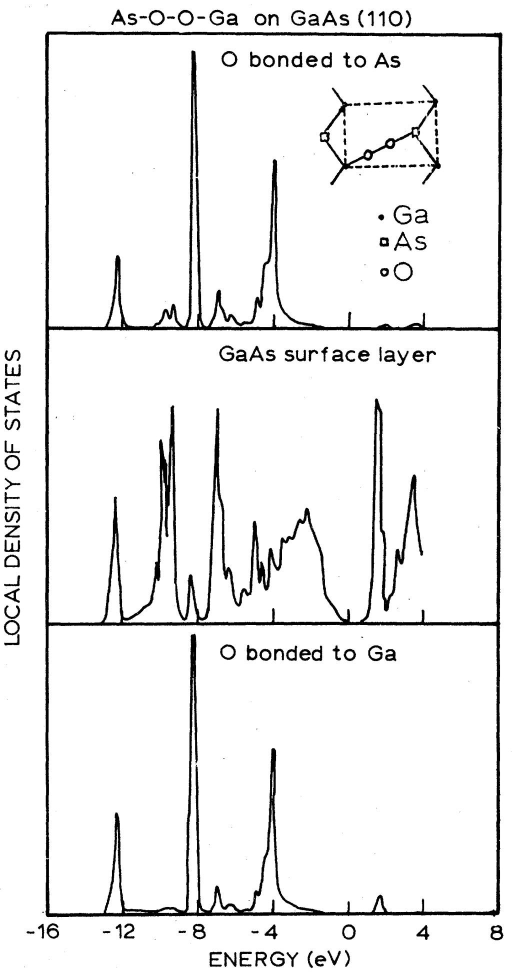

FIG. 9. Local densities of states when a peroxide bridges zig-zag chains on GaAs(110). The hypothetical geometry is given in the inset in the top panel. The As–O–O and Ga-O-O bond angles are ≈ 150°.

constraint there *does* exist a bridging configuration which is consistent with bond-length constraints on the surface. This is shown schematically in the inset on Fig. 9. The geometry involves an O_2 molecule bridging second-neighbor surface Ga and As atoms or neighboring zig-zag chains. With an O–O bond length of 1.4 Å and O-substrate bond length of 1.8 Å this requires O–O–Ga and O–O–As bond angles of roughly 150° on the unrelaxed surface.

We have calculated the electronic spectrum for O_2 bonded to the surface in this geometry. The local densities of states are given in Fig. 9. The top panel is the local density of states on the oxygen bonded to the As, the lowest panel is the projection onto the cation-bonded oxygen, and the central panel refers to the substrate surface layer. The most significant feature of this spectrum is that the oxygen-substrate bonds are evidently somewhat weaker. We see that the shift of states to higher binding energy in the lowest valence band is not nearly as dramatic as in the previous geometries, and the Ga–O bonding state is weak in the heteropolar gap. Similarly, the antibonding As–O states are not moved as far into the conduction band as observed in Fig. 5. The character of the oxygenlike spectra is also changed somewhat. For O_2 chemisorption on GaAs in the ideal and relaxed geometries in the O_2-like states displayed all the prominent electronic features of the free molecule. Here we can easily identify the remnants of the π bonding and antibonding levels at -8 and -4 eV, respectively, but the σ and σ^* levels are somewhat less apparent. This occurs in the bonding geometry since the oxygen p orbitals which lie along the O_2 axis also primarily compose the bonding orbitals to the substrate. These σ-like states are then strongly mixed with the substrate and lose their localized molecular character. The weakened bonds between the oxygen and the substrate also result from the competition for these orbitals between the O–O bond and the O-substrate bonds. In fact, the tendency for electrons to be removed from the O–O σ-bonding orbitals in this geometry makes the peroxy bridge susceptible to dissociation. In addition, this surface configuration would be negatively charged and is probably structurally unstable in the sense we have discussed with O–Ga bonds on the relaxed surface.

B. Broken surface bonds

Physical intuition suggests that oxygen chemisorption will eventually weaken the surface bonds as a precursor to the growth of a thicker oxide layer. In fact, we have previously discussed several bonding geometries in Sec. V which are likely to be structurally unstable. As an example of an oxidation-induced structural defect, we have artifically broken a surface bond between nearest-neighbors Ga and As while saturating the original dangling bonds with atomic oxygen. The electronic spectra for such a system are given in Fig. 10. In this configuration the reduced coordination number of the surface species reduces the competition from back bonds with the chemisorbed oxygen for the substrate electrons. This produces stronger, more localized chemisorption bonds. In the central panel, we see the As–O bonding state near -9 eV is similarly localized and quite strong. The two prominent features near the band gap correspond to the dangling broken bonds in the plane. The lower state near the valence-band edge is anion derived, the state near the

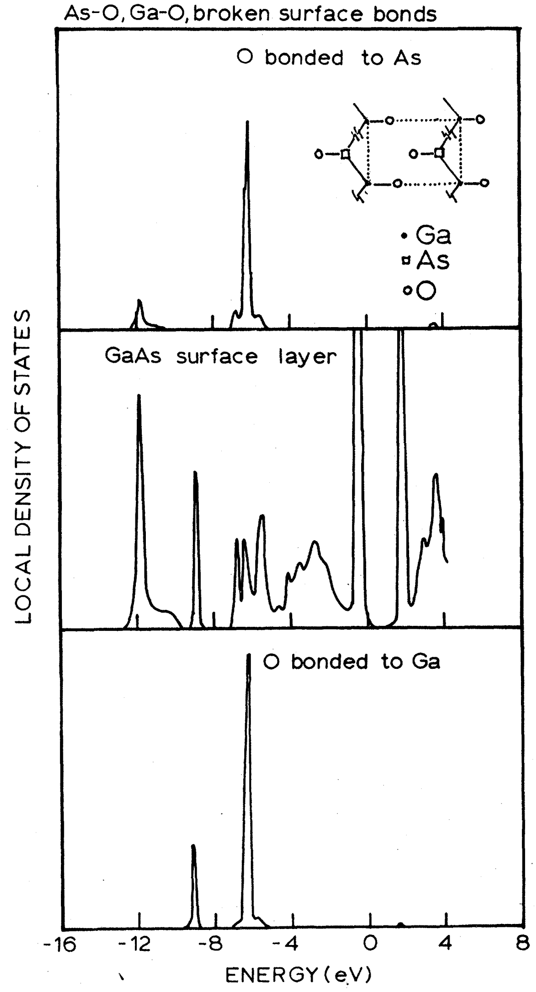

FIG. 10. Local densities of states when all the dangling bonds on the unrelaxed GaAs(110) are saturated, and a single bond to a nearest neighbor in the surface is broken as shown in the inset.

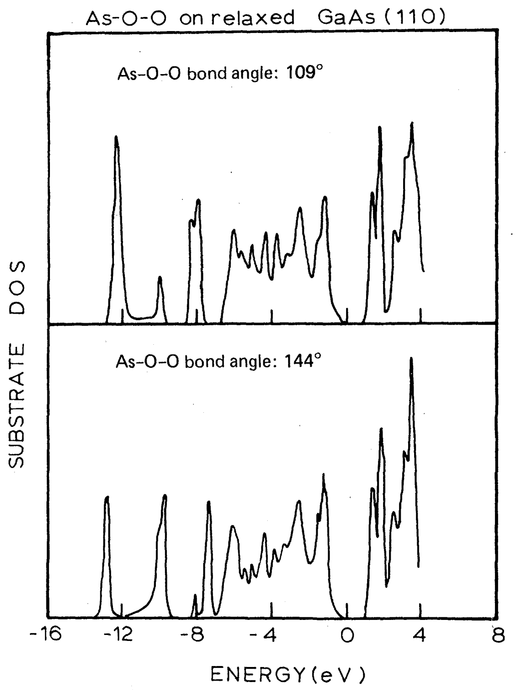

FIG. 11. Surface densities of states when As–O–O bonds are formed on the unrelaxed GaAs (110) surface, with an As–O–O bond angle different from the nominal 90° assumed in Figs. 5 and 8. The top trace has the oxygen bonding at a tetrahedral angle. The lower trace corresponds to O_2 pointing parallel to the surface normal.

conduction-band minimum is a Ga-like state. The prominent oxygen states near −6 eV are again primarily of nonbonding character.

C. Bond-angle variations

For O_2 chemisorption on the ideal and relaxed surfaces, we have assumed a simple geometry in which the O–O axis is directed at right angles to the O-substrate bond direction. We have investigated the effect of changing this bond angle on the electronic spectra. For O_2 chemisorbed on As in the relaxed geometry, the results are shown in Fig. 11. The top curve is the projection on the GaAs surface layer when the As–O–O bond angle is the tetrahedral angle, 109°; the lower curve represents the spectrum when the angle is 144° (with the O–O pointing along the surface normal). The effects of such large bond-angle variations are slight, but noticeable. In general, we see that increasing the bond angle slightly decreases the As–O bond strength; states in the lowest valence band are pushed back from −12 to −10 eV.

Again, we attribute this to the increased competition from the O–O bond for electrons in the As–O bond as these two axes become more parallel. The interesting features in the band gap change very little with this bond angle. The general insensitivity of the bonding states to this angle is noteworthy since it implies that the As–O–O bond angle in this system will be principally determined by electrostatic considerations, i.e., repulsion or attraction of the free end of the peroxy radical with the surface.

VII. EXPERIMENTAL DATA

There have been numerous experimental studies of various properties of oxygen chemisorbed on both polar and nonpolar GaAs surfaces.[7,9,18-21] Recently there has been some controversy[8-10] over the interpretation of several experiments which have addressed the question of which site on the nonpolar GaAs surface is the preferred bonding target. The notion that a preferred bonding site exists on this surface seems to be rooted in the observation by early workers that saturation coverage appears to occur for exposures equivalent to half-monolayer coverage.[18] Our theoretical results relate directly to experimental data from x-ray photoelectron spectroscopy (XPS)[9] core-level studies, ultraviolet photoemission spectroscopy (UPS) valence-band studies,[21] and electron ELS investigations[8,19] of empty localized surface states.

Core-level photoelectron spectroscopy[9] has shown quite clearly that with increasing oxygen exposure the As $3d$ core level shows a larger chemical shift (~2.9 eV) while the Ga $3d$ core level remains unperturbed. This has been interpreted as evidence of the involvement of only As atoms in the early states of oxidation on the surface. Our calculations tend to support this conclusion. First, we find that for all configurations in which only the anions are oxidized the As loses 0.6–0.8 e^-, with the charge generally redistributed among both the oxygen- and cation-derived substrate orbitals. This is a large charge transfer which could reasonably account for the 2.9 eV as $3d$ core shift. Note that this is a larger charge transfer per oxide bond than occurs in As_2O_3 for instance,[22] indicating that it is difficult to successfully interpret the chemical shifts at the oxidized surface by analogy with molecular chemical shifts. Second, it has been questioned whether the absence of a core shift of the Ga $3d$ state indicates that it is not an oxidized species.[7,8] We have found that for all stable configurations in which Ga–O bonds are formed at the surface, there is a sizable charge transfer (~0.25 e^-) from the Ga and in fact there is some charge transfer (0.15 e^-–0.26 e^-) from the As as well. A charge discrepancy of this magnitude is presumed to exist between elemental Ga and Ga in bulk GaAs, resulting in a 1.1-eV core shift.[22] Moreover, in view of the large core shift of the similar As 3d core state induced by a comparable charge transfer, we certainly expect an observable (i.e., ~0.3–0.5 eV) chemical shift of the Ga 3d state if the cation is an oxidized species. In addition, if Ga is oxidized, we should also expect a second core shift on the neighboring As 3d state in excess of 0.6 eV since Ga–O bonds are formed at the expense of some surface-anion charge. Neither a chemical shift of the Ga 3d core state *nor* a second chemically shifted peak on the As 3d core state are observed, arguing against the presence of oxidized Ga on the surface.

In conflict with these core-level spectroscopy results, electron-energy-loss spectroscopy results which probe transitions from the Ga-3d-state core to empty cation-derived states near the conduction-band edge on the (110) surface have shown these states shifting in energy uniformly with oxygen exposure.[7] Similar results have been reported for the Ga-rich polar (100) and (111) surfaces.[19] In these latter cases, this observation is quite certainly evidence of the formation of Ga–O bonds at the surface. Note that these crystal planes contain partially filled dangling-cation orbitals which could hardly be stopped from reacting with oxygen. However at the (110) surface the situation is quite different; the unsaturated Ga orbitals are empty and the virtual charge in these states is not of a dangling-bond character. Indeed, our calculations have shown that these states are more sensitive to oxide formation on the surface *anions*. Hence, the ELS observation of the states moving with oxygen exposure could well be further evidence of chemisorption on the surface As atoms. The situation is further confused by the surface exciton which decreases the apparent energy of these states, a shift which may well be modified after the surface is exposed to oxygen.

Note that the results of Sec. V show that the x-ray core photoelectron spectroscopy results and the ELS data are not contradictory, and may in fact be supportive. For the configuration in the upper panel of Fig. 8 we assume chemisorption of O_2 to the only As on the relaxed surface, calculate a large charge transfer from the surface As (~0.63 e^-), almost no charge transfer from the surface Ga (~0.01 e^-), and observe movement of cation-derived surface states above the conduction band. This system also displays empty states near midgap, in agreement with observed Fermi-level position for oxidized n-type samples.[21]

Finally, with the aid of recent UPS data[21] we wish to address the question of whether oxygen chemisorbs as O or O_2 on GaAs. From the oxygen projections of Figs. 3, 5, 7, and 8 we see that when O is present on the surface, a strong single state near −6 eV is evident in the valence band. These are of course the nonbonding oxygen p electrons. When O_2 occurs on the surface, the strong O-O interaction splits this state into Σ-like and Π-like states at −10, −8, and −4 eV. UPS data (Fig. 12) taken with a photon energy of 21 eV show peaks at these energies growing uniformly with oxygen exposure. This is strong evidence for the chemisorption of O_2 on the surface. Finally, in these experimental spectra we can discern the strength of the lowest valence band shifting from −10 to −13 eV. Following the results of Secs. IV and V this provides further evidence for chemisorption to the surface As atoms.

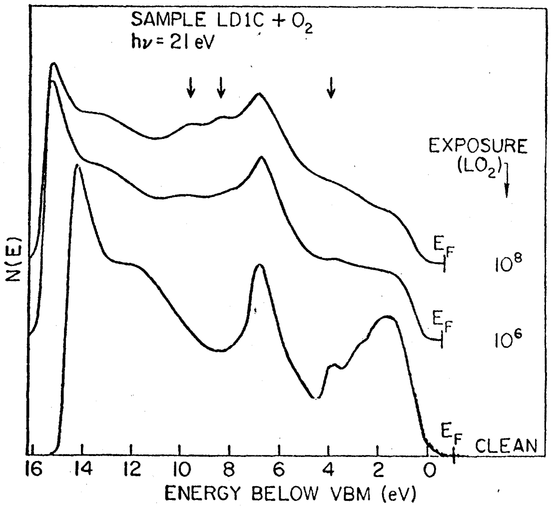

FIG. 12. Experimental 21-eV UPS spectra from Ref. 21 for clean and oxidized GaAs (110) surfaces. The exposures are given in the right-hand side of the figure. VBM: Valence-band maximum.

VIII. SUMMARY

This study of oxygen chemisorption on GaAs (110) yields several results which relate generally to chemisorption semiconductors, and other results which specifically relate to phenomena at GaAs(110).

In general, we see that the presence of a crystal surface can modify considerably the chemical reactivity of the individual constituent elements. This follows from the fact that the solid is a cooperatively bonded entity. In addition, the structure of a particular crystal face can be quite important in exposing or shielding localized surface states, a factor which can seriously affect the reactivity of these states at the surface. Finally, we see that correlations must be introduced in some manner into the localized adsorbate states which generally arise in these problems. For these systems, it is clear that not all the states which are calculated in the usual one-electron theory are adequately represented by one-electron band theory.

For GaAs(110) we see that relaxation significantly alters the reactivity of the surface Ga atoms. In addition, we find the surface chemistry to be sufficiently complex that the surface anions and cations are not properly treated as uncoupled. Oxidation of either species generally rearranges charge on *both* species, and can generally redistribute the character of valence states in a complicated manner. Further, we claim that the data from XPS, ELS, and UPS studies of the oxidation of GaAs can be understood from a single model in which O_2 bonds to the surface As in its relaxed geometry. We find core-level spectroscopy and electron-energy-loss spectroscopy not to be in conflict, but to be mutually supportive of this model.

Finally, it would be quite interesting to extend such calculations into the regime where a thicker oxide layer is formed, providing information about the electron structure and the chemical composition of real oxides on GaAs surfaces.

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*Present address: Xerox Webster Resource Center, Webster, N. Y. 14580.

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