Electronic Structure of the Oxygen Overlayer on Al(100)

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We present detailed electronic structure, total– and orbital–density-of-states information for an ordered overlayer of oxygen on Al(100). Our calculations show that O($2p$) levels are split upon chemisorption. We attribute the oxygen-related structure reported in photoemission experiments to O($2p_\sigma$) levels broadened by band-structure and crystal-field effects. The O($2p_z$) levels are predicted to disperse significantly due to hybridization with the substrate and may be observable in angularly resolved photoemission experiments.

Recently, photoemission data for oxygen chemisorbed on aluminum have been reported by various workers[1-5] as reproduced in Fig. 1(a). A common gross feature of all these experiments is that a broad resonance level due to oxygen appears at about 7 eV below E_F. At the higher coverages (i.e., 5–100 L; 1 Langmuir = 10^{-6} Torr sec), the spectra[2-4] shows a pronounced shoulder on the resonance 2.6 eV below the main peak and the width of the resonance increases. In this Letter we investigate the electronic structure of an overlayer of oxygen chemisorbed on Al(100) surface. Our calculations show that the O($2p$) levels split upon chemisorption. Specifically it is found that (i) the broad oxygen resonance at about −7 eV is derived primarily from the O($2p_\sigma$) (i.e., $2p_x$, $2p_y$) levels; (ii) the broadening of this peak arises from important *band-structure effects* associated with the monolayer in the crystal field; (iii) the O($2p_z$) orbitals are distributed over about 6-eV energy range as a result of hybridization with the substrate. These are predicted to lie at lower binding energies than O($2p_\sigma$) levels but presumably have not been detected in angle-averaged photoemission experiments.[1-5] These results are of great importance in understanding the nature of chemisorption of oxygen and the oxidation of metal surfaces.

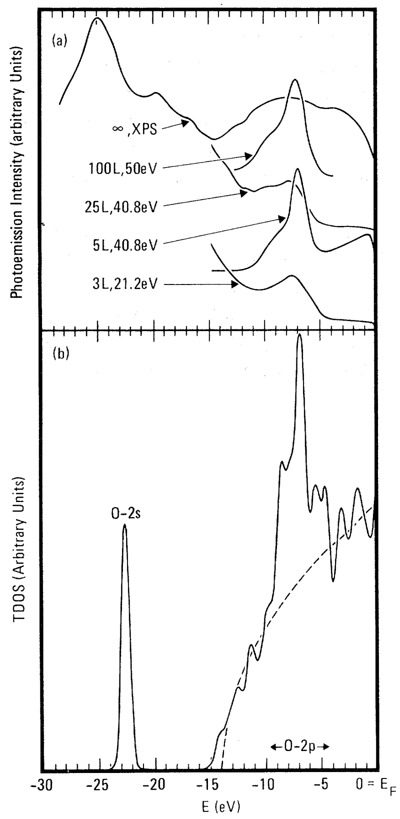

FIG. 1. (a) Photoemission spectra for Al at various oxygen exposures (given in Langmuirs) and incident photon energies (reproduced from Refs. 1–5). The curve labeled "∞" is for oxidized aluminum. (b) Calculated total density of state (TDOS) for Al at a monolayer oxygen coverage. The dashed line gives the free-electron density of states.

To understand the origin, width, and location of the observed oxygen resonance at −7 eV, we proceed systematically in three steps. First, we calculate the bandwidth associated with the oxygen overlayer itself in the absence of any substrate. Next, we "immerse" the overlayer in the substrate or crystal potential and recalculate the electronic structure. We are able to show that this provides much insight into the adsorbate-induced structure. Finally, we investigate the electronic structure of oxygen in the presence of eight layers of substrate atoms.

The chemisorption of oxygen on aluminum has recently been investigated using an atom-jellium approach[6] and cluster models.[7,8] We modeled the chemisorption by an ordered (1×1) oxygen overlayer and eight layers of aluminum substrate in a slab configuration in a manner discussed earlier.[9,10] Oxygen was placed in every central fourfold site of the first surface plane (x-y) of Al in a configuration appropriate to Al(100) surface. For this geometry, nearest-neighbor Al-O distance is 3.8 a.u., and d(O-O) = 5.4 a.u. The oxygen-incorporation model is consistent with the observation[1] of negligible change in work function. This model has also been established by cluster-model investigations[8] and generalized atom-jellium studies.[1,6] Our calculations were performed non–self-consistently within the framework of the extended tight-binding (ETB) method[11] using the Hartree-Fock-Slater ($\alpha = 1.0$) approximation for the potential. Even though our results are non–self-consistent, it is known[12] that a judicious choice of α can lead to results which are "nearly self-consistent." Judging from the calculated position of the O(2s) peak (see below), we concluded that a choice of $\alpha = 1.0$ is appropriate for this oxygen-aluminum system. Thus, incorporation of "true" self-consistency might change the bandwidth somewhat, but is not expected to alter our principal conclusions. A detailed discussion of our calculations along with the description for potential and Gaussian basis sets will be presented elsewhere.

The chemisorption model being investigated here has the advantage of a complete two-dimensional periodicity. Unlike the case for a small cluster model[7] we include distant neighbors (typically fifth) direct and indirect (through substrate) interactions among adatoms. Our model explicitly takes into account the atomic nature of the substrate in contrast to the atom-jellium approach.[6] Finally, since we treat up to eight layers of the substrate in the third dimension, the possibility of any spurious edge effects on the adatom levels is minimized. In Fig. 1(b) we have depicted the calculated total density of states for our model system. The dashed line gives the free-electron density of states and the O(2p) resonance appears on top of this free-electron–like background. It is noted that the relative oxygen and aluminum contributions depend on the thickness of the slab. The calculated position of the O(2s) peak at – 23 eV is to be compared with the O(2s) peak in the x-ray photoemission experiments[5] observed at – 24 eV [curve ∞ in Fig. 1(a)].

So far we have only discussed the spectral-peak positions. To understand the nature of interaction between the substrate and overlayer, we further performed a band calculation for the oxygen monolayer with a lattice constant corresponding to (1×1) structure (~5.4 a.u.). The dispersion of the three oxygen p bands along various directions in the two-dimensional Brillouin zone (BZ) is shown in Fig. 2(a). At Γ, the p_z band lies below the doubly degenerate p_x, p_y states because the latter form an antibonding combination at $\vec{k}_{11} = 0$. As one moves from Γ towards X, the p_x band becomes more and more bonding and its energy is gradually lowered. The p_y band is antibonding here and has the highest energy. The p_z band is nonbonding in practically all directions and is relatively dispersionless. Along the XK direction, the p_y band becomes bonding and starts to dip in energy, but p_x becomes less bonding. At K, the two bands become degenerate and continue to be nearly degenerate along the $K\Gamma$ direction because $p_x \pm p_y$ combinations have about equal energies. The total bandwidth arising from the overlayer is about 1.3 eV. It should be emphasized that this bandwidth is also a function of the exchange parameter α and increases to 2.2 eV for $\alpha = 0.7$. However, our main conclusions are independent of the choice of α. Band dispersions reported above for the oxygen overlayer are in remarkably good agreement with those found by Liebsch,[13] but the bandwidths are different because of differences in lattice constants and the choice of α.

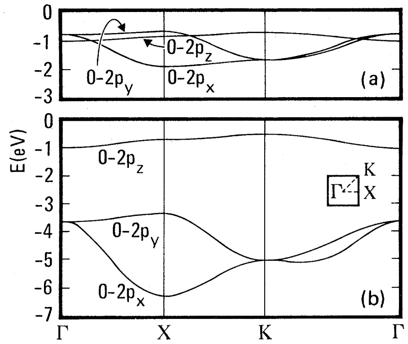

FIG. 2. Energy bands for a two-dimensional monolayer of oxygen (2p region) (a) in the absence, and (b) in the presence of the crystal potential of the eight layers of aluminum. The inset shows the BZ.

Next we performed the band calculation for the overlayer in the presence of the substrate potential. The results (using an arbitrary energy scale) are illustrated in Fig. 2(b). By comparing Figs. 2(a) and 2(b), one notices that the total width of the oxygen p_x, p_y bands has increased by about 2 eV. The nondispersive p_z orbitals are located at higher energy. Such on ordering can be readily justified using simple crystal-field arguments. However, the most novel finding is that the state distribution due to O($2p_{\sigma}$) bands, in the presence of crystal field alone, resembles quite closely the oxygen resonance observed in Fig.

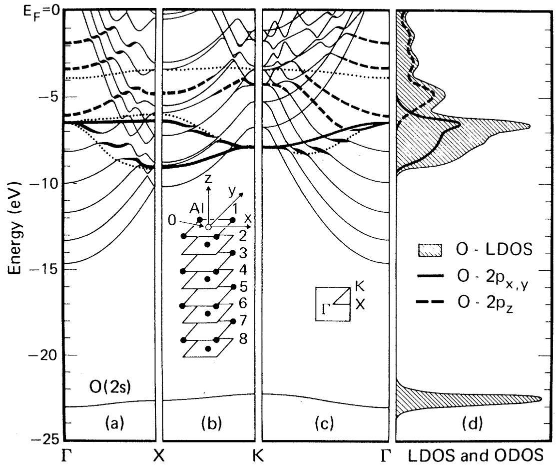

FIG. 3. (a)–(c) Energy bands for a monolayer of oxygen and eight layers of aluminum along $\Gamma-X-K-\Gamma$. Dotted lines give the bands for oxygen monolayer in the crystal field. The insets show the chemisorption model and the BZ; (d) local and orbital densities of states for oxygen.

1(a). If such a situation holds for a general chemisorbed system, then we have found a scheme for calculating the adsorbate-induced structure at tremendously reduced computational cost. We now explore the effect of including basis functions on the substrate atoms.

The band structure for oxygen chemisorbed on Al(100) surface along various symmetry directions in the BZ is shown in Figs. 3(a)–3(c). Let us first discuss the bands derived from O($2p_x$) and P($2p_y$) orbitals shown by heavy lines. Oxygen-monolayer bands in the crystal potential alone [from Fig. 2(b)] are superimposed (dotted lines). It is clear that the substrate hybridization makes O($2p_\sigma$) bands discontinuous at certain $\vec{k}_{11}$ points and reduces dispersion. The latter comes about as a result of implicit core orthogonalization that occurs upon incorporating basis on aluminum atoms. However, the overall shape of these bands is not drastically altered. One can further understand the implications of this band structure by examining the local and orbital densities of states[14] (LDOS and ODOS) for oxygen shown in Fig. 3(d). From the ODOS for O($2p_x$) [or O($2p_y$)], it is clear that the peak at about -7 eV is due to the flat O($2p_y$) band along the ΓX direction [or O($2p_x$) along the ΓY direction]. The shoulder below the main resonance arises due to lower-energy O($2p_x$, $2p_y$) bands which have been distorted due to interaction with the substrate orbitals. Thus the broad resonance observed in photoemission experiments[1-5] has its primary origin in O($2p_\sigma$) levels broadened due to oxygen-band-structure effects in the crystal field.

The otherwise flat O($2p_z$) band of oxygen monolayer undergoes drastic changes due to interaction with the substrate orbitals (see dashed lines in Fig. 3). The O($2p_z$) character is dispersed in the energy range extending from E_F to about -6 eV and practically loses its "identity" due to hybridization with Al(3*s*) and Al($3p_z$) orbitals. It is evident from the position of E_F in Fig. 3(d) that in addition to O($2p_\sigma$), a large fraction of O($2p_z$) orbitals are also occupied. The system may thus be thought of as "ionically" bound. A gross Mulliken-type population analysis[14] revealed that approximately 1.5 electrons have been transferred from aluminum to oxygen.

It should be noted that most of the weight for the O($2p_z$) orbital lies above the O($2p_\sigma$) orbitals [Fig. 3(d)]. To our knowledge, no experiments have yet been reported which attempt to separate the orbital symmetries of oxygen states. It should be extremely valuable to perform *angularly resolved* photoemission experiments of the type reported[15] for transition metals to understand further the oxidation of simple metals. As a by-product of such experiments one would also learn the role played by *d* electrons in transition-metal oxidation.

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Mobility in Tetrathiafulvalene–Tetracyanoquinodimethane (TTF–TCNQ)

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I account for the magnitude and temperature dependence of the mobility of TTF-TCNQ in the range 150–300 K by scattering of the carriers by optical phonons derived from the symmetric molecular vibrations. The only adjustable parameters are the widths of the conduction bands on TCNQ and TTF chains, chosen as 3000 and 1500 K, respectively. I also obtain estimates of the coupling to acoustic phonons and the unbroken chain lengths by fitting conductivity data down to 70 K.

TTF-TCNQ first attracted attention because its conductivity is very high for an organic material. Recent reports, based on measurements at the University of Pennsylvania of many carefully prepared and mounted samples, give the room-temperature conductivity $\sigma_{\rm RT}$ as 660 ± 130 Ω^{-1} cm^{-1}.[1] With decreasing temperature σ increases, reaching a peak σ_p at about 58 K, reported for some samples to be as high as $(100-150)\sigma_{\rm RT}$.[1] From neutron-scattering studies it has been deduced that there is a charge transfer of $\rho = 0.59$ electrons from TTF to TCNQ.[2] With the carrier density n calculated from this, I deduce from $\sigma = ne\mu$ (where μ is mobility) that the sum of electron and hole mobilities, in cm^2/V sec, is 3 ± 1 at room temperature, and 300–450 at the peak. These values of μ and its temperature dependence are similar to those I have deduced recently for electrons along the TCNQ chain in *N*-methyl-phenazinium tetracyanoquinodimethane (NMP-TCNQ).[3] I have been able to account well for the magnitude and behavior above 60 K of μ in that case by the interaction of electrons in a tight-binding band with the molecular vibrations. Here I have succeeded in extending these calculations to TTF-TCNQ.

Different explanations have been offered for the magnitude and temperature dependence of σ above 58 K. One theory is that many-body collective effects are involved. Specifically, contributions to σ are supposed to arise from charge-density wave fluctuations which slide via time-dependent phases.[1] From a one-dimensional (1D) calculation, Lee, Rice, and Anderson found that fluctuations are important, reducing the Peierls-transition temperature $T_{\rm P}$ to about one-fourth the mean-field value, $T_{\rm P}^{(0)}$.[4,5] This makes $T_{\rm P}^{(0)} \simeq 250$ K for TTF-TCNQ. For $T_{\rm P} < T < T_{\rm P}^{(0)}$, they showed that the density of states $D(\epsilon)$ at the Fermi energy $\epsilon_{\rm F}$ is reduced by 50% or more below $T_{\rm F}^{(0)}/2$. More recently, however, Horovitz, Gutfreund, and Weger, by including the effect on $T_{\rm F}$ of interchain coupling, showed that, for TTF-TCNQ, fluctuations are *not* important and $T_{\rm P} \simeq T_{\rm P}^{(0)}$ as determined by a 1D calculation.[6] As a consequence, $D(\epsilon)$ and the conduction are not expected to show deviations from single-particle behavior until T is close to $T_{\rm F}$, i.e., 54 K.

The evidence cited for a collective-mode contribution to σ is the strong dip observed in $\sigma(\omega)$ at low frequencies.[7] This has been interpreted as representing a gap or pseudogap of 1100 cm^{-1} (0.14 eV) in the density of states.[7] Since $\sigma(\omega)$ drops by more than an order of magnitude at 300 K, as well as at lower temperatures, it has been suggested that at the higher T's, rather than representing $D(\epsilon)$, "... the pseudogap in $\sigma(\omega)$ is in essence a mobility gap caused by the strong dynamic fluctuations ... below the mean-field temperature."[7] This is in conflict with the findings of Ref. 6 and even Ref. 5. It should be noted also that the dip in $\sigma(\omega)$ changes little from 300 to 5 K, where there is a real gap. From studies of photoconductivity, Eldridge[8] finds strong evidence that the peak at 1100 cm^{-1} is part of an absorption band that begins at ~ 315 cm^{-1}, the latter corre-