Electronic mechanism for alkali-metal-promoted oxidation of semiconductors

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An electronic mechanism for the experimentally observed alkali-metal-promoted oxidation of semiconductor surfaces is proposed. The mechanism is based on the assumption that the rate-limiting step for oxidation is dissociation of the oxygen molecule. The role of the preadsorbed alkali-metal atoms is to supply the empty surface-dangling-bond bands with electrons, which will lead to metallization of the surface, reduction of the work function due to the formation of a surface a dipole layer, and a positive shift of the surface Fermi energy. Eventually, as the oxygen molecule approaches the surface, transfer of charge from the dangling-bond bands to the partly occupied antibonding $2\pi^*$ orbital of the oxygen molecule takes place. We assume that the activation energy for dissociation of the oxygen molecule, chemically interacting with a Si surface, is given by the energy, 0.9 eV, corresponding to the excitation from the ground triplet state to the excited singlet state in the gas phase, 1 eV. The rate of dissociation is estimated by the probability for this excitation by hot electron-hole pairs, weighted by the amount of electron charge transferred to the molecule. It is found that this electronic mechanism for thermally activated dissociation of an oxygen molecule impinging on the semiconductor surface is substantially increased when an alkali-metal overlayer is preadsorbed on the surface. The proposed electron-hole–pair mechanism introduces a strong density of states and temperature dependence, which could be tested experimentally.

I. INTRODUCTION

In the past few years, increasing attention has been paid to alkali-metal-promoted oxidation (APO) of semiconductors,[1-4] although this catalytic effect, using preadsorbed alkalides, has been known for a decade.[5] It has been shown by several experimental groups, for example, that very pure SiO_2 can be grown on a silicon surface using this technique. These observations will presumably have a large impact on the industry of microelectronics. Conventionally, the formation of a SiO_2-Si interface requires relatively high temperatures and oxygen pressures, which limits the purity of the SiO_2 formed. With this new technique the alkali-metal precovered surface is typically exposed to oxygen at room temperature, and then the alkali-metal atoms are desorbed when annealing the sample to about 700 K, leaving a stoichiometric SiO_2 behind. It has been shown that this procedure can be repeated over and over again.[2,3]

As the APO reaction is complex and involves several steps, it is, from a theoretical point of view, of interest to investigate how individual reaction steps are influenced by alkali-metal additives. On single-crystal metal surfaces, it is found that the sticking coefficient of oxygen and similar molecules, CO and N_2, increases with increasing predeposited alkali-metal amounts.[6] The APO effect has also been observed for graphite (semimetal).[7,8] In a model calculation[7] it was shown that the APO of graphite could be explained by alkali-metal promotion of the charge transfer from the substrate to the oxygen molecule, which will increase the probability for dissociation of the oxygen molecule. For these surfaces, metals and semimetals, it is believed that the high dissociation ener-

gy of the oxygen molecule (5.1 eV in the gas phase) constitutes the bottleneck for sticking, followed by reaction. In an experimental study of APO of Ge(111)-(2×1) by Surnev,[9] it is found that the initial sticking coefficient of oxygen, S_0, as a function of alkali-metal coverage Θ, increases with approximately 2 orders of magnitude with increasing Θ, while further uptake of oxygen is not very dependent on Θ. In this work, we investigate the influence of preadsorbed alkali metal on S_0 for some semiconductor surfaces which have been extensively studied both experimentally and theoretically.

The dangling bonds formed when a semiconductor surface is created are of central importance for the chemistry at its surface. From a large number of experiments and calculations it is possible to obtain information about the electron structure of clean and alkali-metal adsorbed semiconductor surfaces. Recently, a summary of data obtained from photoelectron spectroscopy studies of surface states on semiconductors has been published by Hansson et al.[10] We will focus our attention to the class of surfaces with a (2×1) structure, e.g., Si(100)-(2×1), Si(111)-(2×1), and Ge(111)-(2×1), for which APO has been observed. For the Si(100)-(2×1) surface, the most consistent model for the surface reconstruction is the asymmetric dimer model,[11] while for Si(111)-(2×1) and Ge(111)-(2×1) it is the π-bonded-chain model.[12] From the photoelectron spectroscopy data,[10] we conclude that for these semiconductor surfaces a common feature of the electron structure is present in the region of the bulk band gap. The surface-dangling-bond bands in the region of the bulk valence-band edge is pictured schematically in Fig. 1. Two of the four unpaired electrons of a surface dimer (two surface atoms) are found in a band far below
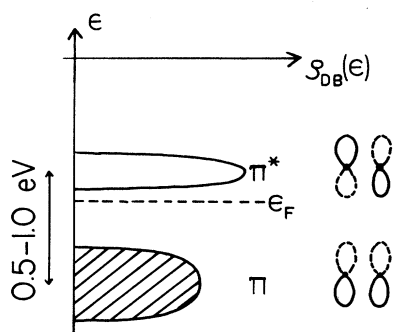
FIG. 1. Schematic drawing of the dangling-bond bands in the region of the bulk valence-band edge of a (2×1) surface of e.g., Si(100), Si(111), and Ge(111). The right-hand side of the figure shows the combination of the $3p$ atomic orbitals in the direction of the surface normal, which forms the bonding (π) and anti-bonding (π^*) band. The typical band separation is 0.5–1.0 eV.

the band gap, and two will fill up a band of π symmetry with bonding character. This band is typically found just below the bulk valence-band edge (hatched in Fig. 1). In the bulk band gap a narrower band of π symmetry with antibonding character is found, which is empty for the clean surface. This antibonding band has been identified by Mortensson et al.[13] in normal photoemission experiments on n-doped Si(111)-(2 $\times$ 1).

The major effect when alkali-metal atoms are adsorbed is that its outermost s electron is transferred to this antibonding band, giving rise to weakening of the intradimer bond and a surface dipole which reduces the work function.[14(b)] When the surface then is exposed to oxygen, it is energetically favorable for an electron to be transferred from the dangling-bond bands into the antibonding $2\pi^*$ orbital of the oxygen molecule as it reaches a typical chemisorption distance from the surface. The result is a weakening of the intramolecular bond of the oxygen molecule, which will cause a relaxation of its bond length. At this point, when a chemical interaction takes place, there is a possibility that thermally excited electron-hole pairs will excite the molecule to its first excited electronic state. If this excitation is activated, a

possibility for transferring an additional electron opens up which will lead to dissociation.

When the molecule reaches the chemisorption region, the molecular electron affinity will increase compared to the gas-phase value. The increase will be greater when alkali-metal atoms are preadsorbed on the surface, due to the lowering of the work function by typically a few eV in this case. This will cause an enhancement of the probability for thermally activation of the excited state, which will lead to dissociation. This forms the proposed basis for APO of the semiconductor surface. To be more specific, we will, from now on, consider the interaction between the oxygen molecule and a Si(100)-(2 $\times$ 1) surface. In this case, the excitation energy to the first excited electronic state is 0.9 eV.[15]

II. THEORY AND CALCULATION

In this section, we develop a procedure to calculate the electron structure and charge transfer from the semiconductor surface to the antibonding $2\pi^*$ molecular orbital of the O_2 molecule, as a function of the alkali-metal coverage and surface-molecule distance. This enables us to estimate, to lowest order, the increase of the probability for thermally activated dissociation of the oxygen molecule, when the surface is preadsorbed by alkali-metal atoms. The lowest-order approach refer to the fact that the electron structure is calculated in the absence of coupling to the first excited electronic state. Finally, the probability for this excitation, which is assumed to determine the probability for dissociation of the oxygen molecule, is estimated by applying the golden rule.

When the O_2 molecule approaches close enough to the surface, additional charge might be transferred to the originally half-filled $2\pi^*$ orbital (two electrons in the gas phase). We argue that the $2\pi^*$ orbital will predominantly interact with the dangling-bond bands π and π^*, which are formed by the surface atom p orbitals (e.g., $3p$ for Si and $4p$ for Ge) pointing in the direction of the surface normal (see Fig. 1). To describe the interaction between the states of the surface-dangling-bond bands and the $2\pi^*$ orbital, we consider the following model Hamiltonian in the Hartree-Fock approximation:

$$H = \sum_{i,\sigma} \varepsilon_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{i\sigma,k\sigma} \{ V_{i\sigma,k} c_{i\sigma}^\dagger c_{k\sigma} + \text{H.c.} \} + \sum_{i\sigma \neq j\sigma'} \tfrac{1}{2} U_{i\sigma,j\sigma'} n_{i\sigma} c_{j\sigma'}^\dagger c_{j\sigma'} , \qquad (1)$$

where

$$n_{i\sigma} = \langle c_{i\sigma}^\dagger c_{i\sigma} \rangle .$$

The first term represents the energy of the occupied unperturbed one-electron levels of the $2\pi^*$ orbital of the oxygen molecule. The one-electron energies of the oxygen molecule are $\varepsilon_{i\sigma}$, where $i = (2\pi^*)_x$ or $(2\pi^*)_y$ and $\sigma = \uparrow$ or $\downarrow$. The second term is the energy of the occupied unperturbed surface-dangling-bond states, while the third and fourth terms originate from the molecule-surface interaction and the intramolecular Coulomb interaction in the

$2\pi^*$ orbital of the oxygen molecule, respectively. The Coulomb interaction matrix, $U_{i\sigma,j\sigma'}$, is renormalized by image effects and the factor $\tfrac{1}{2}$ appears as the matrix is symmetric.

The Hamiltonian in Eq. (1) can be simplified further as we consider the following. We define the x and y coordinates perpendicular to the molecular axis of the oxygen molecule as shown in Fig. 2 [note that in the figure the O-O distance is exaggerated compared to the Si-Si distance of Si(100)-(2 $\times$ 1) with factor of 1.7]. In the ground state in the gas phase, the oxygen molecule is in a triplet
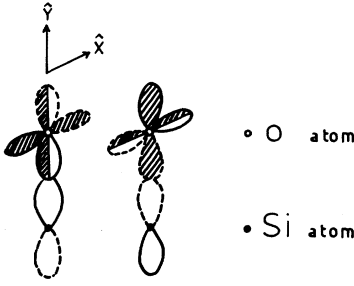
○ O atom

● Si atom

FIG. 2. Schematic drawing of the $2p_x$ and $2p_y$ orbitals of molecular oxygen, perpendicular to the molecular axis (solid line), attached to the $3p$ orbitals of the surface dimer of Si pointing in the direction normal to the surface. The two missing electrons, one in the $(2\pi^*)_x$ orbital and one in $(2\pi^*)_y$ orbital of the oxygen molecule, are represented by the unhatched regions of the orbitals $2p_x$ and $2p_y$ of the left-hand- and right-hand-side oxygen atom, respectively. The O-O distance in the figure is exaggerated in comparison with the Si-Si distance. These distances are in reality given by 2.5 a.u. (Ref. 21) and 4.1 a.u. (Ref. 7), respectively.

state with one unpaired electron in the $(2\pi^*)_y$ orbital with spin σ, and one in the $(2\pi^*)_x$ orbital with spin σ.[16] As the ionization level of the neutral molecule in the gas phase, $I_{O_2} = 12.07$ eV,[17] is well below the bottom of the dangling-bond band, we can consider these two electrons to be frozen on the molecule. This approximation has been tested numerically and is found to be good even when the interaction with the surface is strong.

The affinity of O_2 in the gas phase is positive, $A_{O_2} = 0.44$ eV,[17] and will increase when the interaction with the surface states is considered. At typical chemisorption distances from the surface, this affinity level will cross the Fermi level, leading to a transfer of an electron to the oxygen molecule. The transfer of a second electron is neglected as the affinity of O_2^- in the gas phase is negative and large, $A_{O_2^-} = -5.9$ eV.[18] This implies that the O_2^{2-} state of the molecule is strongly dissociative. As the oxygen molecule approach the surface, $A_{O_2^-}$ will increase twice as fast as A_{O_2} as it corresponds to a state with an initial excess charge of one electron. However, if we consider the contribution from image interaction to the total energy, the O_2^- state will exceed the O_2 state by as much as 2.5 eV at a close molecule-surface distance of 2 a.u. We can also exclude the transfer of a second electron, considering the orbital geometry. As one of the half-filled orbitals of the oxygen molecule is oriented parallel to the surface [$(2\pi^*)_x$ in Fig. 2], the overlap with the surface p orbital, which supply electrons, is much less compared to the half-filled orbital, $(2\pi^*)_y$, which overlaps more strongly with the surface p orbital.[15] The Hamiltonian can then be reduced to

$$H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + E_a c_a^\dagger c_a + \sum_{k\sigma} [V_{ak} c_a^\dagger c_{k\sigma} + \text{H.c.}] ,\qquad (2a)$$

where

$$E_a = \varepsilon_a + U_0 - 1/2d \quad \text{with index } a = (2\pi^*)_y, -\sigma ,$$

$$(2b)$$

$$U_0 = U_{a,(2\pi^*)_x\sigma} + U_{a,(2\pi^*)_y\sigma} ,$$

where we have assumed, according to the previous discussion, that $n_{(2\pi^*)_y,\sigma} = n_{(2\pi^*)_x,\sigma} = 1$. ε_a is the molecular level of the gas-phase oxygen molecule, $\varepsilon_a = -I_{O_2}$. The Coulomb energy U_0 is estimated from $U_0 = I_{O_2} - A_{O_2}$, which implies that $E_a = -A_{O_2} - (2d)^{-1}$. The $(2d)^{-1}$ term is added to take into account the image interaction. The image term should be multiplied by the factor $(\varepsilon_r + 1)/(\varepsilon_r - 1)$, where ε_r is the substrate dielectric function. But as we will consider the surface to become metallic when alkali-metal atoms are preadsorbed, ε_r goes to infinity and this factor becomes unity. The surface metallization will be further discussed below.

From the Newns-Anderson-type of Hamiltonian[19] in Eq. (2a) we can define the chemisorption function $\Delta(\varepsilon)$ and its Hilbert transform $\Lambda(\varepsilon)$:[19]

$$\Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_a) \approx \pi V^2 \rho_{DB}(\varepsilon) \qquad (3a)$$

and

$$\Lambda(\varepsilon) = \pi^{-1} P \int_{-\infty}^{\infty} \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' . \qquad (3b)$$

The hopping matrix elements V_{ak} are considered energy independent. This is a reasonable approximations as we only consider the coupling between the oxygen level E_a and the relative narrow surface density of states, $\rho_{DB}(\varepsilon)$, formed by the two dangling-bond bands, π and π^* (pictured schematically in Fig. 1). Given the band density of states, $\rho_{DB}(\varepsilon)$, and coupling strength V, we can calculate the amount of electron transfer form the dangling-bond bands to the oxygen molecule. However, we have to take into account the effect of preadsorbed alkali-metal atoms. The alkali-metal coverage Θ is defined as follows. Full coverage, $\Theta = 1$, corresponds to one alkali-metal atom per surface dimer, see, e.g., Ref. 14(a).

According to a recent calculation by Batra et al.,[14(b)] the displacements of the Si atoms are not significant when a full monolayer of potassium is adsorbed on a Si(100)-(2×1) surface. Furthermore, it is found, both experimentally[20] and theoretically,[14(b)] that no potassium-induced states appear in the bulk band gap. Batra et al. conclude that the dominant effect of alkali-metal adsorption is that the $4s$ electron of potassium is transferred into the empty dangling-bond band, leaving a completely ionized potassium atom in between two surface dimers.[14(b)]

Based on these observations, we will consider two effects of the preadsorbed alkali-metal atoms. First, it introduces a coverage dependence in the density of states projected on the oxygen molecule, $\rho_a(\varepsilon)$, due to the buildup up of a surface dipole layer. This layer is formed by the ionized alkali-metal atoms and their lost electrons donated to the antibonding dangling-bond band of the surface. The projected density of states is written

$$\rho_a(\varepsilon) = \pi^{-1} \frac{\Delta(\varepsilon)}{[\varepsilon - E_a' - \Lambda(\varepsilon)]^2 + \Delta^2(\varepsilon)} , \qquad (4a)$$

where

$$E_a' = E_a + \Delta\Phi_{SD} . \qquad (4b)$$

The last term in Eq. (4b) is the surface dipole contribution to the change of the work function due to alkali-metal adsorption, $\Delta\Phi$. We adopt the Fermi level of the clean surface as energy zero.

The second effect of preadsorbed alkali-metal atoms is the shift of the Fermi level, $\Delta\varepsilon_F$, due to electron transfer from the alkali-metal atoms to the antibonding dangling-bond band. The work-function change is given by

$$\Delta\Phi = \Delta\Phi_{SD} - \Delta\varepsilon_F . \qquad (5)$$

Information about the total work-function change as a function of coverage, $\Delta\Phi$, can be deduced from experiments, e.g., for potassium on Si(100)-(2×1) in Refs. 21 and 22. The coverage dependence of $\Delta\Phi_{SD}$, to be inserted in Eq. (4b), is then given by Eq. (5) as the coverage dependence of $\Delta\varepsilon_F$ is determined by the following equation (assuming complete ionization of the alkali-metal atoms):

$$\int_0^{\Delta\varepsilon_F} \rho_{DB}(\varepsilon) d\varepsilon = \Theta . \qquad (6)$$

The fraction of an electron charge transferred to the oxygen molecule, which will depend on Θ, is given by[19]

$$n_a = \int_{\varepsilon_B}^{\Delta\varepsilon_F} \rho_a(\varepsilon) d\varepsilon + \langle n_a \rangle_{loc} , \qquad (7a)$$

where

$$\langle n_a \rangle_{loc} = \left[1 - \frac{d\Lambda(\varepsilon)}{d\varepsilon} \Big|_{\varepsilon = \varepsilon_{a,loc}} \right]^{-1} . \qquad (7b)$$

The energy ε_F refers to the lower band edge of $\rho_{DB}(\varepsilon)$ and the second term of Eq. (7a) is the contribution from localized states below the Fermi energy.

Finally, we will investigate the probability for dissociation of the oxygen molecule and its dependence of alkali-metal coverage. The probability per time unit for dissociation at a given distance from the surface is given by $P = P(d)$. In a semiclassical approximation, the total probability for dissociation could be estimated by integrating P over a prescribed trajectory of the molecule in the molecule-surface interaction region.

Cluster calculations by Goddard et al.[15] for molecular oxygen chemisorbed on silicon indicate that if the molecule is electronically excited from its ground state to the first excited state (excitation energy $\varepsilon_0 = 0.9$ eV), the activation energy for dissociation is considerably decreased. We assume accordingly, that this excitation forms the rate-limiting step for dissociation of the oxygen molecule. In the gas phase, this excitation corresponds to the triplet-to-singlet transition of 1 eV.[23] According to Fig. 2, this excitation in the gas phase corresponds to the transfer of one electron from the half-filled $(2\pi^*)_y$ orbital to the half-filled $(2\pi^*)_x$ orbital.[15] In the excited state, the oxygen molecule will most likely bridge the dimer, lead-

ing to additional charge transfer into the $(2\pi^*)_y$ orbital. If we consider the extreme case of one electron transferred when the excitation takes place, $n_a = 1$, it is possible that after the excitation the molecule will be found in a O_2^{2-} state, which is strongly dissociative. Therefore, it is reasonable that P is given by the probability per time unit for the electronic excitation of energy ε_0, p_e, weighted with n_a. P is then written

$$P = n_a p_e . \qquad (8)$$

We assume that the excitation is driven by thermally excited electron-hole pairs in the covalent bond formed between the dangling-bond bands and the oxygen molecule. p_e is estimated by the following golden-rule expression:

$$p_e \propto \sum_{k_a, k_a'} |\langle k_a' | v | k_a \rangle|^2 [1 - f(\varepsilon_{k_a'})] f(\varepsilon_{k_a})$$
$$\times \delta(\varepsilon_{k_a} - \varepsilon_{k_a'} - \varepsilon_0) , \qquad (9)$$

where v represents the coupling between the ground and the first excited electronic state of the molecule, $f(\varepsilon)$ the Fermi-Dirac distribution function, and $|k_a\rangle$ are the adsorbate projected states,

$$|k_a\rangle = |a\rangle\langle a|n\rangle . \qquad (10)$$

where $|n\rangle$ are the eigenfunctions (spin included) of the Hamiltonian in Eq. (2a). In the gas phase this excitation by electron impact corresponds to the triplet-to-singlet transition. This implies that the potential v is spin dependent, as the outgoing electron must have the opposite spin compared to the ingoing electron. In the case of a .chemisorbed oxygen molecule, a covalent bond is formed between the surface and the molecule, and thus the total electronic spin of the molecule is not a well-defined quantity. For this reason we argue that spin conservation is not required for the excitation event. Equation (9) can be rewritten as an energy integral,

$$p_e \propto |v_a|^2 \int_{-\infty}^{\infty} d\varepsilon \, \rho_a(\varepsilon) \rho_a(\varepsilon + \varepsilon_0)[1 - f(\varepsilon)] f(\varepsilon + \varepsilon_0)$$
$$\approx |v_a|^2 e^{-\beta\varepsilon_0} \int_{\varepsilon_F - \varepsilon_0}^{\varepsilon_F} d\varepsilon \, \rho_a(\varepsilon) \rho_a(\varepsilon + \varepsilon_0)$$

$$\text{when } \beta\varepsilon_0 \gg 1 , \qquad (11)$$

where $v_a = \langle a | v | a \rangle$ and $\beta = (k_B T)^{-1}$. The integral in Eq. (11) can be evaluated with the projected density of states given by Eq. (4a). An alkali-metal coverage dependence is introduced by $\rho_a(\varepsilon)$ [see Eqs. (4a) and (4b)], and by $f(\varepsilon)$ as the Fermi energy is coverage dependent [see Eq. (6)]. In this model study, we only show results from calculations of the relative change of P as we are mainly interested in the change of P with alkali-metal coverage Θ and surface-molecule distance d.

III. RESULTS

In the calculations, we model the dangling-bond density of states, $\rho_{DB}(\varepsilon)$, by two identical semielliptical bands corresponding to a lower bonding π band and an upper antibonding π^* band [see Fig. 3(a)]. The choice of equal-

ly shaped bands, with no energy gap in between, is made in order to minimize the number of parameters but still retain the essential qualitative features of the surface-dangling-bond bands. The value used for the clean-surface work function, $\Phi_0 = 4.9$ eV, corresponds to Si(100).[24] We model the coverage dependence of the total work-function change with the analytical function $\Delta\Phi(\Theta) = -2[1 - \exp(-10\Theta)]$ eV, which approximately reproduces the work-function measurement for potassium on Si(100)-(2×1).[20]

In Figs. 3(b)–3(d) results are shown for the projected density of states for different surface-molecule distances d and coupling constants V. V is chosen to be 0.6 at the distance $d = 2$ a.u. in order to reproduce the amount of transferred charge to the oxygen molecule, $n_a = 0.9$, which was obtained in a cluster calculation by Barone et al.,[25] for d equal to the equilibrium distance, approximately 2 a.u. The values of V for larger d values in Fig. 3(c) and 3(d) are tentative to mimic a plausible exponential decay of V with d. We use $V(d) = V_0\exp[-a(d - d_0)]$, where $V_0 = 0.6$, $a = 0.27$ a.u.,$^{-1}$ and $d_0 = 2$ a.u.

The result for $d = 6$ a.u. in Fig. 3(d) shows that for the clean surface, $\Theta = 0$, the molecular level is almost unperturbed and empty, while for the alkali-metal covered surface, $\Theta = 1$, the level is shifted down into the region of the surface-dangling-bond band, giving rise to charge transfer of about half of an electron from the surface to the oxygen molecule. At a distance somewhat closer to the surface, $d = 4$ a.u. [Fig. 3(c)], the molecular level is strongly interacting with the band in the case of a clean surface and for $\Theta = 1$, a split-off state is formed below the band bottom. The split-off state corresponds to a localization of about 0.8 of an electron charge on the oxygen molecule. In the equilibrium position, $d = 2$ a.u. [Fig. 3(b)], essentially one electron is localized on the molecule, independent of Θ.

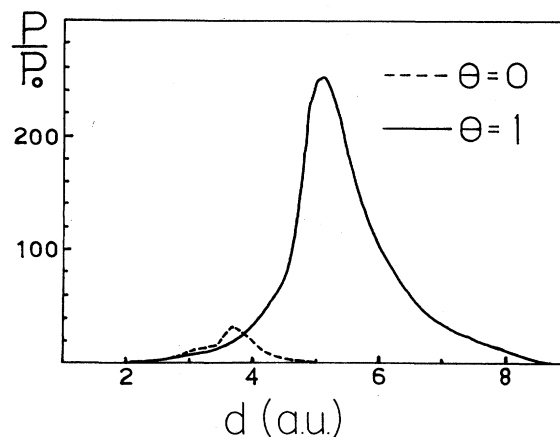These results show that for an oxygen molecule ap-

FIG. 4. The estimated relative increase of the probability for dissociation of the oxygen molecule, $P(d,\Theta)/P(2,0)$. P is given by Eq. (8). The results for $\Theta = 1$ and $\Theta = 0$ are given by the solid and dashed line, respectively. The value of $P(5,0)/P(2,0)$ and $P(6,0)/P(2,0)$ is 1 and 0.02, respectively. The temperature is 500 K, but the result remains the same for temperatures $kT \ll \varepsilon_0$.

proaching the surface, considerable charge transfer takes place in a region of about 2–4 a.u. outside the equilibrium position. In the terms of diabatic potential energy surfaces, this relates to jumping from a O_2 potential energy surface to a O_2^- potential energy surface as the oxygen molecule reaches this region when approaching the surface. These results indicate that the charge-transfer process is initiated further out from the surface when the surface is covered by alkali-metal atoms.

When the molecular level is in resonance with the band at a relatively large distance from the surface, e.g., in Fig. 3(d) for $\Theta = 1$, sharp structures in the projected density of states appear, and no localized states outside the band energies appear. In this case, the number of thermally activated electron-hole pairs on the molecule is enhanced,
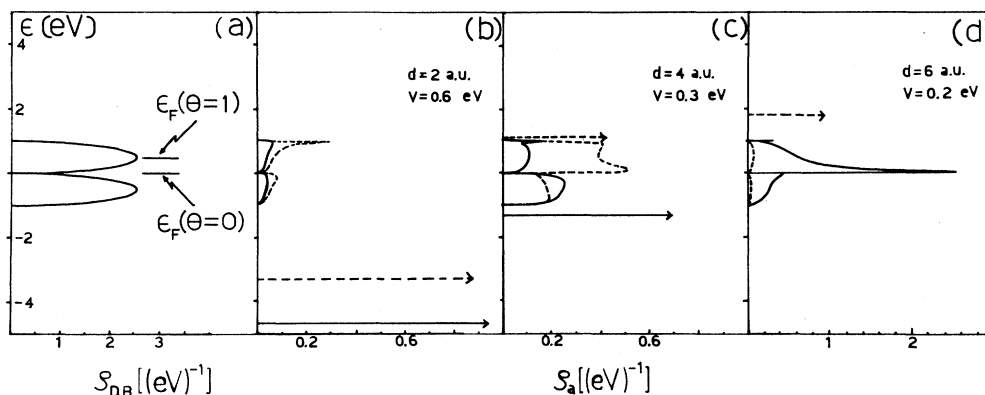

FIG. 3. (a) The modeled dangling-bond bands used in the calculation. The lower is the bonding π band (filled) and the upper is the antibonding π^* band. The π^* band is empty for the clean surface, $\Theta = 0$, and half-filled for one monolayer of alkali-metal atoms, $\Theta = 1$. (b)–(d) The projected density of states, $\rho_a(\varepsilon)$, for different distances, d, and coupling constants V; the dashed line corresponds to $\Theta = 0$ and the solid to $\Theta = 1$. The horizontal arrows represents localized states outside the dangling-bond bands with the strength given by the arrow length.

leading to a relatively large probability for the electronic transition. The estimated relative probability for dissociation P, shown in Fig. 4, illustrates this effect.

IV. DISCUSSION

The electronic mechanism for dissociation is strongly promoted for a molecule approaching an alkali-metal-covered surface compared to a clean surface. We want to point out that the electron-hole–pair mechanism has been proposed by Newns[26] in explaining the observed vibrational excitation of a NO molecule impinging on a Ag(111) surface. In that case the coupling λ between the thermally excited electron-hole pairs and the internal vibrational coordinate of NO is considered. The mean number of localized phonons of the molecule, $\langle n \rangle$, which corresponds to the probability for the vibrational excitation, takes a similar form as p_e in Eq. (11),

$$\langle n \rangle = \left[\frac{2}{\pi} \right] \lambda^2 \varepsilon_v e^{-\beta \varepsilon_v} \rho_a^2(\varepsilon_F) , \tag{12}$$

when $\beta \varepsilon_v \gg 1$ and the variation of $\rho_a(\varepsilon)$ is small in the interval $\varepsilon_F < \varepsilon < \varepsilon_F + \varepsilon_v$. As the vibrational energy, $\varepsilon_v = 230$ meV, is large compared to maximum substrate phonon energy, the experimentally observed temperature dependence, $\exp(-\beta \varepsilon_v)$, indicates that the electron-hole–pair mechanism is important in this case. When considering the activation energy for dissociation of an oxygen molecule approaching a semiconductor with appropriate surface bands, we argue, based on the study by Goddard et al.,[15] that the coupling to the first excited electronic state is most important. In this case the phonon mechanism can be ruled out for the same reason as

$\varepsilon_0 = 0.9$ eV. However, the electron-hole pair coupling to the vibrational excitation of the oxygen molecule (in the gas phase $\varepsilon_v = 190$ meV) might be an alternative channel leading to dissociation. It is important to note that both of these processes have same density-of-states dependence, apart from different activation energies ε_0 or ε_v, given by the integral in Eq. (11).

The electron-hole–pair mechanism introduces a strong temperature dependence. For temperatures $T \ll \varepsilon_0/k_B$, where ε_0 is the excitation energy of about 0.9 eV, corresponding to the triplet-to-singlet transition in the gas phase of 1 eV, the probability for dissociation, P, has the temperature dependence $P \propto \exp(-\varepsilon_0/k_B T)$. An experimental study of the temperature dependence of the alkali-metal-promoted oxidation of semiconductors would be valuable in order to judge the importance of the proposed electronic mechanism. It might also be possible to create a high electronic temperature, using laser light with appropriate frequency. This would certainly be a crucial test of an electronic mechanism of the proposed form.[27] In addition to the temperature dependence, it would also be valuable to obtain experimental information of the variation of the alkali-metal-promoted effect for different semiconductor surfaces with qualitatively different dangling-bond bands. For example, in the case when both the width of π^* band and the separation between the π and π^* band exceeds ε_0, the alkali-metal-promoted effect is expected to be large according to the model.

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