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METAL OXIDATION AND SURFACE STRUCTURE

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The chemisorption of oxygen on a thin oxide film on a metal is discussed, and compared with that on the oxide in bulk. If the oxide film is thin, chemisorption of oxygen as ions is larger on the composite system. Oxygen ions account for almost all the chemisorption on *n*-type oxides, but on *p*-type oxides the main chemisorption occurs as neutral pairs. In both cases sufficient oxygen ions are present to give a significant electrical potential difference across the film as is required in Mott's theory of film growth.

1. Introduction

Mott [1,2] first emphasized the important part played by oxygen adsorbed at the oxide/oxygen interface in determining the rate of growth of a thin oxide film on a metal. He pointed out that oxygen adsorbed as atoms on the oxide surface should provide surface traps for electrons. When the oxide film is thin, these traps can be filled by electrons transferred from the underlying metal, and by this process a strong electric field is established in the film. Because of this field, the oxide film can grow even at low temperatures where ionic diffusion is negligible. If we accept this theory of the formation of thin oxide films on metals, the rate of growth of the film is connected with the mechanism of oxygen chemisorption on the oxide. The current theory of this latter process [3] assumes that oxygen is chemisorbed as the anion O^-, and a space charge is established in the oxide near the surface. The theory is not therefore directly applicable to thin oxide films where space charge effects are unimportant. Moreover, for a thin oxide film on a metal, the presence of the metal means that chemisorption at the oxide surface takes place in a reducing environment. The adsorbent is not really the oxide at all, but the whole system, metal plus thin oxide film. Even so, the space charge in the bulk oxide, and the electrical potential difference across the thin oxide film on the metal are established by similar processes, and both depend upon the electronic structure at the oxide surface.

Interest in these composite adsorbents is not confined to the problem of film growth alone. Surface processes involving oxygen on the systems Cu/Cu_2O (film thickness 500-1000 Å) and Ni/NiO (film thickness 25-180 Å) have been investigated [4-7] at temperatures where the oxidation rate is negligible. For both these systems, the oxide is a *p*-type semiconductor. Work on systems with *n*-type oxides, though difficult because of the very low surface coverages (see § 2) would be valuable.

2. *n*-Type oxide

We assume that associated with each adsorbed oxygen atom there is a localized surface level lying in the gap between the top of the valence band and the conduction band of the oxide. Recent work on the interaction between an atom and a crystal surface [8,9] shows how such surface levels are formed. They may be cationic (electron concentrated on the surface crystal atoms), anionic (electron

concentrated on the foreign atom) or even homopolar (electron shared equally between the foreign atom and the crystal). With oxygen on an *n*-type oxide like Al_2O_3, it seems likely that although the oxygen atom is adsorbed over a lattice cation, the important interaction problem will be between the 2*p* orbitals of oxygen and the valence band of the oxide. This band is associated largely with the lattice anions. Each oxygen atom brings three extra levels to the system but only four electrons. One of the extra levels is therefore unoccupied, and if this is an anionic surface level we have a charge distribution which corresponds, more or less, to adsorption of oxygen as atoms. When the anionic surface level is occupied we have the picture of anionic chemisorption.

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THIN OXIDE FILM ON THE METAL

Let there be N_s surface levels, and let N be occupied by electrons. N is the number of O^- ions and $(N_s - N)$ the number of oxygen atoms adsorbed on the oxide surface. If ϵ is the depth of the surface levels below the bottom of the conduction band then, with respect to the bottom of the conduction band as the energy zero, the chemical potential of electrons at the surface is

$$\mu = -\epsilon + kT \ln [N/(N_s - N)]. \tag{1}$$

If V is the electrical potential at the oxide surface measured from zero at the metal/oxide interface then

$$-eV = \epsilon - \chi - kT \ln [N/(N_s - N)], \tag{2}$$

where χ is the depth of the Fermi level in the metal below the bottom of the conduction band in the oxide. If space charges can be neglected, the energy level diagram is that shown in fig. 1. The dotted line is the Fermi level (the electro-chemical potential), and we note that the surface level lies below it by an amount $kT \ln [N/(N_s - N)]$. Now the electrical potential across the film is due to the transfer of electrons from the metal to the surface levels so that when space charges are unimportant,

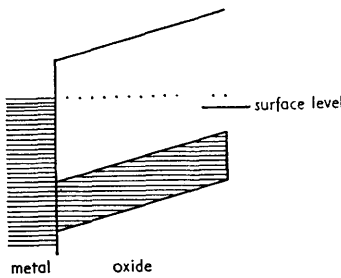

FIG. 1.—The energy level diagram for oxygen chemisorption on a thin oxide film on the metal. The dotted line is the Fermi level.

$$-(V/X) = (4\pi e/\kappa)N, \tag{3}$$

where X is the thickness and κ the dielectric constant of the film. $(N_s - N)$, the number of adsorbed oxygen atoms will be given by the usual Langmuir isotherm

$$N_s - N = (M - N_s)Kp^{\frac{1}{2}}. \tag{4}$$

Here M is the number of surface sites, p the oxygen pressure and K the equilibrium constant. From eqn. (2)-(4) we derive the adsorption isotherm for *ions* as

$$\theta/(1 - \theta) = [Kp^{\frac{1}{2}}/(1 + Kp^{\frac{1}{2}})]\Gamma \exp(-X\theta/\lambda), \tag{5}$$

where $\theta = N/M$ is the fraction of the surface covered by oxygen ions, λ is a characteristic length for the oxide defined by

$$\lambda = \kappa kT/4\pi e^2 M, \tag{6}$$

and

$$\Gamma = \exp[(\epsilon - \chi)/kT]. \tag{7}$$

We note that with $M = 10^{15}\ \text{cm}^{-2}$ and $\kappa = 10$, $\lambda = 0{\cdot}015$ Å at 300°K. Also with $V = 1$ V. eqn. (3) gives $\theta = 0{\cdot}056$ for $X = 10$ Å. Now θ decreases with X, so for film thicknesses greater than about 10 Å we can assume that $\theta \ll 1$. Further,

there is no experimental evidence that oxygen is adsorbed as atoms to any extent on n-type oxides so that we also have $Kp^{\frac{1}{2}} \ll 1$. Thus eqn. (5) degenerates to

$$\theta \exp (X\theta/\lambda) = \Gamma K p^{\frac{1}{2}}. \tag{8}$$

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This isotherm is illustrated in fig. 2 for several film thicknesses between 20 and 80 Å. The important feature is that, provided $\Gamma K p^{\frac{1}{2}}$ is not too small, θ is nearly independent of the oxygen pressure, and for practical purposes we can regard the adsorption as saturated although only a small fraction of the surface is covered.

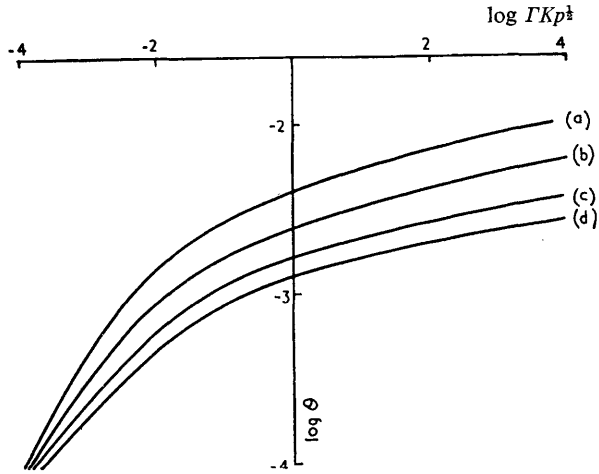

FIG. 2.—The adsorption isotherm for oxygen ions according to eqn. (8). Film thickness:
(*a*) 20 Å; (*b*) 40 Å;
(*c*) 60 Å; (*d*) 80 Å.

For the oxidation problem we need an expression for the electrical potential difference across the film. If we put $\alpha = -eV/kT$ then $\theta = \alpha\lambda/X$, and the potential difference is calculated from

$$\alpha \exp \alpha = (X/\lambda)\Gamma K p^{\frac{1}{2}}.$$

As X goes from 10 to 1000 Å, (X/λ) goes from about 10^4 to 10^7 at 300°K. Hence if $\Gamma K p^{\frac{1}{2}} > 1$, α is given approximately by

$$\alpha \simeq \ln \Gamma K p^{\frac{1}{2}} + \ln (X/\lambda)$$

and varies only slowly with X. In this way we obtain Mott's equations for the rates of growth of thin and very thin films. It should be noticed that the potential difference across the film is given by

$$-eV \simeq (\epsilon - \chi) + kT \ln (X/\lambda) + kT \ln Kp^{\frac{1}{2}}. \tag{9}$$

It is not equal to $(\epsilon - \chi)$.

BULK OXIDE

The surface levels associated with the adsorbed oxygen are filled with electrons transferred from the donor levels in the interior, and a space charge is established in the oxide. The equation for V, the electrical potential at the surface is [3]

$$-V = 2\pi e N^2/\kappa M' \tag{10}$$

if $e|V| \gg kT$. Here M' is the concentration of donor levels in the oxide. This equation replaces eqn. (3) for a thin film on the metal. Eqn. (1) and (4) still hold, and we can retain eqn. (2) if χ is replaced by $\frac{1}{2}\epsilon'$ with ϵ' equal to the depth of the donor levels below the bottom of the conduction band. The adsorption isotherm for ions is now easily derived as

$$\theta/(1-\theta) = [Kp^{\frac{1}{2}}/(1 + Kp^{\frac{1}{2}})]\Gamma' \exp(-M\theta^2/\lambda M'),$$

with

$$\Gamma' = \exp[(\epsilon - \tfrac{1}{2}\epsilon')/kT].$$

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For $M' = 10^{16}$ cm^{-3} and $V = 1$ V, eqn. (10) gives $\theta = 3 \times 10^{-4}$. Thus we can assume that $\theta \ll 1$, and if adsorption as atoms is also small then

$$\theta \exp (M\theta^2/\lambda M') = \Gamma' K p^{\frac{1}{2}}, \tag{11}$$

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which is the analogue of eqn. (8). The isotherm, eqn. (11), is illustrated in fig. 3 for $(\lambda M'/M) = 1{\cdot}5 \times 10^{-9}$. Comparison with the isotherms in fig. 2 shows that even if Γ' exceeds Γ by a factor of 10^{30}, adsorption of oxygen as anions on

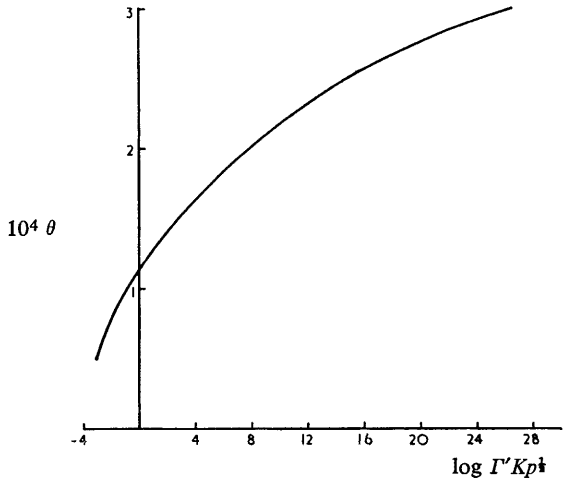

FIG. 3.—The adsorption isotherm for oxygen ions according to eqn. (11).

a thin oxide film on the metal should be some ten times greater than that on the bulk oxide. We have no experimental information on this matter, although it is an important consequence of Mott's theory of the rate of growth of a thin oxide film.

3. *p*-TYPE OXIDE

In the molecular-orbital theory [8, 9] of the chemisorption of oxygen on a *p*-type oxide, the main interaction problem is likely to be between the $2p$ orbitals of oxygen and the valence band of the oxide. For Cu_2O, the valence band is associated largely with the Cu^+ ions. Of the three extra levels which an oxygen atom brings to the system, suppose that the highest is a *homopolar* surface level lying in the gap between the normally filled and empty crystal bands. When this surface level is unoccupied, the charge distribution corresponds to oxygen adsorbed as the O^- ion but with a positive hole trapped at the crystal surface near the oxygen ion. This is the molecular-orbital description of oxygen chemisorption with the formation of " neutral pairs " at the oxide surface.[4, 10] There seems to be no reason why this sort of chemisorption should not proceed to complete surface coverage, and this is in fact the situation [11] with oxygen on Cu_2O. We note, however, that at complete surface coverage, interactions between the discrete surface levels should result in the formation of a surface *band*.

The simple band approximation fails for the transition metal oxides. For these oxides it seems that the cation levels are not broadened into bands in the crystal, but remain as discrete levels lying in the gap between the valence and conduction bands of the O^{2-} lattice.[12] When oxygen is adsorbed on the oxide, we might suppose that, as a result of the interaction between the oxygen $2p$ orbitals and the valence band of the O^{2-} lattice, an anionic surface level is formed in the gap between the filled and empty bands. If this level is vacant, oxygen is adsorbed as the atom, but if the surface level lies below the occupied discrete cation levels, it will be filled by an electron from one of these levels. In this case oxygen is adsorbed as the O^- ion and a positive hole is formed in the oxide. This positive

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hole will probably be trapped on the lattice cation over which the O^- ion is adsorbed because of the favourable electrostatic environment there. This gives the picture of chemisorption with the formation of neutral pairs once again. The same picture is obtained if the surface level, instead of being anionic and lying below the discrete cation levels, is homopolar and lies above them. Evidently there is no difficulty in describing oxygen chemisorption with the formation of neutral pairs for Cu_2O where the simple band approximation is adequate, and for NiO where it is not.

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THIN OXIDE FILM ON THE METAL

We assume that, associated with each oxygen *ion* adsorbed, there is a surface level lying in the gap between the filled and empty oxide bands. For the transition metal oxides, these levels lie above the occupied discrete levels of the lattice cations. Let there be N_s such surface levels, and let N be occupied by electrons. N is the number of oxygen ions and $(N_s - N)$ the number of neutral pairs on the surface. With these definitions, and with the energy zero at the bottom of the empty band, eqn. (1)-(3) still hold, and the energy level diagram is that in fig. 1. The surface level lies below the Fermi level by an amount $\boldsymbol{k}T \ln [N/(N_s - N)]$, but this quantity will be negative if neutral pairs predominate. We have the Langmuir isotherm, eqn. (4), for the number of neutral pairs, and eqn. (5) is the adsorption isotherm for oxygen *ions*. Again $\theta \ll 1$ for film thicknesses greater than about 10 Å, but for p-type oxides the experimental evidence is that oxygen is adsorbed to complete surface coverage.[8, 11] This means that $Kp^{\frac{1}{2}} \gg 1$ so that the adsorption isotherm for ions degenerates to

$$\theta \exp (X\theta/\lambda) = \Gamma, \tag{12}$$

and θ is independent of the oxygen pressure.

The potential difference across the film is given by

$$\alpha \exp \alpha = (X/\lambda)\Gamma, \tag{13}$$

and since (X/λ) is large, we have the approximation

$$-eV \simeq \epsilon - \chi + \boldsymbol{k}T \ln (X/\lambda),$$

if $\Gamma > 1$. These equations have been used [10] to discuss the oxidation rate for the system Cu/Cu_2O within the framework of Mott's theory. For the system Ni/NiO, the fact that the cations are doubly charged means that a quartic law (rate proportional to X^{-3}) with the rate constant varying as $p^{\frac{1}{2}}$ replaces the cubic law for the oxidation of Cu. Some evidence for such a law is to be found in the experiments of Campbell and Thomas [13] and of Gulbransen and Andrew,[14] but more work on the oxidation of Ni is needed.

BULK OXIDE

Our picture of oxygen chemisorption is that for each oxygen ion adsorbed there is a vacant surface level lying above any normally occupied levels in the oxide. At temperatures above the absolute zero, some of these levels will be filled by electrons transferred from the interior. This gives a surface charge, and a space charge in the oxide. The surface charge is, however, very small. If ϵ is the depth of the surface levels below the bottom of the empty band, and χ is the depth of the Fermi level in the interior below this same energy zero, eqn. (1) and (2) hold, with N the number of oxygen ions and $(N_s - N)$ the number of neutral pairs. The Langmuir isotherm, eqn. (4), gives the number of neutral pairs, but eqn. (3) is replaced by [3]

$$\exp \alpha = (2\pi e^2 N^2/\kappa \boldsymbol{k}TM'), \tag{14}$$

where M' is the concentration of positive holes in the interior of the oxide. The

adsorption isotherm for *ions* is now easily derived as

$$\theta^3 = [Kp^{\frac{1}{2}}/(1 + Kp^{\frac{1}{2}})]\Gamma(\lambda M'/M).$$

With $Kp^{\frac{1}{2}} \gg 1$, we have

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$$\theta^3 = \Gamma(\lambda M'/M). \tag{15}$$

Γ in this equation has, of course, a different value from Γ in eqn. (12).

In eqn. (15), $\Gamma < 1$ if positive holes really are trapped at the surface when oxygen is chemisorbed. Thus, with $(\lambda M'/M) = 1{\cdot}5 \times 10^{-9}$, the fraction of the surface covered with ions cannot exceed about 10^{-3}. This means that the concentration of positive holes in the space charge region cannot exceed 10^{19} cm^{-3}, and eqn. (14), which is based on classical statistics, is valid, even though, as with Cu_2O, the positive holes are formed in the highest filled band. With NiO, classical and quantum statistics give the same results since the positive holes are formed in the discrete cation levels.

The coverage on a thin oxide film on the metal is given by eqn. (12), but here we must have $\Gamma > 1$ if a significant potential difference, such as is required in Mott's theory of oxidation, is to exist across the film. This means that with thin films, the adsorption as ions will exceed that on the bulk oxide. For example, with $\lambda = 0{\cdot}015$ Å and $\Gamma = 10$, we get $\theta = 10^{-2}$ for a film 10 Å thick on the metal, and $\theta = 10^{-3}$ for a film 100 Å thick. It is not obvious how this difference in the character of oxygen chemisorption on the composite system and on the bulk oxide might be detected, because in both cases the surface is completely covered with oxygen adsorbed as neutral pairs.

4. Conclusion

Our picture of oxygen chemisorption on an *n*-type semiconductor is that the main chemisorption occurs as ions with electrons transferred to the surface levels. On a *p*-type semiconductor, the main adsorption occurs as neutral pairs (oxygen ions and trapped positive holes) and most surface levels are vacant. We have indicated briefly how the required surface levels might arise in a molecular-orbital treatment of chemisorption. However, the first steps in such a treatment have only just been made, and so far no consideration has been given to chemisorption on an adsorbent consisting of a thin oxide film on a metal. It is clear from fig. 1 that such adsorbents might involve new features because the electronic structure of the system is considerably modified by the strong electric field across the film. Because of this, the nature of the bond between oxygen and the adsorbent must change as electronic equilibrium is established by electron transfer from the metal to the surface levels. A similar effect must occur on the bulk oxide as the space charge is built up. These effects are not important for our present purpose which has been to show how the basic ideas of Mott's theory of film growth, and those of the boundary-layer theory of chemisorption, are connected.

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