UNDERSTANDING OXIDE-METAL INTERFACES

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Abstract. One of the most important features of the interface between an oxide and a metal is the sharp change in dielectric constant between the two materials. This suggests that the stabilisation of charges (lattice ions and defect centres) in the non-metal by the polarisation of the metal may contribute strongly to the interfacial adhesion. This effect can be treated in classical electrostatics by the method of images. We present the application of this theory to the adhesion of bulk materials and to the properties of thin films and coatings. The predictions of the continuum theory are compared with atomistic calculations of interfaces. Finally, we consider how, in light of this theory, how interfacial adhesion can be influenced and controlled.

1. Introduction.

The interface between a metal and a non-metal is of vital interest in many areas of technology. For example, corrosion of metals depends on the stability, properties and adhesion of the growing oxide film. In catalysis, a metal may be supported by a high surface area ceramic. Clearly, adhesion and the stability of the high surface area form is important but even the catalytic properties of the metal can be influenced through the so-called strong metal-support interactions. In semiconductor technology, there are the obvious device applications but of potentially equal importance are the more mundane questions of packaging. Here the adhesion of metals with ceramics and other materials is crucial.

The theoretical treatment of such interfaces has inevitably lagged behind that of interfaces within a single class of materials such as metals or oxides. At an atomistic level, models have been developed that can predict the structure and properties of a wide range of surfaces and boundaries. Such a treatment of the metal-non-metal interface would certainly be of great value. However, approaching this task from the modelling of either the metal or, for example, the oxide seems unlikely to lead to much success. The potential models derived to describe the interatomic interactions in either the oxide or the metal are fundamentally different and quite inapplicable to the other material. A complete quantum mechanical description would be appropriate but is almost certainly intractable without oversimplifying assumptions. Instead, we have examined the fundamental characteristics of such interfaces to identify the dominant physical processes that contribute to adhesion.

One of the most striking features of almost all metal-non-metal interfaces is the large dielectric mismatch across the boundary. Thus, while a metal has a nearly infinite dielectric constant, a typical value for an oxide is around 10. Furthermore, the non-metal may have a high degree of ionic bonding and can almost certainly support charged defects and impurities. We argue, therefore, that a leading attractive interaction between the two materials can be described in terms of classical image interactions. This concept enables us to interpret such diverse phenomena as the wetting and non-wetting of oxides by liquid...
metals, the spatial variation in the stoichiometry of the oxide films grown on metals, the dependence on thickness of oxide film grown on silicon of the wetting of the film by water and some features of radiation enhanced adhesion. The theory has consequences for the stability of interfaces and how that may be influenced, the kinetics of high temperature oxidation etc.

2. Image Theory.

2.1 Simple interfaces.

If we consider any single planar interface with a dielectric mismatch \( \varepsilon_1 \) and \( \varepsilon_2 \) being the two dielectric constants, then the presence of a charge, \( Q \), in region 1, introduces an additional term in the interfacial energy \( E_{im} \).

\[
E_{im} = \left( \frac{Q^2}{4\varepsilon_1 a} \right) \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)
\]

where \( a \) is the distance of the charge from the boundary. We can see that if region 2 is a metal \( (\varepsilon_2 = \infty) \) then the additional term lowers the boundary energy and is attractive. If we consider a free surface for the non-metal, \( (\varepsilon_2 = 1) \), then the additional is repulsive and de-stabilises the surface. For adhesion, we are interested in the binding energy of the interface, \( W_a \),

\[
W_a = \gamma_{OM} - \gamma_O - \gamma_M
\]

where \( \gamma_{OM} \) is the interfacial energy; \( \gamma_O \) and \( \gamma_M \) are the surface energies of the oxide and metal respectively. The image term, \( E_{im} \), contributes to both \( \gamma_{OM} \) and \( \gamma_O \) and in both cases increases the adhesion of the boundary. Indeed for static charges, it is often the effect on the surface energy that is the more important. This is a general but often neglected point that one cannot assess the influence of defects or impurities on interfacial adhesion without considering both the interface and the free surfaces.

If we consider an ionic or partly ionic material being brought up to a metal surface, there are two sources of image attraction. Firstly, the ionic charges of the material will gain stabilisation through the proximity of the metal. Secondly, there will be additional attraction if charged defects or impurities are near the ionic surface. Note that in both cases, the effect is not dependent on the charge of the defect or ion but overall charge neutrality does reduce the total binding through the cross-terms between charges and their images. Physically, the simple image interactions represent the stabilisation of charges by a polarizable medium. Thus, the energy is lowered by the presence of the highly polarizable metal and raised near the unpolarizable vacuum of the free surface. At large distances, the classical image term gives a good representation of the attractive interaction. Indeed, this description seems to hold down to distances of around two Angstroms although there are the usual problems of identifying the position of the image plane \( (\delta) \). At closer distances, the overlap of electron density in the ionic material and the metal cannot be ignored and this provides the necessary balancing repulsive terms.

2.2 Thin oxide films.

In many cases of practical interest, we are concerned with coatings or the growth of thin films. Here the same principles apply but the simple continuum result must be generalized \( (\delta) \). We consider a three layer system with a thin region sandwiched between two semi-infinite regions. There are two cases illustrated in Figure 1. The first consists of the charges in the semi-infinite region 1 near two parallel dielectric interfaces. This might represent an oxide with a thin layer of metal on the surface and above that gas or vacuum. Following the methods of Smythe \( (\delta) \), we can show that the image contribution to the energy of the system, \( E_{im} \), is given by
CASE I

Figure 1: Three regions of differing dielectric constants with the middle region of finite thickness, L. In Case I, we consider the influence of charges in region 1; in Case II, the charge is in the finite region 2. After ref.5.

\[ E_{im} = \frac{Q^2}{2\varepsilon_1} \int_0^\infty dkA(k) \]

where

\[ A(k) = \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \exp(-2ka) + \left( \frac{2\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \frac{2(\varepsilon_2 - \varepsilon_3)\exp(-2ka)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)\exp(2kL) + (\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)} \]

where \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) are the dielectric constants of the three regions, \( a \) is the distance of the charge, \( Q \), from the interface and \( L \) is the thickness of the thin layer. Clearly, when \( \varepsilon_2 = \varepsilon_3 \), the expression simplifies to that for the single interface. We can generalize this expression to consider the interaction between two charges within region 1 (\(^6\)).

The second important case is also illustrated in Figure 1. Here the dielectric region containing the charges is the middle region 2. This might represent an oxide film or coating on a metal surface. Now the image contribution to the energy is given by,
3. Adhesion between bulk phases

3.1 The ideal lattice.

Let us start by considering the symmetry of the ideal interface between an ionic material and a metal. We can compare the charge interactions that lead to crystal cohesion in the perfect ionic crystal with that at an interface with appropriate image charges. Figure 2 illustrates this for an ionic crystal with the rocksalt structure, for example magnesium oxide. The top diagram shows the structure of the (100) direction in magnesia both continuing into the bulk and terminating at an interface with a metal. If the position of the image plane is half an oxide interplanar spacing from the oxide surface, the pattern of charges is identical to the bulk. Thus we would expect the adhesion of the interface to be close to the surface energy of the oxide. In the second example in Figure 2, we consider the (110) face of magnesia. Here, the pattern of ionic charges reflected in the metal is very different from the simple continuation of the bulk. Potentially, we could achieve much greater adhesion from this interface.

In order to quantify these ideas, we have calculated the adhesion using a simple atomistic model. In this model, we have represented the repulsive terms between the oxide and metal as a hard barrier to penetration of the oxide. Thus we have positioned the ionic material one oxygen ion radius above the
jellium edge of the metal. We have also placed the image plane to coincide with the metal surface/jellium edge. For the (100) surface we calculate an adhesion of 0.74 Jm\(^{-2}\) which compares with the surface energy of 1.1 Jm\(^{-2}\). The adhesion is lower in our calculation because our repulsive force prevents the ionic crystal getting to half a planar spacing from the jellium edge. The different sizes of the magnesium and oxygen ions enable the bulk structure to interlock and minimise the interplanar spacing. The calculated adhesion of the (110) surface is 1.33 Jm\(^{-2}\). Although this is larger than for the (100) surface, this is not due to the charge symmetry. We should expect the adhesion to be about twice that for (100) due to the much higher surface energy of the (110) surface. In fact, the calculated adhesion is relatively low because the ionic material cannot approach the image plane sufficiently closely.

Clearly, the example shows that the adhesion between an oxide and a metal is likely to depend on the crystal plane of the oxide. It also depends crucially on the spacing that can be achieved across the interface. This could be the origin of the lock-in structures suggested by Gleiter (6). Rather than gaining stability from the relatively small epitaxial interactions, such structures permit the maximising of the image interactions by minimising the interfacial separation.

3.2 The influence of defects.

Since charges in the non-metal contribute to the adhesion of the interface with the metal, introducing more charges should increase the adhesion. For an ionic material, intrinsic defects such as vacancies and interstitials carry charge as do most impurities. Experimental support for this idea comes from the data on the wetting of oxides by non-reacting liquid metals (7). The systematics of the data reveal two important results (8). Firstly, there is no correlation between the wetting behaviour and the van der Waals (dispersion) interactions that are often discussed. Secondly, the wetting appears to be determined entirely by the substrate non-metal with no dependence on the metal as long as it does not react chemically. However, there is a correlation between the wetting (which implies good interfacial adhesion) and those non-metals which can disorder or go non-stoichiometric. For example, NiO, UO\(_2\), and V\(_2\)O\(_3\) are all wetted while MgO, ThO\(_2\) and Al\(_2\)O\(_3\) are not. The disorder in the oxides provides a high concentration of defect charges and hence strong image interactions.

<table>
<thead>
<tr>
<th>Oxide Structure</th>
<th>Adhesion Jm(^{-2})</th>
<th>Fit to Adhesion 0.74 + 0.09Q + 0.15Q(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) Surface</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>(110) Surface</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>Q=-2 Ni vacancies at surface</td>
<td>1.14</td>
<td>1.16</td>
</tr>
<tr>
<td>Q=-1 Ni(^+) ions at surface</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Q= 0 Perfect surface</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>Q=+1 Ni(^{3+}) ions at surface</td>
<td>0.98</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 1: Energies of adhesion calculated from an atomistic model of oxide surfaces near a metal. The defect structures consist of a regular 1/4 coverage in the surface layer with deeper compensating charge.

We can use our simple atomistic model to estimate the consequences of high concentrations of charged defects in the oxide. The results are summarised in Table 1. The defect configurations considered are vacancies, ions of enhanced and reduced charge, all on the cation sublattice. This produces defect charges of -2, -1 and +1 respectively. Our model is a realistic description of nickel oxide with the latter two defect configurations involving Ni\(^{2+}\) and Ni\(^{3+}\) ions. In all cases the defect centres were introduced at a quarter coverage in the surface of the oxide with a sub-surface space-charge region of compensating charge. This provides a rather realistic defect distribution but because the image interaction is dipolar the additional adhesion is not as great as would be estimated by considering the charges individually. Qualitatively, the
results are as we expected with all defect distributions increasing the adhesion. Because of the defect interactions, the maximum effect on the adhesion may be produced by lower concentrations than we have considered here. An interesting observation is that although the more highly charged defect produces more binding than the singly charged centres, the results are not the same for the +1 and −1 charge cases as expected from the simple image theory. This is because in an atomistic model there are additional Madelung terms in the energy that effect the result. The Madelung terms are linear in the net defect charge, $Q$, while the image terms are quadratic. The table shows that the binding energies can all be fitted to an expression $(0.74 + 0.09Q + 0.15Q^2)$ Jm$^{-2}$ which allows for both contributions.

3.3 Atomistic surface calculations.

![Figure 3](image)

**Figure 3:** The calculated cation vacancy formation energy near the (100) surface of MgO compared with the classical image calculation. After ref. 9.

Although a complete lattice relaxation calculation using realistic potentials has not been achieved for an oxide-metal interface, the influence of the image interactions can be seen in calculations on oxide surfaces. This, of course, is still an interface between two regions of abruptly different dielectric constants and should show analogous behaviour. The most relevant case is the analysis of the vacancy formation in MgO near a free surface ($^\circ$). The calculation shows that to form a cation vacancy near a surface, three corrections to the bulk energy are needed. Firstly, there is a term arising because the Madelung potential in the outer surface layer is not the same as in the bulk. This represents a short-range term which no continuum treatment will handle. Secondly, there is a term which remains finite even at great depths from the surface, due to the dipole layer associated with rumpling of the outer layers of ions. Thirdly, there is a term corresponding to the image effects that we have been discussing. Figure 3 shows the comparison between the lattice calculation and the continuum image term. The continuum analysis describes the calculated situation well up to a few Angstroms from the surface.

Another example is given in Figure 4. Here we consider an interstitial defect in MgO which enables us to take the charge right through the surface. Within the crystal lattice, the calculation shows the influence
of the lattice structure as the interstitial moves through the lattice planes. Superimposed on this is the image repulsion that the defect feels in approaching the free surface. Outside the surface, the image effects operate in the opposite sense, attracting the charge to the interface. The most stable position for the ion is just outside the surface where both the image terms and lattice terms are optimised.

4. The Properties of Thin Films.
4.1 The oxidation of silicon.

Water does not wet the surface of pure silicon while once an oxide film of more than 40 Angstroms has grown the surface can be wetted completely. The data of Williams and Goodman (10) are shown in Figure 5 which indicates how the contact angle of the water varies with film thickness. Originally, there has been no convincing explanation for this variation but the phenomenon can be interpreted in terms of fixed charges present in the silicon substrate (11). The experimental data fall into two groups depending on the temperature of the measurement. They are shown separately in the Figure. The observed contact angle depends on the interfacial energy and on the surface energies of the oxide and water. The first two of these are influenced by the presence of charges in the silicon. The observed variation in contact angle reflects the changing influence of these fixed charges as the oxide film grows thicker. In fact, the data can be very well fitted by a density of charge of a few times $10^{13}$ per square centimetre just below the surface. An
Figure 5: The variation of the contact angle of water on the surface of oxide grown on silicon as a function of oxide film thickness. The circles and triangles are experimental measurements (10) and the lines are calculated from the image theory. After ref.11.

optimal fit is obtained with the charges 3.2 Angstroms below the surface at high temperature and at 5.4 Angstroms for the low temperature case. These charges may well be $F^-$ ions left from the etching silicon by HF. The exact details of the fit are less important than the interpretation of an unexplained phenomenon in terms of simple and plausible image effects.

4.2 Cabrera-Mott theory.

In oxidation, both the rate of oxidation and the rate-limiting process depend on the thickness of the oxide. Interfacial processes, like chemical reactions, limit growth for very thin films, giving the linear regime. Diffusion controls growth for thick films, giving the parabolic regime. At intermediate thicknesses, perhaps a few nm, Cabrera and Mott (12) proposed that injection of ions into the oxide films is rate-determining, giving a characteristic near-logarithmic growth law. In their model, injection is controlled mainly by the electric field set up across the oxide by adsorbed charges at the oxide surface. This field, which enhances the injection rate, is taken to have the form

$$E = V/x$$

with $x$ the thickness and $V$ given by the difference between the metal work function and the electron affinity of the adsorbed species. Charge is transferred until the gain in energy in moving from the metal Fermi level to the molecule is balanced by the work done against the electrical field set up by the electrons which have transferred to species adsorbed at the gas-oxide interface.

Image terms have three main effects on oxidation in the Mott-Cabrera regime (5). First, the energy gain on adsorbing a charged molecule is increased for thinner films by the proximity of the metal. Secondly, there is a stabilisation because the delocalised electrons in the metal become localised electrons after
transfer. Thirdly, charged ions injected into the oxide are themselves subject to an image term affecting their motion. These terms are all ones which would be small for thicker oxides, but which cannot be ignored for the thinner oxides of the logarithmic regime. They have qualitative differences too. Thus the polarisation-driven motion within the oxide film speeds oxidation for the inward motion of oxygen ions, but enhances the outward motion of metal cations, so that the change in rate depends on the mobile species.

The demonstration of effects from image terms presents problems, mainly because most experimental results are presented in forms which do not aid tests of mechanism. One useful comparison is to look at plots of oxidation velocity \( v = (dx/dt) \) versus thickness, rather than the standard \( x \) or \( x^2 \) versus \( t \). If presented in terms of the velocity and thickness normalised to their values \( v_0 \) and \( x_0 \) at some reference time, then the qualitative shape of the curve is quite different for the Mott–Cabrera case and for the standard linear/parabolic (or Deal–Grove) case. Moreover, there is a dimensionless parameter, the logarithmic derivative of the normalised velocity with respect to the normalised thickness, which is bounded by 0 and 1 if the oxidation is limited by diffusion and interface limited processes, but which is observed to lie well outside this range whenever other mechanisms are found. There is little doubt that careful measurements should distinguish between the control of injection by the Cabrera Mott field and the standard diffusion and reaction control, with a significant effect of image terms on the parameters deduced. (13).

4.3 Consequences for oxidation

The effects of image terms on oxidation, other than those just discussed on injection, are of several types, affecting the defect nature and population within the oxide, the motion of charged ions, and the extent to which the oxide remains in intimate contact with the metal (section 5).

Consider first the nature and numbers of defects in the oxide. Close to the metal, there is a significant energy advantage in having ions with high charges, since these can gain polarisation energy. In oxides like NiO or CoO or FeO, the proportion of ions in the higher (3+) oxidation state should be greater adjacent to the metal. This is observed (14–15). There is a corollary: the oxide immediately adjacent to the metal should be oxygen-rich, not metal-rich as one might first think. Close to the surface of the oxide, however, there will be a polarisation energy advantage in neutral species (neutral relative to the perfect lattice for substitutional species, apart from the adjustment for the altered surface Madelung potential). So vacancy charge states may be different, a point noted elsewhere in the removal of colour centres from microcrystals.

Clearly, any such change of charge state for those ions which are mobile will affect the oxidation rate. This will happen both because the ionic mobility is usually charge-state dependent and because of the Mott–Cabrera field. A further effect relates to the charge transport that may take place along with ionic motion. Even in oxides for which the carriers are large polarons (most oxides for which the cation does not readily change charge state) the polarisation energy gain on localising a carrier near to a metal substrate could suffice to stabilise the small polaron form. This would, of course, dramatically affect carrier mobility. We know of no examples where the effect has been seen, but it should be observable in transport in thin films.

5. Consequences for Adhesion.

Given the role of image terms in adhesion, the natural question asked is whether the charges can be modified so as to enhance adhesion (or perhaps to reduce it). There are two main methods by which this can be done, namely radiation-enhanced adhesion and electrostatic bonding. In both cases there are several contributing phenomena. One is morphological: when there is an electric field across an interface, there is an energy gain by deforming the interface to eliminate air-filled regions. Another is the issue of chemical reactions; this will lie outside our discussion, if only because even after a reaction has occurred one still has to explain the adhesion of the product with its adjacent phases.
5.1 Radiation enhanced adhesion.

Since 1984 there have been tens of studies of the effects of ion beams on interfaces and especially on adhesion. These studies have been conducted largely in the regime in which there is no ion-beam mixing across the interface. Yet in many cases there is good evidence for significantly enhanced adhesion. Some such cases — notably involving metal-polymer or polymer-polymer adhesion — it is likely that the effect of radiation is the production of free radicals, with subsequent reactions which lead to adhesion in a reasonably clear way. For other systems, however, the role of image charges seems probable (1) and is, to our knowledge, the only explanation of some of the data. A full interpretation remains difficult, however, for the data available are often in the form of qualitative tests: the Scotch tape (or Peel) Test, for instance, which checks if adhesive tape will strip the metal from a non-metallic substrate, or the Cotton bud abrasion (or Rub) test, which checks how easily the metal can be wiped off.

The most interesting examples are those where a non-reactive metal (like Au; cases like Cu or Ag are often regarded as relatively non-reactive, whereas Al or such transition metals as Fe are clearly reactive) is encouraged to adhere to an oxide like MgO or alumina. The features which suggest a charged-defect contribution (and hence an image contribution) are these. First, in many cases nuclear energy deposition is involved: it would seem that point defect creation is either useful or necessary. Secondly, electronic processes are also involved, for there is dependence on the electronic stopping power, so that charge transfer among the defects may play a role. Thirdly, there is dependence in some cases on the film thickness, though this is less reproducible or clear-cut. Fourthly, there are aging effects, in which the strength of the binding depends on the delay between processing and testing. This suggests diffusional processes, though it is not clear if it is ionic or electronic charge which is moving. Fifthly, heat treatment affects the adhesion after radiation. Again, the effects are consistent with defect processes which (in most cases) lead to improved binding. The broad conclusion is, therefore, that radiation-enhanced adhesion arises principally from the creation of charged defects in the non-metal close to the metal/non-metal interface.

5.2 Electrostatic bonding.

A related approach is used widely in the electronics industry, especially for the bonding of non-reactive metals to glasses and glass ceramics. In this, the metal is placed against the glass, and an electrostatic field applied such that the metal forms the anode (hence the alternative name anodic bonding). After a period of time the field can be removed, leaving a formed bond. One of the processes involved is certainly the morphological effect mentioned at the start of the section, which ensures intimate contact over more of the interface; this effect is also aided by the electrolysis of asperities. There is, however, a second component. Here charged defects in the silicate network move towards the interface, and they will do so as to contribute an image term, raising adhesion. It is interesting to contrast this with the effect at the cathode: mobile alkali ions move to the cathode where, in principle, they might aid adhesion; instead, they react with moisture to produce hydroxide, which easily breaks. Here there is another parallel with radiation enhanced adhesion: NaCl on a silica substrate loses chlorine under irradiation, leaving sodium, which again forms only a weak hydroxide link.

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References.

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(6) H. Gleiter, J de Physique 46 (1985) C4-393.
N.W. Ashcroft. The question has to do with the use of microscopic vs macroscopic fields. Your energy was Fourier decomposed, but macroscopic dielectric constants were apparently used for all wave-vectors. This would be reasonable if the energy was dominated by small values of k in the Fourier decomposition. The issue is: what length scales are important?

P. Tasker. When you calculate the polarization around a charged defect in an ionic material, the effect falls off slowly with distance and a significant contribution to the energy comes from large distances. [The polarization contribution only falls off as \( R^{-1} \)]. In atomistic calculations, you cannot explicitly model a large enough region to accurately obtain the defect energy and you must match to a continuum described by a macroscopic dielectric constant. Indeed, you can get a good estimate of the vacancy energy (for example) by having a very small inner region (e.g. 1 atom) and using the dielectric constant to calculate the polarization, as was done at least 50 years ago. When an interface is present, you must allow for detailed interface structure affects in the energy. This effect is rather short range. The calculation of the vacancy near an oxide surface (Fig. 3) shows that the atomistic calculation agrees with the continuum estimate after about 7 planes from the surface, and is qualitatively in agreement from about 3 planes.

J.M. Blakely. Could you comment on how a step on the ionic surface would contribute to the image contribution to bonding? This may be of interest in explaining the effect of roughness on interfacial adhesion.