

LETTER TO THE EDITOR

Metal–non-metal and other interfaces: the role of image interactions

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Abstract. We argue that many phenomena associated with metal/non-metal interfaces and similar situations with a large dielectric constant mismatch can be understood in terms of the image interactions due to charges in the non-metal. The effects are additional to the traditional interactions, and are especially significant when no reactions between the phases occur. The image-charge concept allows us to rationalise much apparently unrelated information concerning: (a) the systematics of wetting and non-wetting of oxides by liquid metals; (b) the systematics of strong metal-support interaction in catalysis; (c) the spatial variation of stoichiometry in oxides grown on metals; (d) the dependence on thickness of the observed changes in the wetting by water of oxide grown on silicon; (e) some features of radiation-enhanced adhesion; and (f) a number of correlations of behaviour with non-metal properties in which the precise choice of metal is not critical.

The idea of an image charge is long established. If there is a planar boundary dividing space into two regions of different dielectric constant ϵ' , ϵ'' (e.g. metal/non-metal, vacuum/solid, liquid/solid) then the polarisation energy of any charge will be affected by the existence of the boundary. In a simple case, the effect on a charge in region I can be represented by imagining region I extended to fill all space, but including interaction with an image charge whose magnitude depends on both the actual magnitudes of the dielectric constants (ϵ' in I, ϵ'' in II) and whose position is the mirror image of the charge, regarding the boundary as a reflecting plane (Smythe 1939, Landau and Lifshitz 1960). Thus, at distance z from the boundary, a charge Q causes an image term

$$U(z) = (Q^2/2z\epsilon')(\epsilon' - \epsilon'')/(\epsilon' + \epsilon'')$$

thus lowering the energy near a metal (ϵ'' infinite (Landau and Lifshitz 1960, p 40)) and increasing the energy near a vacuum (ϵ'' unity). This simple expression does not cover all cases we shall need, though the other cases can be obtained by standard means (see Smythe 1939). Nevertheless, the equation and its generalisations have been applied widely in situations as varied as electron motion near interfaces, electron–phonon coupling in inelastic tunnelling, and many instances of classical electrostatics. Our application is different, and appears to be far reaching in a wide range of interface behaviour. We note that the change in polarisation energy due to the boundary (which we may call loosely the image energy) affects the interfacial energy too, i.e. the energy needed to cleave the two dielectrics at the boundary depends on charges present near the interface. This simple feature allows us to rationalise a large number of observations. A full comparison will be given in later papers; for the moment we give an overview.

We consider first metal/non-metal adhesion. In some cases this is well understood, with major contributions from chemical reactions and the formation of interfacial compounds. In such cases the image contribution, whilst present, will be hard to isolate. In the case of non-reactive, especially noble, metals, we believe the image terms provide a significant part of the adhesion. Consider first the broad order of magnitude, for a charge Q in a medium of dielectric constant ϵ' adjacent to a medium of dielectric constant ϵ'' (ϵ'' is infinite for a metal, unity for the vacuum) at distance z from the boundary. For $\epsilon' = 10$, $z = 2 \text{ \AA}$ and $Q = 1e$ the image interaction energy is 0.18 eV; if we were simply to superpose 10^{15} such charges per square cm, there would be an energy 290 erg cm^{-2} of increased binding. Moreover, since this energy is quadratic in Q (and clearly independent of the sign of Q) and since the outermost layer of ions in the non-metal is more like 1 \AA from the image plane, midway between the boundary planes of metal and non-metal, these terms can easily approach the magnitude of typical energies of adhesion, i.e. $500\text{--}1500 \text{ erg cm}^{-2}$. Of course, we should not merely superpose contributions at such high densities. Nevertheless, we can reach the same conclusion in another way. Consider a lattice of ions adjacent to a metal (for present purposes we may ignore the metal's atomic structure; see Stoneham (1981) for further discussion; we shall also ignore any lattice relaxation for the present). This will generate a lattice of image charges. The precise relation of the image charge lattice to that of the original ions depends on both the lattice structure and the choice of boundary plane. There are at least five distinct classes of such continuation, which we shall discuss elsewhere. The simplest is for a (100) plane in the NaCl structure, where the images simply continue the existing ionic lattice. The interfacial energy from image charges is readily seen to be equal to the (unrelaxed) surface energy, i.e. again of the order of observed interfacial energies.

Experimental support comes from the tabulated data of Naidich (1981), and especially from the data for the wetting of oxides by non-reacting liquid metals surveyed before by one of us (Stoneham 1982/3). Our analysis showed two clear results. First, the van der Waals (dispersion) interactions often discussed gave a miserable description of the wetting behaviour overall. Secondly, the wetting appeared to be determined entirely by the substrate non-metal, i.e. there was no dependence on metal provided it was not chemically active. Stoneham noted a correlation with optic dielectric constant. Our reanalysis of the same data (to be described further elsewhere) shows an equally good separation of wetting and non-wetting cases as follows. Wetting occurs when either (a) the ions are ones which can readily change valence or (b) the static dielectric constant exceeds a critical value of about 25. Just these conditions correspond to a high degree of non-stoichiometry or disorder: NiO, UO₂ and V₂O₃ are wetted, whereas for example MgO, ThO₂ and Al₂O₃ are not. The disorder provides high concentrations of defect charges and hence strong image interactions. The same oxides can further enhance their image interactions by valence changes on one sublattice, since the image interaction is quadratic in charge Q . In NiO 2Ni^{2+} going to Ni^{3+} plus Ni^{+} increases the sum of $Q \times Q$ from 8 to 10, i.e. a 25% increase per ion pair.

Further evidence comes from other phenomena, though it is less direct and is included mainly to indicate the implications of the concept of image interactions as a significant part of the interfacial energy. First, as noted before (Stoneham 1982/3), the empirical rules just mentioned for wetting by liquid metals also apply to the existence of strong metal-support interaction in catalysis; as we shall discuss elsewhere, both the previous and new rules appear to work well. It is widely believed that strong metal-support interactions are partly associated with the geometric form the supported metal catalysts adopt on the substrate. It is interesting to note therefore that the way in which the

morphology of metals evaporated onto surfaces evolves (e.g. islands or layers: see Venables and Spiller 1983) depends on the substrate in a way which correlates with and so could perhaps be associated with image terms. Cases where there are no likely image terms form layers (e.g. rare gas atoms adsorbed on graphite) and ones where image terms are possible (e.g. Au on alkali halides) form islands. One important and intriguing case is Al on GaAs, where the most plausible interpretation of the rapid development of the full Schottky barrier height at very low coverages (Zunger 1981, Margaritondo and Franciosi 1984) proposes Al island formation. Metal adhesion to glass introduces another factor, for the image charge term is enhanced by the presence of mobile ions in the framework (typically borosilicate). When a metal is deposited, the image terms attract the mobile ions (e.g. alkalis). This is reversible in principle, i.e. slow removal of metal would allow relaxation back to the distribution in which mobile ions are repelled from the vacuum interface by image terms. Fast removal of metal, as in fracture, needs a high energy, since it would result in a particularly alkali-rich, unstable surface.

Image terms influence interface energies whenever there is a change in dielectric constant across the boundary. What appears to be a clear example can be seen from the work of Williams and Goodman (1974), who observed that when one grew oxide on Si, the wetting angle for water on the outer surface of the oxide changed from non-wetting for no oxide to wetting for oxide a few tens of angstroms thick. We find (see figure 1;

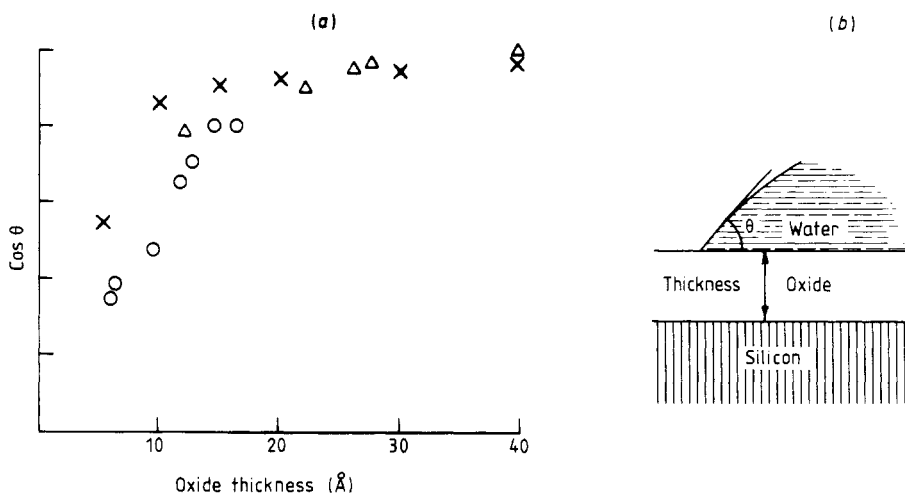


Figure 1. (a) Variation of $\cos \theta$ ($\theta =$ contact angle) for water on a layer of oxide on Si. Experimental data (O, room temperature growth; Δ , 600°C growth) from Williams and Goodman (1974) and theory (x) from our present work, assuming the effect is entirely that described in the text. (b) Geometry to define contact angle and oxide thickness.

details to be given elsewhere) that the variation of contact angle with thickness can be explained quantitatively by assuming charged defects in the oxide; good agreement, possibly not unique, is found for a defect of charge $|e|^2 \text{\AA}$ below the oxide/vacuum interface every 27 surface SiO_2 units. In this case, of course, the electrostatic problem goes beyond the simple method of images. Whether or not the charges needed to explain wetting are the same as the fixed charges known to be formed in the thermal oxidation of Si remains to be seen.

The charges responsible for the image interaction may be of several kinds. They may

be fixed charges, whether the normal components of an ionic lattice or immobile defect charges; they may be defects created (either by ionic reorganisation or by charge transfer) to establish equilibrium in the presence of an interface; or they may be mobile charges, as in our discussion of metal–glass adhesion. We now look at a variety of systems which appear to show the influence of image terms on the defect populations (and hence indirect effects on other behaviour).

One clear example is the atomistic modelling of oxide–vacuum interfaces by Duffy *et al* (1983). They showed that the vacancy formation energy had a characteristic dependence on depth from the surface, dominated by two terms: (a) the very localised effect from the altered Madelung energy, which affected essentially the outer layer only; and (b) an image term, falling more slowly with depth, which raised the energy needed to create charged defects, irrespective of charge. As noted previously (Stoneham and Tasker 1984), the energy can be reduced if trapped carriers are available. In particular, for anion vacancies in MgO, where a single trapped electron gives the F^+ centre (net charge $+|e|$) and a second trapped electron gives the neutral F' centre, the energy falls as electrons are moved to the outer region to give F'' centres; in principle, this can be done optically, and indeed one can identify several cases where adhesion might be improved optically. In fact, electron transfer to the outer layers may occur anyway under normal thermal conditions. This is suggested by the observations of Elovich kinetics for oxygen adsorption on neutron-irradiated MgO microcrystals (Nelson *et al* 1968), where the decay of surface (F_3^+) and bulk (F^+) centres was monitored by spin resonance. The Elovich kinetics show (Low 1960) that adsorption becomes increasingly slow, beyond the effects of site blocking, with increased coverage; the precise numbers in this case also showed an apparently excessive initial F^+ centre concentration. This can be rationalised by assuming (a) an initially uniform distribution of anion vacancies (irrespective of whether electrons are trapped; strictly, we need only the absence of a surface excess of vacancies); (b) adsorption limited by electron transfer from traps to oxygen molecules to give adsorbed $(O_2)^-$; and (c) the electrons preferentially trapped at vacancies near the surface because of the reduced image energy. The rapid depletion of the electron-rich near-surface centres would imply both the fall-off typical of Elovich kinetics and the apparent high initial concentration.

In the last example, as indeed in our discussion of silicon oxidation, charged defects were discouraged near to a dielectric/vacuum interface. The image terms do encourage charged defects near to dielectric/metal interfaces, however, a point noted in other contexts by Duffy and Stoneham (1983) and by Harrison (1976). This feature also allows one to understand the otherwise puzzling results reported for non-stoichiometric oxide growth on metals. The conventional description of oxide growth suggests, naturally, that the oxide close to the metal would be relatively metal-rich, and that close to the oxide/gas interface relatively oxygen rich. In fact, data for both Ni (Dose 1983) and Fe (Sakisaka *et al* 1984) show the oxygen-rich M_2O_3 forming adjacent to the metal, albeit for a very thin region. This is readily rationalised by the image terms, since the higher charges present ($+3$ in M_2O_3) take advantage of the Q^2 dependence of the image energy. The situation is somewhat different from the Si oxidation discussed earlier, both in the disposition of the charges and in the precise energies involved, but the parallels are considerable. Clearly in the case of a thin oxide layer the image term is inhomogeneous, and structures which change from one atomic plane to another can emerge.

The striking enhancement of adhesion, induced by radiation, between solids normally showing little or no adhesion, also finds a possible explanation in terms of the image contribution to adhesion. In some cases, of course, the explanation could well be

different, e.g. for polymer substrates, adhesion may involve reactions with free radicals induced by bombardment. Nevertheless, for ceramic substrates, there are strong suggestions of an image component. All cases seem to need some degree of nuclear energy deposition, i.e. defect formation, with electronic energy deposition often an aid. Thermal treatment, which would allow redistribution of carriers so as to aid adhesion, can have pronounced effects. Adhesion is effective in those cases where electrical contact remains diode-like (e.g. Au on n-GaAs, Tombrello 1984) but weak when ohmic contact is obtained, and presumably there is a sufficiency of carriers near the interface to negate the effect of the boundary (e.g. Au on p-GaAs, Tombrello 1984). One anticipates that irradiation prior to metal deposition might aid adhesion, though this may be hard to separate from the established ion-beam and plasma cleaning phenomena.

Finally, we remark on a smaller consequence of image terms which may, nevertheless, be of importance in barrier heights. This is associated with the surface rumpling, i.e. the extent to which the anions move out relative to the cations. Tasker (1982) has given a general argument suggesting, in agreement with other work, that the rumpling is positive at a free surface. It is straightforward to generalise the argument to include image terms, and to show that the replacement of the vacuum by a metal enhances the outward anion motion. The rumpling leads to a dipole which makes it harder to move an electron from the metal to the oxide.

We have argued that image interactions provide a substantial term in interfacial energies, especially metal/non-metal energies of adhesion. Moreover, careful attention to image terms allows one to rationalise a wide variety of interfacial phenomena. We do not suggest, of course, that these contributions are the only ones; they are additional to terms discussed previously by us and by others. The image terms do, however, have a particularly simple conceptual form, and appear to vary considerably from case to case. We are aware of a number of potential experimental tests and of a range of applications based on these ideas.

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