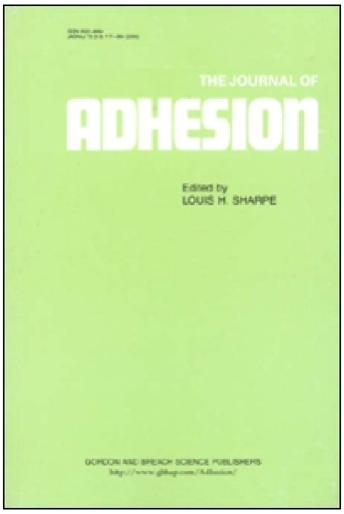

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Simple Views on Metal/Oxide Interfaces: Contributions of the Long-Range Interactions to the Adhesion Energy*

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The image and van der Waals contributions to the metal/oxide work of adhesion are compared through the extent to which they follow the known prevalent trends, *i.e.* the increase in work of adhesion (a) with narrowing oxide band gap and (b) with increasing conduction electron density of the metal. The van der Waals interaction is shown to follow both trends, while the image term is suggested to be significant only for dense metals in contact with very ionic oxides. The relative contribution of these long-range interactions to the overall metal/oxide work of adhesion is found to be maximized for systems involving metals with low electronic densities and oxides with wide band gaps. At variance, high metallic electronic densities and narrow oxide gaps likely favour short-range interactions arising from charge transfer.

KEY WORDS: Work of adhesion; metal/oxide interface; van der Waals interaction; image interaction; short-range interaction; dielectric constant; band gap; conduction electron density.

1. INTRODUCTION

Metal/oxide interfaces are encountered in many technological areas such as electronics, optics and the glass industry. One of the most striking questions arising about both the manufacturing process and lifetime of devices including these interfaces is the understanding of adhesion properties. For non-reactive interfaces, the existing models suggest that the metal/oxide adhesion is dominated by a unique long-range contribution but disagree about its nature. McDonald and Eberhardt[1] and Naidich[2] favour van der Waals (vdW) interactions on the basis of a pair interaction model. At variance, Stoneham and coworkers[3,4] support the idea that the prominent interaction at non-reactive metal/oxide interfaces is due to the image term arising from the polarization of the metal by the Madelung field of the oxide. The crux of the question is that adhesion is brought about through several conflicting contributions, so that it is quite difficult to unravel the role played by each of these in the phenomenon as a whole.[5]

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Therefore, trends in work of adhesion (WA) are believed to offer better criteria of comparison than absolute values of WA.

Several correlations between metal/oxide WA and parameters characteristic of the two media in contact have been proposed. In fact, as shown in the following, these correlations belong to two categories which suggest the existence of two main trends in metal/oxide WA. A simple classifying rule was suggested by Stoneham.[6] He has observed that the WA of a given metal on various oxide substrates increases with increasing oxide refractive index, *n*, or, consequently, with increasing values of the high frequency limit, $\varepsilon_{O\infty} = n^2$, of the dielectric function. Furthermore, it can be derived from the Lorentz form of the dielectric function that wetting behaviours could be classified[6] according to the ratio $\Delta/\omega_{pO} = [\varepsilon_{O\infty} - 1]^{-1/2}$, where $\omega_{pO} = (4\pi ne^2/m)^{1/2}$ is the oxide plasma frequency and Δ is the energy difference between the centroids of the valence and conduction bands.[7,8] The expectation is an increase in WA with decreasing Δ/ω_{pO}. Alternatively, a classifying parameter can be Δ only, since ω_{pO}, which depends on the density of valence electrons in the oxide, is almost constant (close to 20 eV)[9] for most oxides (The quantity Δ is more appropriate than the band gap δ – which is the energy difference between the band edges – to the description of electronic excitations between valence and conduction band. However, the gap energy, δ, of the oxide can also be correlated[2,10] with the metal/oxide WA). This trend, which characterizes the oxide substrate by means of either the high frequency limit of the dielectric constant (the refractive index) or the energy difference between the centroids of the valence and conduction bands, is herein labelled trend A.

Another correlation has been observed which relates to dependence on the metal. From a series of experimental values of metal/alumina WA, Eustathopoulos *et al.*[11,12] inferred that the WA is in inverse ratio to the atomic volume of the metal. Supported by an atomistic simulation of Finnis,[13] this trend can be expressed by saying that, on a given oxide, the adhesion is favoured for those metals having a high conduction electron density.[10] It is labelled trend B in the following.

The goal of the present work is to compare the contributions of the image and vdW interactions with the overall WA at metal/oxide interfaces through the extent to which these quantities follow the above general trends. To describe the behaviour of the image term, the oxide is represented by a charge distribution. The vdW term is calculated[14] by means of a continuum dielectric model.[15] A more general approach of the metal/oxide adhesion is then sketched in the discussion.

2. CONTRIBUTIONS FROM LONG-RANGE FORCES TO METAL/OXIDE ADHESION

The Image Contribution

The image contribution to a metal/oxide interface energy arises from the interaction of the ionic charge distribution, ρ_{ion}, with the part of its own Madelung field that is reflected at the interface. In classical electrodynamics, this reflected field can be regarded as being due to a fictitious image charge distribution, ρ_{image}, located in the metal. The ionic charge distribution, ρ_{oxide}, of the oxide can be related to ρ_{image}

as follows:

$$\rho_{\text{image}}(\vec{r}') = \frac{\varepsilon_{O\infty} - \varepsilon_M}{\varepsilon_{O\infty} + \varepsilon_M}\rho_{\text{oxide}}(\vec{r}) \quad (1)$$

where $\vec{r}'$ is the symmetric of $\vec{r}$ with respect to the interface plane and ε_M is the dielectric constant of the metal.[16] The image contribution, $W_{\text{adh}}^{\text{im}}$, to the metal/oxide WA, which is given by the energy of interaction between the ion distribution and the fictitious image charge distribution, can be written in the form

$$W_{\text{adh}}^{\text{im}}(\text{M},\text{O}) = \frac{1}{2\varepsilon_{O\infty}}\int d^3\vec{r}d^3\vec{r}'\rho_{\text{oxide}}(\vec{r})\rho_{\text{image}}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|} \quad (2)$$

In such a model, since the interaction potential between the ions and their images is in inverse ratio to the high frequency limit, $\varepsilon_{O\infty}$, of the dielectric constant (Eq. (2)), the energy, $W_{\text{adh}}^{\text{im}}(\text{M},\text{O})$, decreases with increasing values of this dielectric constant or, in other words, with narrowing Δ (of course, this does not show up if the static dielectric constant is always taken equal to 1, irrespective of the differences between oxides). This trend, which is the exact opposite of the trend A, is reinforced by the fact that the absolute values of the net charges on the oxide ions decrease with increasing polarisability of the oxide, *i.e.*, again, with decreasing gap energy.[17]

In the simplest description of the metallic medium, the dielectric constant, ε_M, is taken equal to ∞, yielding $\rho_{\text{image}}(\vec{r}') = -\rho_{\text{oxide}}(\vec{r})$ (Eq. (1)). This indicates that the Madelung field is totally reflected at the interface. However, the description of all metals as perfect electrostatic mirrors does not introduce any distinction between metals. This is due to the fact that the spatial dispersion is neglected. To understand the role of the wave vector dependence of the dielectric function, let the metal dielectric function be described, for example, by means of the well-known Lindhard expression:[18]

$$\varepsilon_M(\vec{q}) = 1 - \frac{4\pi e^2}{q^2}\chi_M(\vec{q}) \quad (3)$$

with

$$\chi_M(\vec{q}) = \left(\frac{-4mk_F}{\hbar^2}\right)\left\{\frac{1}{2} + \frac{1-(q/2k_F)^2}{2(q/k_F)}\text{Log}\left|\frac{q+2k_F}{q-2k_F}\right|\right\} \quad (4)$$

where e is the electronic charge, m is the electron mass and k_F is the Fermi wave vector which is defined by $k_F = (3\pi^2 n)^{1/3}$, where n is the electron density of the jellium. In such a model, the susceptibility, $\chi_M(\vec{q})$, vanishes for $q > 2k_F$, indicating that the metal does not polarize under short wavelength external charge fluctuations. If, in reciprocal space, one considers both the Fourier components of the charge distribution which mimics the (periodic) oxide and the dielectric susceptibility of the jellium metal (Fig. 1), the extent to which an oxide Fourier component is reflected at a metal/oxide interface is directly determined by the dielectric susceptibility of the metal at the corresponding wave vector.[18]

In Figure 1, the Fourier components corresponding to the cubic lattice of the magnesium oxide, MgO, are shown along with a series of Lindhard dielectric susceptibilities. As a result of the rapid decrease of the quantity $\chi_M(\vec{q})$ for $q > 2k_F$, the coupling

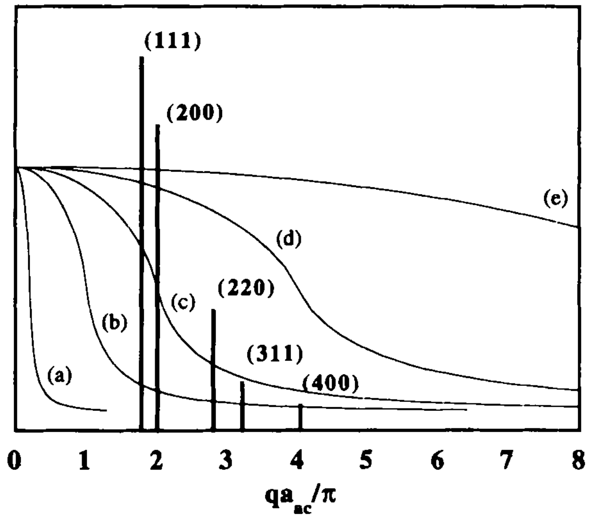

FIGURE 1 In reciprocal space, Fourier components of the ionic charge distribution of MgO and Lindhard dielectric susceptibility curves for various values of the Fermi wave vector, k_F: (a) $k_F = 0.1\pi/a_{ac}$; (b) $k_F = 0.5\pi/a_{ac}$; (c) $k_F = \pi/a_{ac}$; (d) $k_F = 2\pi/a_{ac}$; (e) $k_F = 5\pi/a_{ac}$ (a_{ac} is the oxygen-cation nearest-neighbour distance, which is 2.1 Å in the MgO case).

between Fourier components and dielectric susceptibility depends strongly on the Fermi wave vector. As shown in Figure 1, for small values of k_F, the region of the reciprocal space where oxide Fourier peaks appear corresponds to low values of the dielectric susceptibility. The poor reflection of the Fourier components by the metal thus leads to a weak image interaction (Fig. 1a). When k_F increases, the image term becomes more effective since there are more Fourier peaks to fulfill the condition $q < 2k_F$ (Figs. 1b to 1d). Finally, the perfect electrostatic mirror limit is reached for $k_F \rightarrow \infty$ (Fig. 1e). Therefore, consistent with the calculation of Duffy *et al.*,[19] the present qualitative approach shows that spatial dispersion weakens the reflected potential and its interaction with the ionic distribution. In addition, Duffy *et al.*[19] clarify to some extent the connection between the image interaction and the position of the image plane. They demonstrate that accounting for the short-wavelength fluctuations in the direction perpendicular to the interface is equivalent to shifting the image plane into the metal.

For representative metals, the quantity k_F ranges between 0.65 Å^{-1} (cesium) and 1.75 Å^{-1} (aluminium).[18] Therefore, the cases illustrated in Figures 1b to 1d are rather realistic. Now, since the coupling between the Fourier components and the dielectric susceptibility strengthens very much along that 1b–1d series, the image term $W^{\mathrm{im}}_{\mathrm{adh}}(\mathrm{M, O})$ is expected to increase for dense metals – *i.e.* to follow the trend B.

The van der Waals Interactions

To our knowledge, the only formalism that yields an analytic expression of the vdW interactions at metal/insulator interfaces (semi-infinite media) is the dielectric continuum model due to Barrera and Duke.[15] Assuming that each medium is characterized by a nonlocal dielectric function, these authors have expressed the interface energy as a difference between the zero-point energies of interface and bulk collective excitation modes. The vdW contribution, $\gamma_{1/2}^{\mathrm{vdW}}$, to the interface energy between media 1 and 2 is thus derived by subtracting both the energies of the bulk longitudinal modes, $\omega_{pi}(i = 1$ or $2)$, given by $\varepsilon_i(\omega_{pi}) = 0$, and those of the transverse modes, ω_{ti}, given by $\varepsilon_i(\omega_{ti}) = \infty$, from the interface mode energies, ω_{pint}, which satisfy $\varepsilon_1(\omega_{\mathrm{pint}}) + \varepsilon_2(\omega_{\mathrm{pint}}) = 0$ and whose degeneracy is consequently 2 in the present continuum model. Neglecting plasmon damping, this vdW interface energy is written in the form

$$\gamma_{1/2}^{\mathrm{vdW}} = \frac{\hbar q_c^2}{16\pi}(2\omega_{\mathrm{pint}} - \omega_{p1} - \omega_{p2} - \omega_{t1} - \omega_{t2}) \tag{5}$$

The parameter q_c is a cutoff wave vector characteristic of the solids in contact, which can be viewed as the wave vector for which plasma excitations enter the continuum of single-particle excitations. By means of Drude and Lorentz models for the metal (M) and the oxide (O), respectively

$$\varepsilon_{\mathrm{M}}(\omega) = 1 - \omega_{p\mathrm{M}}^2/\omega^2 \quad \text{and} \quad \varepsilon_{\mathrm{O}}(\omega) = 1 + \omega_{p\mathrm{O}}^2/(\Delta^2 - \omega^2),$$

analytic expressions are found for the interface energy, $\gamma_{\mathrm{M/O}}^{\mathrm{vdW}}$, and for the surface energies, $\gamma_{\mathrm{M/V}}^{\mathrm{vdW}}$ and $\gamma_{\mathrm{O/V}}^{\mathrm{vdW}}$, where V stands for vacuum.

Such a simple model has the advantage of yielding interface energies as functions of three parameters only, the energy difference between valence and conduction bands Δ, the metal plasma energy, $\omega_{p\mathrm{M}}$, and the oxide plasma energy, $\omega_{p\mathrm{O}}$. However, it is based on the assumption that the dielectric functions are independent of the wave vector, which amounts to neglecting the contribution of individual excitations in the vdW interface energies.[20,21] For metal surfaces, this leads to overestimations (by a factor of about 2).[22] In addition, the model supposes (i) that the interface is abrupt and (ii) that, at the vicinity of the interface plane, the electronic structure inside each medium is unchanged compared with that in bulk (neither surface state nor gap narrowing). However, since the vdW interaction is long-range, it is reasonable to assume that it is not much affected by the electronic structure of the interface.

The vdW contribution to the work of adhesion at metal/oxide interfaces can be calculated[14] by means of the Dupré equation:

$$W_{\mathrm{adh}}^{\mathrm{vdW}} = \gamma_{\mathrm{M/V}}^{\mathrm{vdW}} + \gamma_{\mathrm{O/V}}^{\mathrm{vdW}} - \gamma_{\mathrm{M/O}}^{\mathrm{vdW}} \tag{6}$$

with the help of Equation (5). This contribution is shown in Figure 2 as a function of the metal plasmon energy, $\omega_{p\mathrm{M}}$, for different values of the oxide gap, Δ. The quantity Δ is calculated via the Lorentz formula, by setting $\Delta = \omega_{p\mathrm{O}}/(\varepsilon_{\mathrm{O}\infty} - 1)^{1/2}$. Such a definition of Δ as the energy difference between the centroids of the valence and conduction bands,[7,8] has been proved[23] to be well adapted to the calculation of vdW interface energies by means of Equation (5). It is straightforward to see (Fig. 2) that $W_{\mathrm{adh}}^{\mathrm{vdW}}$ meets the experimental trends in work of adhesion, since it increases with both narrowing oxide band gap (increasing dielectric constant) and increasing metal plasma frequency (increasing conduction electron density). The qualitative agreement of the present

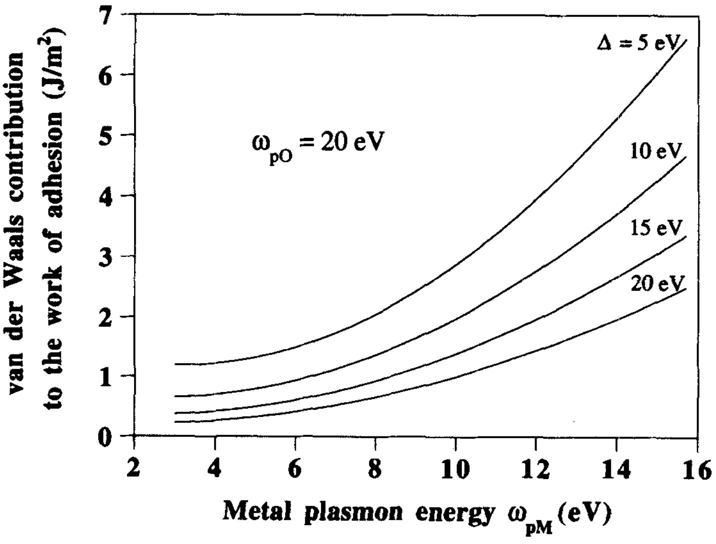

FIGURE 2 The van der Waals contribution to the work of adhesion at metal-oxide interfaces, as directly calculated from Equations (5) and (6), for different values of the energy difference, Δ, between the centroids of the valence and conduction bands.

model with experimental data has been previously considered in more detail for metal/silica, metal/alumina and metal/gas interfaces.[14,23]

From these comparisons it appears that vdW interactions account for the prevalent experimental trends.

3. DISCUSSION

To decide whether the long-range interactions are contributing significantly to the overall WA, some estimates of the quantities $W_{\mathrm{adh}}^{\mathrm{im}}(\mathrm{M,O})$ and $W_{\mathrm{adh}}^{\mathrm{vdW}}(\mathrm{M,O})$ are needed.

The Contribution of Image Forces

The Ag/MgO(100) system is expected to give rise to a sizeable image term since it meets the criteria discussed in Section 2 – *i.e.* a wide gap and a strong ionic character for the oxide and a rather large Fermi wave vector (1.2 Å^{-1}) for the metal. Assuming for MgO net charges of $+2$ and -2 on the cation and anion, respectively, Duffy *et al.*[19] have found for $W_{\mathrm{adh}}^{\mathrm{im}}(\mathrm{M,O})$ a value (0.37 J/m^2) which is 25% of the overall WA value they have calculated (1.44 J/m^2). This does not run counter to the idea [Finnis[13]] that, if MgO is fully ionic, the image interaction significantly contributes to the Ag/MgO(100) WA (moreover, this calculated $W_{\mathrm{adh}}^{\mathrm{im}}(\mathrm{M,O})$ value is of the same order of magnitude as the experimental value (0.45 J/m^2)[24] of the overall WA). However, bearing in mind that the image term is quadratic in charge, the result would be quite different if, following recent calculations,[25] the net charges on magnesium and oxygen ions were assumed to be ± 1.1 only. In that case, the image contribution to the WA would become marginal. More generally, and whatever the ionicity of MgO may be, it is worth noting that MgO is one of the most ionic oxides[26] and that number of oxides, as for example SiO_2 and TiO_2,[27] are much more covalent. Therefore, in the case of many oxides, the image interaction is expected to contribute much less to the WA.

The van der Waals Contribution

The van der Waals contribution, $W_{adh}^{vdW}(M, O)$, has been often calculated by means of a short-range pair interaction model, which accounts only for vdW forces between interface atoms. Estimates obtained by using such a model, 0.2 to 0.5 J/m^2 for various metal/oxide systems,[1,2] can be regarded as a lower limit of $W_{adh}^{vdW}(M, O)$. The comparison of these values with the overall metal/oxide WA, which in non-reactive cases ranges between 0.2 and 1 J/m^2 for most metal/oxide systems,[2,12,28] indicates that vdW forces could indeed play a non-negligible role in the adhesion at metal/oxide interfaces.

Short-range Contributions

In addition to long-range interactions, a complete description of the WA involves a short-range contribution arising from charge transfer at the interface. To date, self-consistent calculations of metal/oxide systems did not lead to an unambiguous description of the energetics at the interface. In fact, there are very few such calculations and most of these deal with the Ag/MgO(100) system. For that interface, the calculated WA values (1.44[19,29] and 1 J/m^2 [30]) are systematically overestimated with respect to the experimental finding (0.45 J/m^2).[24] This discrepancy is crucial since these calculated values suggest that silver should wet MgO(100), with contact angles close to 80°, while a non-wetting behaviour is observed, with contact angles ranging between 135°[24] and 139°.[31]

The charge transfer contribution to the interface energy, $\gamma_{O/M}$, arises from the electron overlap and the subsequent formation of bonding states near the interface. Therefore, since a conduction state of the metal needs to be close to an oxide band to hybridize strongly with it,[32] a narrow metallic state whose energy is located at the middle of a wide gap should not hybridize very much and the delocalization it experiences at the interface should be close to that of the free surface of the metal – *i.e.* charge transfer contributions to $\gamma_{M/V}$ and $\gamma_{O/M}$ should not differ much. In such a case, when calculating the WA by means of the Dupré equation (Eq. 4), the short-range contributions should partly cancel[14,23] in the $(\gamma_{M/V} - \gamma_{O/M})$ difference. Finnis[13] draws a rather similar conclusion in his quantum mechanical description of the general features attached to the interaction of metal with an ionic material. Representing the ionic medium *via* the rare gas model and expressing interactions in terms of perturbation theory, he suggests that the chemical binding of ionic materials to metal surfaces is mainly bought about by trough image interactions, not short range interactions.

In other words, our approach suggests[23] that the conditions which produce weak metal/oxide adhesion are those which favour long-range *versus* short-range interactions: (i) low conduction electron density, n_C, for the metal; (ii) large energy difference, Δ, between the centroids of the valence and conduction bands of the oxide (or, more

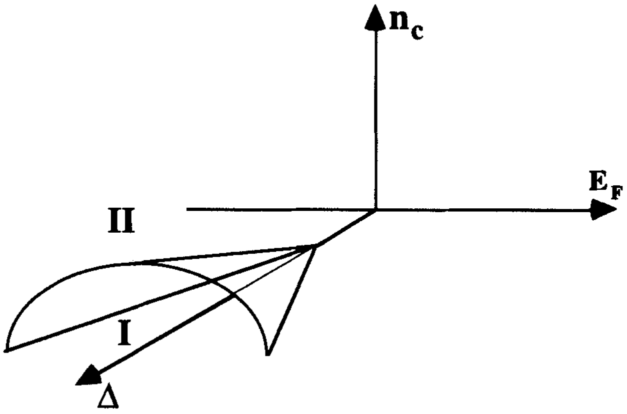

FIGURE 3 Schematic representations of the prevalent contributions to the metal/oxide work of adhesion, represented in a (n_c, Δ, E_F) space, where n_c is the conduction electron density of the metal, Δ is the energy difference between the centroids of the valence and conduction bands and E_F is the position of the Fermi level at the interface (with respect to the middle of the band gap). In region I, the role of the van der Waals interaction in the work of adhesion is maximized while, in region II, the relative contribution of short-range interactions increases.

simply, wide oxide band gap, δ); (iii) interface Fermi level far enough from the conduction and valence band edges of the oxide. These conditions can be expressed *via* a schematic representation (Fig. 3) of the metal/oxide WA as a function of the parameters n_C, Δ and also the Fermi energy, E_F, to indicate the position in energy of the Fermi level. Two regions are distinguished. In the region I, which corresponds to contacts between low-density metals on wide band-gap oxides, interfaces are mostly non-reactive, the adhesion is poor, and the relative contribution of vdW interaction to the overall WA is maximum. Furthermore, for high values of the gap energy and depending on the ionic character of the oxide, the image term could play a role. In region II, gaps narrow, metals become increasingly dense and interface Fermi levels get closer to the oxide band edges. As a result, the contribution of short-range interactions due to charge transfer increases (this case involves reactive interfaces).

It must be noted that the different contributions can not simply be added to obtain the overall WA, and that only a self-consistent procedure can lead to a realistic description of the interface. Nevertheless, this schematic view, though simplified, possibly yields some leads for a general understanding of the adhesion properties. In particular, the conclusion that the relative importance of the vdW interactions increases in certain conditions shows that these interactions should be included in calculations of the work of adhesion at metal/oxide interfaces.

4. CONCLUSION

The long-range contributions to the work of adhesion at metal/oxide interfaces have been examined through the extent to which these follow the known trends – *i.e.* the increase in work of adhesion as the oxide band gap narrows (as the dielectric constants increase) or as the conduction electron density of the metal increases. Two important conclusions have been drawn. Firstly, the van der Waals interactions account for the two trends and might contribute significantly to the overall work of adhesion. Secondly, the image term does not follow the first trend and is expected to play a role only in the case of systems involving very dense metals and highly ionic oxides.

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