Bonding along metal-oxide interfaces
Haarsma, Hendrik

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CHAPTER 1

Objectives

Their obvious technological importance notwithstanding, our basic understanding of heterophase interfaces is still rudimentary, particularly in relation to materials properties. This thesis concentrates on a fundamental understanding of the bonding between dissimilar materials such as metals and ceramic materials from a theoretical point of view. As a matter of course, availability of accurate descriptions of the interatomic forces is crucial in the physical description of the metal-ceramic interfaces. In fact, it forms the central objective of this thesis that combines quantum mechanical calculations with a semi-empirical approach in terms of pairwise interaction functions. In this chapter, the objectives from a theoretical viewpoint are placed in perspective with experiments.

It goes without saying that important properties of materials in high-technology applications are strongly affected or controlled by the presence of solid interfaces. For example, a great deal of the electronic industry is based on the interesting electrical properties of semiconductor interfaces, with ceramic-semiconductor-, metal-semiconductor- and metal-ceramic interfaces playing a crucial role. Interfaces are also important in the field of surface engineering. For techniques designed to enhance corrosion resistance of surfaces or optimize their performance in catalytic or tribological applications, interfaces play a decisive role. In the field of semiconductor technology as well as in the area of surface engineering, metal-oxide interfaces are frequently encountered. Interfaces between metals and oxides have been the subject of extensive research in recent years because they control to a great extent properties of metal-ceramic composites, protective coatings, thin metal/ceramic films in electronic devices, etc. For these reasons it would be of practical importance to
have a fundamental understanding of the bonding between dissimilar materials such as metals and ceramic materials.

Their obvious technological importance notwithstanding, our basic knowledge of interfaces, even relatively simple interfaces like grain-boundaries, is still rudimentary, particularly in relation to materials properties. The importance of interfaces is determined primarily by their inherent inhomogeneity, that is, the fact that physical and chemical properties may change dramatically at or near the interface itself. It should be realized that physical properties, like elastic moduli, thermal expansion, or electrical resistivity might differ near interfaces by orders of magnitude from those in bulk regions. Because of these sharp gradients, an isotropic bulk solid may change locally into a highly anisotropic medium. Consequently, all processes that are controlled by interface phenomena, such as decohesion, segregation, cavitation and diffusion, occur in a very narrow region, of the order of a few lattice spacings, where the two materials join. Thus, the atomic structure of interfaces needs to be understood in order to establish the physical mechanisms of various boundary phenomena. In recent years, considerable progress has been made (see review\(^1\)), including by our group (for a review reference is made to\(^2\)), in understanding of interfaces between dissimilar materials at the atomic structure level, using high-resolution (transmission) electron microscopy (HRTEM) as the experimental methodology.

To scrutinize the basic behavior of heterophase interfaces also theoretical work has been carried out in recent years on model systems. These model systems are well-defined simple interfaces that are boundaries with known orientation and high symmetry between simple, known constituents. The hope is that general concepts governing adhesion, structure, chemistry, mechanical behavior, and their interdependence can be elucidated. An important property of a heterophase interface is its surface and interface energy per unit area, and the closely related work of adhesion. Thermodynamic and mechanical properties of the interface have been found to depend on these parameters. It is relevant here to recall the precise definition of the work of adhesion, surface, interface and adhesion energies because it will play a central role in the calculations in the following chapters. In addition, some confusion exists in literature about the precise definition\(^3,4\).

Different energies will be used:

- \(E_x\) represents the total energy of an infinite bulk crystal \(X\) per surface area.
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- $E_{X}$ and $E_{X'}$ are the total energies of semi-infinite bulk crystals $X$ per surface area, where the free surface is either on the right or on the left hand side (having identical value).

- $E_{X}$ and $E_{X'}$ are the number of unit cells in the semi-infinite bulk crystals times the number of unit cells per surface area (since they have the same values, each is half of $E_{X}$).

The work required to form two interfaces from two infinite bulk crystals A and B is related to the interface energy $\gamma_{A/B}$

$$E_{A/B} + E_{A/B} - E_{A} - E_{B} = \gamma_{A/B} + \gamma_{B/A}$$ (1.1)

Here $E_{A/B}$ is the energy of a semi-infinite crystal A with next to it a semi-infinite crystal B, and $E_{B/A}$ is similar only the crystals switched places. Since these two situations are the same the values of $E_{A/B}$ and $E_{B/A}$ are equal, this also means that the interface energies are equal ($\gamma_{A/B}$ and $\gamma_{B/A}$). The interface energies are found by correcting the energies of the semi-infinite crystals by the bulk energy of the crystals ($E_{A}$ and $E_{B}$).

Equation (1.1) can be simplified to:

$$\gamma_{A/B} = E_{A/B} - E_{A} - E_{B}$$ (1.2)

Within the same framework the surface energy with respect to the bulk is

$$\gamma_{A} = E_{A} - E_{A} \text{ or } \gamma_{A} = E_{A} - E_{A}$$ (1.3)

The work of adhesion is the work to cleave the A/B interface into semi-infinite crystals A and B

$$W_{A/B} = E_{A/B} + E_{A/B} - E_{A/B}$$ (1.4)

Here we assume that the free surfaces are unreconstructed. From the definitions of the interface and surface energy, Eqs. (1.2) and (1.3), it can be seen that the work of adhesion is:

$$W_{A/B} = \gamma_{A} + \gamma_{B} - \gamma_{A/B}$$ (1.5)

If A is equal to B the work of adhesion becomes the cleavage energy, $\gamma_{A} + \gamma_{A}$ because $\gamma_{A/A}$ vanishes. The adhesion energy is defined as the change of the surface energies of A upon contact over a certain contact area $S$ due to the interactions with B, or simply:
Experimental determination of the interface energy is an important step towards understanding heterophase interfaces. In principle, there are several ways in which information on the interface energy can be extracted from experiments, for example, either by measurement of wetting angles or by study of interface fracture behavior by four point bending tests. Another possibility is that of using high-resolution (transmission) electron microscopy, and the information it can provide on the atomic structure of an interface. The link between atomic structure and interface energy is provided by the interaction, which takes place at the interface between the bonding across it and the geometrical misfit.

The experimental determination of the work of adhesion is not as easy as it looks. Delamination from a substrate is not only driven by applied stresses in the materials, but, sometimes rather, by residual stresses. Such stresses are inevitable in certain manufacturing techniques and are enhanced when the materials have vastly different thermo-physical properties, such as metal/ceramic. These stresses are still rather extrinsic due to deposition or to thermal expansion mismatch, but they can relax by annealing or by plastic deformation of some kind. In fact, the energy stored in the system, which becomes available when failure occurs depends on the thickness of the layers and on residual stresses in the layer or film.

Besides extrinsic stresses, intrinsic stresses exist and they refer to stresses that are not the result of differences in thermal expansion coefficients or applied loads. In general, the lattice parameters of a heterophase interface do not match, leading to a geometrical misfit. If both materials are unstrained up to the interface, there is a period at the interface that may be much larger than either of the equilibrium lattice periods, and that normally is incommensurate with these. In this case, the interface is incoherent. It is clear that not all atoms near the interface have the same local environment and consequently do not have the same energy. Some atoms will be in a more favorable position than others will. Depending on the strength of the interaction some atoms will move to positions that are more favorable and the atomic structure near the interface, predominantly that of the elastically softer material, will relax so as to lower the interface energy. If the lattice parameters at the interface are equal, it is possible that all atoms have the same, favorable, local environment. In that case, the interface is coherent. However, the fact that work has to be exerted on the system to bring the lattices into registry leads to an energy balance. In practice an interface is usually neither incoherent nor coherent, but semicoherent. The interface in this case is characterized by regions in which coherence has increased, and by regions in which coherence has decreased. Because the misfits
are concentrated in the latter regions and they resemble dislocation character, they are called “misfit dislocations”. This phenomenon was first noted in the case of epitaxial layers and widely studied in this context\textsuperscript{5,6,7}.

If the solid phases A and B become strained to an amount $d\varepsilon_{ij}$ along the interface, the area of the interface is increased by $dS$ and the work, $dW=\gamma_{A/B} dS$ is provided by an intrinsic stress, which is called the interface stress\textsuperscript{8}:

$$\sigma^I_{ij} = \gamma_{A/B} \delta_{ij} + \frac{\partial \gamma_{A/B}}{\partial \varepsilon_{ij}}$$  (1.7)

The physical origin of the interface stress lies in the long-range interactions and the specific structure of the interface. Although the interface energy is a scalar, the interface stress in Eq. (1.7) is a tensor and different interfaces may have different interface stresses.

In this thesis, it is assumed that the interfaces and consequently the work of adhesion refer to atomically flat interfaces. However, in making a comparison between theoretical predictions and experimental observations, it is important to emphasize that experimental measurements of the interface stress can be considerably affected by the roughness along the interface. With a simple sinusoidal roughness, it was shown\textsuperscript{8}, that with increasing ratio of oscillation amplitude over oscillation wavelength (rougher interface), the measured stress is 60% smaller than the actual interface stress.

The effect of a simple sinusoidal roughness could be extended\textsuperscript{9} to the more general cases of random self-affine and mound rough interfaces, which are commonly observed during multi-layer growth\textsuperscript{10,11,12,13}, as well as mound interface roughness that develops during epitaxial growth\textsuperscript{14,15,16,17}. Denoting the interface height profile by $h(\vec{r})$ which is assumed to be a single valued function of the in-plane position vector $\vec{r}(x,y)$, the work $dW$ necessary to stretch a rough interface elastically to an amount $d\varepsilon_{ij}$ becomes\textsuperscript{9}

$$dW = \sigma_{ij} d\varepsilon_{ij} \int \frac{d^2 \vec{r}}{\sqrt{1 + (\nabla h)^2}}$$  (1.8)

For a weak roughness $|\nabla h|<<1$ the effect of the roughness in Eq.(1.7) can be simplified to:

$$\frac{1}{\sqrt{1 + (\nabla h)^2}} \approx 1 - \frac{1}{2} (\nabla h)^2 + \frac{1}{4} (\nabla h)^4 + ...$$  (1.9)
Similarly, the adhesion energy, which is assumed proportional with the contact area $S$ (see Eq. (1.6)) will be affected by the roughness along the interface\(^{18}\). The adhesion energy is given by

$$U_{ad} = -W_{AB} \int d^2 r \sqrt{1 + \nabla h \cdot \nabla h}$$

and assuming Gaussian random roughness fluctuations\(^{19}\) yields after ensemble averaging over possible random roughness configurations:

$$U_{ad} = -W_{AB} S_{\text{flat}} \langle \sqrt{1 + \nabla h \cdot \nabla h} \rangle < \langle \sqrt{1 + \nabla h \cdot \nabla h} \rangle = \int_0^\infty du \left( \sqrt{1 + \rho^2 u} \right) e^{-u}$$

with $A_{\text{flat}}$ the average macroscopic flat contact area and the average local surface slope of the rough interface. For small local surface slopes such that $\rho < 1$, we can rewrite the integral for the adhesive term (Eq. (1.11)) in a closed integral form:

$$\int_0^\infty du (1 + \rho^2 u)^{1/2} e^{-u} = \rho \, e^{\rho^2} \Gamma\left(\frac{3}{2}, \rho^2\right)$$

where $\Gamma(x,a)$ represents the incomplete $\Gamma$-function\(^{18}\). For small $\rho$ the asymptotic expansion leads to:

$$\rho \, e^{\rho^2} \Gamma\left(\frac{3}{2}, \rho^2\right) = 1 + \frac{1}{2} \rho^2 + \sum_{n=2}^{\infty} R(n) \rho^{2n}$$

with $R(n) = \{1 \cdot 1 \cdot 3 \cdot 5 \cdots (2n-3)\} / 2^n$.

The balance between the interface energy and the strain energy governs the transition from the coherently strained interface to a semi-coherent interface with interface dislocations. Unlike dislocations in the bulk, it should be emphasized that the interface dislocations are not defects in the usual sense but an integral part of the interfacial structure. In fact, the Burgers vector of the interface dislocation depends on the elastic properties of the two materials on either side of the interface, i.e. in contrast to the Burgers vector of a lattice dislocation in the bulk. The interface dislocations are positioned either at or very near the interface, and they reduce the misfit strain with respect to the unrelaxed fully coherent interface by locally decreasing the interfacial coherency\(^{20,21}\).
Experimental examples are shown in Fig. 1-1, where the HRTEM images are contracted a factor of 3 more or less perpendicular to the interface to mimic a grazing angular view of the planes continuing across the interface. In this way, the coherency across the interface can be observed more easily. For images taken along <110> it is clear that coherency across the interface is maintained for the main part of the projected interface length, whereas the regions where the misfit dislocations are concentrated are of relatively shorter lengths. These latter regions are encircled in Fig. 1-1a. On the other hand, for the images taken along <100>, the portion in which the disregistry along the interface is concentrated is rather large compared to the other regions where the planes across the interface match smoothly. Again, the regions where the disregistry is concentrated are encircled in Fig. 1-1b. The relative projected lengths of these regions are a consequence that one array of the dislocation lines is observed edge-on with the other array running perpendicular to the viewing direction (giving a short length). The other possibility is that both arrays are inclined 45° with respect to the viewing direction (giving a larger length). Discrimination between the square networks of either ½<110> or ½<100> type Burgers vectors can be made by realizing that the former gives a disregistry along small regions for observation along <110> and along larger regions for observation along <100>. In the latter network, the relative sizes of these regions are reversed.

![HRTEM images](image)

Fig. 1-1: A HRTEM images contracted more or less perpendicular to the interface of a plate-shaped precipitate with (002) of Mn3O4 parallel to (200) of Pd for viewing along (a) <110> (top image); and (b): <100> (bottom image). Regions at the interface of disregistry, that is, where the planes of Mn3O4 and Pd across the interface do not continue in a matched fashion, are encircled. Relatively small regions of disregistry are observed for viewing along <110> and large regions for viewing along <100>.
Hence, from these experimental observations it is clear that networks with line direction <110> and Burgers vector \( \frac{1}{2}<110> \) are present at the interfaces.

It is clear that the misfit at the interface plays an important role, because the elastic strain energy needed to achieve coherence at an interface with large misfit will in general be higher than for an interface with low misfit. Thus, the atomic structure is determined by the interaction between misfit and bonding and atomistic calculations, in combination with atomic structure determination of the core structure of misfit dislocations, can therefore be expected to lead to a better understanding of interfaces between dissimilar materials.

Theoretical studies of interfaces have focused on understanding the cohesion at the interface, principally in the realm of its chemistry and electronic structure. This can be done adequately using ab initio electronic structure calculations and a number of such studies have been made in the past. From a theoretical point of view, ab-initio calculations based on the full-potential linear muffin-tin orbital method (LMTO) and local density approximation (LDA) have been performed for several heterophase interfaces, in particular for interfaces with sapphire and MgO. In various cases, contradicting results are found as far as trends in the bond strength and the positions of the metal with respect to ions are concerned. As these methods are practicable only for rather small period structures, the metal lattice is usually distorted into registry with the oxide. The interface studied is then coherent, and the interface energy can be calculated for different relative positions of the metal and oxide lattices.

As an example, for the Ag-MgO (100) interface it has been found that the most favorable position of Ag will be above the O-atoms of the MgO (100) plane, and not on top of the Mg atoms or in between them. Furthermore, from these calculations conclusions on the nature of the bonding at the interface may be drawn. Full relaxation of the structure is not normally possible using the full potential LMTO. However, the original infinite range LMTO basis set can be transformed precisely into short-range or localized basis sets, with varying degrees of localization in real space. In particular, the tight-binding LMTO (TB-LMTO) method combines the simplicity of empirical tight-binding methods with the precision and rigor of ab-initio approaches. In principle, the TB-LMTO method can be applied to non-periodic and periodic interfaces in solids. It also yields the full non-spherical charge density needed for accurate total energy and force constant calculations. The TB-LMTO approach has not been used extensively to calculate the relaxed structures of metal-oxide interfaces but it is believed to represent an interesting route to explore, see and references therein.
An important contribution to the bonding across metal-oxide interfaces is believed to be the Coulomb interaction between the ions in the oxide and the "image charges" in the metal, or better said the charge density that they induce in the metal. Several experimental observations point in this direction, for example, the frequent occurrence of polar oxide planes at metal-oxide interfaces. However, application of this classical concept at an atomic scale leads to several problems. First of all the concept does not refer to atoms and it does not distinguish between (the band structures of) different metals. Because of this, the classical interaction diverges for separation approaching zero. The main reason that the model does not work at an atomic scale is that the possibilities for charge distribution are unrestricted, whereas in real metals only distributions with a wavelength larger than the Fermi wavelength are permitted. Two ways around this problem have been proposed and applied to model systems with some success. Finnis\textsuperscript{30} treats the metal as an array of charged and polarizable spheres for which the induced fluctuations in the charge density increase the energy, and thus remove the singularity. Duffy, Harding, and Stoneham\textsuperscript{31} have worked out an approach in which the screening of the ions in the metal is explicitly restricted to wavelengths larger than or equal to the Fermi wavelength. Calculations using this modified image interaction compare favorably in some respects with electronic structure calculations, but show remarkable differences as well, notably in assigning the most favorable position for an Ag atom above a MgO \{100\} plane.

The availability of accurate descriptions of the interatomic forces is of course crucial in the physical description of the metal-ceramic interfaces and it forms the central objective of this thesis that combines quantum mechanical calculations with a semi-empirical approach in terms of pair-wise interaction functions. The objectives are:

First: metal-oxide interfaces, where the nature of the bonding across the interface still needs further physical clarification. As discussed by Finnis, for metal-oxide bonding analogous simple schemes for the description of interatomic forces cannot be easily formulated and those employing image charge effects are not fully atomistic. Hence, studies that incorporate atomic structure and bonding are attractive from a scientific viewpoint. (Chapter 2)

Second: the semi-empirical approach that was employed by us in the past could receive a better physical base\textsuperscript{5,22,23}. In fact, this simplified model, while treating the metal atomistically, is close to a continuum treatment. In particular, in the previous model the atomic interactions in the metal are described by Finnis-Sinclair type many-body central force potentials. The ceramic crystal is regarded as a rigid, undeformable substrate so that no description of interatomic forces in this material is needed. The potentials used to describe the
interactions between the metal atoms are of the Finnis-Sinclair type\textsuperscript{34}. In this scheme, the energy of an atom $i$ is given by:

$$E_i = \sum_j V(R_{ij}) - \sqrt{\sum_j \Phi(R_{ij})}$$  \hspace{1cm} (1.14) 

The first term is a repulsive pair part and the second term reflects an attractive many-body part. The functions $V$ and $\Phi$ are short range pair potentials fitted to reproduce experimental data, such as lattice parameter, cohesive energy, and elastic moduli\textsuperscript{35}. Summation is for all atoms $j$ within the cut-off radius of the potentials applied. The interactions across the boundary, between metal and substrate atoms, are modeled with an effective pair potential, $V_{\text{eff}}$. The form is derived from the Finnis-Sinclair potential. It amounts to an approximation to Eq. (1.14), if second and higher derivatives of $\Phi$ are neglected, that is, no large changes in coordination occur. In order to simulate different bond strengths the potential is multiplied by a factor $\alpha$ and takes the following form:

$$E_{\text{Metal-Oxide}} = \alpha V_{\text{eff}}(R) = \alpha \left( V(R) - \frac{\Phi(R)}{\sqrt{\sum_j \Phi(R_{ij})}} \right)$$  \hspace{1cm} (1.15) 

The atomic interactions across the interface could be described by pair potentials, which lead to different bond strengths, depending on the value of $\alpha$.

Third: even from the classical picture, it is quite clear that there is a large difference between the bonding of different crystallographic faces. This is due to the large anisotropy in the surface energy of ceramic materials and to the different symmetry of the reflected image planes. The nature of the interaction suggests that significant bonding can be achieved even in incoherent interfaces. Therefore, the objective is to examine the different crystallographic orientations, f.i. cube-on-cube and cube-on-non cube and for different metal-oxides (Chapters 3,4,5)

Fourth: at interfaces, for instance, contaminating elements can cause charge defects, which may have a profound effect on the interfacial bonding. One may expect an enhanced concentration of charged defects contributing to the stability of the system. (Chapter 2 and Chapter 4)

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OBJECTIVES

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Chapter 1