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R. Benedek, D. A. Shashkov, and D. N. Seidman
Northwestern University, Evanston, IL 60208

D. A. Muller and J. Silcox
Cornell University, Ithaca, NY 14853

M. F. Chisholm
Solid State Division, Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, Tennessee 37831-6030

L. H. Yang
Lawrence Livermore National Laboratory
Livermore, CA 94551

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R. BENEDEK, D. A. SHASHKOV and D. N. SEIDMAN
Department of Materials Science and Engineering
Northwestern University
Evanston, Illinois 60208

D. A. MULLER and J. SILCOX
School of Engineering and Applied Physics
Cornell University
Ithaca, New York 14853

M. F. CHISHOLM
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

L. H. YANG
Condensed Matter Physics Division
Lawrence Livermore National Laboratory
Livermore, California 94551

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ATOMIC STRUCTURE OF A POLAR CERAMIC/METAL INTERFACE: {222}MgO/Cu

R. BENEDEK, D. A. SHASHKOV, D. N. SEIDMAN, Northwestern University, Evanston, IL; D. A. MULLER, J. SILCOX, Cornell University, Ithaca, NY; M. F. CHISHOLM, Oak Ridge National Laboratory, Oak Ridge, TN; L. H. YANG, Lawrence Livermore National Laboratory, Livermore, CA

ABSTRACT

{222}MgO/Cu is one of the most extensively characterized ceramic/metal interfaces, in view of the atom-probe field-ion-microscopy, Z-contrast scanning-transmission-electron-microscopy (STEM), and spatially-resolved electron-energy-loss-spectroscopy (EELS) measurements performed by the present authors, as well as the high-resolution electron microscopy (HREM) of this system by others. Atomistic simulations with local density functional theory (LDFT) and molecular dynamics (MD) have been performed to gain additional insight into the structure of this interface. This presentation describes an interface interatomic potential for {222}MgO/Cu derived from LDFT total energy calculations, and its application to structural properties, including the terminating species, the absence of dislocation standoff, and the symmetry of the interfacial dislocation network.

INTRODUCTION

A fundamental property of ceramic/metal interfaces [1] is their adhesion, which is related to interfacial structure, composition and bonding. Characterization of these interfacial properties has received considerable attention, particularly in model systems, for example, interfaces between the ceramics magnesia, alumina or zirconia and transition or noble metals or Al. These model interfaces differ (in most cases) from engineering interfaces in their sharpness, purity and the absence of chemical reaction zones. High-resolution probes, including primarily field-ion and electron microscopies and x-ray techniques, have in recent years begun to provide an atomic-scale characterization of interface structure and chemistry in some of these model systems. Nevertheless, ambiguities frequently exist in the experimental interpretation, and atomistic computer simulation can be helpful to resolve these ambiguities, as well as address issues inaccessible to experiment. In this presentation, we describe computer simulations of an interface for which extensive experimental results exist, {222}MgO/Cu. With the atom-probe field-ion microscopy [2], Z-contrast STEM [3] and spatially resolved EELS [4] measurements by the authors of this article, in addition to work by others on this system [5,6], {222}MgO/Cu is one of the most extensively characterized ceramic/metal interface on an atomic scale.

Most previous simulations [7] of ceramic/metal interface have addressed neutral interfaces, such as {100}MgO/Ag [8], for which the interfacial bonding is relatively weak (tenths of an eV per interface atom), near the crossover between chemisorption and physisorption regimes. The adhesion of nonpolar ceramic/metal interfaces is known empirically to vary inversely with the enthalpy of formation of the ceramic [9], which is large for many of the most common ceramics, such as magnesia or alumina. Polar interfaces, on the other hand, may exhibit extremely strong adhesion. The MgO-precipitate/Cu-matrix interfaces in internally oxidized Cu(Mg) alloys are found exclusively in the polar {222} orientation [10]. The strong adhesion and ubiquity of these polar interfaces motivate a more thorough investigation of their structure and physical properties.

In common with many microstructural features of materials, ceramic/metal interface structure is determined by a competition between interatomic interactions of electronic origin localized at the interface and strain-field effects that operate on a longer length scale. Determination of an interface interatomic potential at ceramic/metal interfaces suitable for simulation has been more difficult than for other types of interfaces, which discouraged theoretical efforts on these systems. Image-interaction based models have received the most attention, and a discretized version has recently been applied to {100} and {110}MgO/Ag [8]. The image-interaction approach has not been applied to polar interfaces. In this work, we apply *ab initio* local density functional theory (LDFT) calculations, which treat self-consistently the electronic states at the interface, to guide us to an appropriate form of interface interatomic potential [11]. Structural properties of the {222}MgO/Cu interface will be addressed in terms of this potential model.

STRUCTURE AND PROPERTIES OF {222}MgO/Cu

Several atomic-scale probes have been applied to {222}MgO/Cu interfaces in internally oxidized Cu(Mg) specimens. Measurements have been made both on pristine interfaces and on interfaces with Ag segregants, obtained by internal oxidation followed by a low temperature anneal of the Cu specimens containing dissolved Ag and faceted MgO precipitates. The measured properties of the pristine interface include the interface termination [10], misfit dislocation network [3-6], and the local electronic structure [4]. For the Ag-segregated interface, the interface spacing [3], distribution of Ag atoms [2,12], local electronic structure [12] and the misfit dislocation network [3] have been observed. Theoretical calculations that relate to several of these properties have also been performed. Because of space limitations, we address in this presentation only the atomic structural properties of the pristine interface. The discussion is given from a theoretical perspective, and experimental results are quoted but not described in detail.

INTERFACE INTERATOMIC POTENTIAL

Since the unit cells for ceramic/metal interfaces with misfit are too large to be modeled entirely from *ab initio* considerations, we develop an interface interatomic potential to explore interface structure. Local density functional theory (LDFT) total-energy calculations for selected commensurate (coherent and semicoherent) interfaces guide us to an analytical form of the interatomic potential. The plane-wave pseudopotential implementation of LDFT adopted in this work [13] enables the treatment of relatively large periodic unit cells.

Translation state dependence of the interface adhesive energy

A representation of total energy is sought in which bulk interaction potentials that involve atomic coordinates exclusively either in the metal or in the ceramic are complemented by an interface potential that involves atomic coordinates on both sides of the interface. To investigate the interface potential, we perform LDFT total energy calculations for a coherent {222}MgO/Cu interface in which the bulk potential terms are kept constant (by maintaining metal-metal and ceramic-ceramic interlayer spacings at their bulk values), while only the interface coordinates are varied. We consider essentially three interfacial degrees of freedom, one of which corresponds to the interface separation, and the other two to the translation state parallel to the interface of the metal block relative to the ceramic block. Most of the results discussed below correspond to the O termination of the {222}MgO/Cu interface. Similar calculations were also performed for the (so far unobserved) Mg termination.

For fixed interface separation, the energetically favored parallel translation state corresponds to the "hollow" site position, in which each interface Cu atom is equidistant from three nearest neighbor oxygen (or Mg) atoms across the interface. For this translation state, the adhesive energy as a function of interface separation, z, is accurately described by the "universal binding energy" (UBE) function [14]

$$E_u = -\varepsilon(1 + z^*)\exp(-z^*), \tag{1}$$

where the prefactor ε is a specific interface bonding strength (which in our case we normalize per interface Cu atom), and $z^* \equiv (z - z_0)/l$ is a reduced length, expressed in terms of the equilibrium interface separation, z_0, and a scaling length, l. A similar parametrization has been employed previously for neutral ceramic/metal interfaces [14].

Calculations of the adhesive energy as a function of interface separation were also performed for parallel translation states other than the hollow site. These results are accurately described by a superposition of the attractive universal binding energy term and a repulsive core overlap potential across the interface [11,15]:

$$E_i = E_1 + E_2. \tag{2}$$

The one-body potential

$$E_1 = \sum_{z_i} E_u(z_i), \tag{3}$$

is the sum of contributions from Cu atoms at a distance z_i from the ceramic interface layer, which, in our initial treatment, is assumed perfect and flat. For the O termination, ε=2.75 eV/Cu atom, z_0 =1.25 Å, and l =0.62Å.

The two-body potential is a Born-Mayer pairwise repulsive interaction

$$E_2 = A\sum_{i,j} \exp(-br_{ij}), \tag{4}$$

where r_{ij} is the separation of a Cu atom from a terminating plane ceramic (O or Mg) atom, and A and b are parameters; for the O termination $A = 4254$ eV, and $b = 4.73$ Å^{-1}.

Dependence of the interface potential on atomic density of interface layer

This potential parametrization accurately describes LDFT total energy calculations for coherent {222}MgO/Cu interfaces, in which the Cu layers are stretched to match the atomic density of MgO. Realistic interface structure simulations, however, require consideration of a higher Cu layer atomic density. The relative layer atomic density at the interface

$$\rho \equiv \frac{\rho_{Cu}}{\rho_{MgO}} = \left(\frac{a_{MgO}}{a_{Cu}}\right)^2 \approx 1.36. \qquad (5)$$

In the simplest generalization of eqs.(1-4), only the prefactor in eq.(1) is considered a function of ρ. A simple limiting behavior is given by the relation

$$\rho\varepsilon(\rho) = \varepsilon(1), \qquad (6)$$

which implies that bonding is saturated for the coherent interface, so that no increase in bond strength per unit area is achieved by increasing the density ratio ρ above unity. Equation (6) appears to be a reasonable first approximation, although it most likely underestimates interfacial bonding. Molecular statics simulations presented below employed eq. (6) in conjunction with $z_0(\rho)$=const. and $l(\rho)$=const. to model the semicoherent interface with ρ=1.36.

The extent to which eq. (6), or any similar expression, is valid can be investigated through *ab initio* calculations. The LDFT calculations used to establish eqs. (1-4) addressed only the fully coherent case $\rho = 1$. To determine the variation of the potential parameters with ρ, calculations are being performed for interfaces with ρ=3/2 and ρ=4/3. To keep the unit cell size small, the Cu density is varied in only one dimension: cells are constructed with a Cu interatomic spacing in atomic rows parallel to a given close-packed direction in the interface plane reduced by $1/\rho$, but with the spacing between the atomic rows unchanged. The interface is then coherent in one direction (perpendicular to the rows) and incoherent (albeit commensurate) in the direction parallel to the rows. These calculations are in progress. Preliminary results indicate that not only ε, but also z_0 and l vary with ρ.

INTERFACE TERMINATION

The {222}MgO/Cu interface can in principle be terminated by an O or by a Mg layer. Experimentally, the oxygen termination appears to be strongly preferred, and no Mg-terminated interface has been reported in either APFIM [10] or electron microscopy [3,5,6,12] observations of internally oxidized Cu(Mg) specimens. Both thermodynamics and kinetics may influence the distribution of terminations in the facets of oxide precipitates. APFIM and TEM observations of annealed specimens show sluggish precipitate coarsening[16], which indicates that kinetic barriers are significant. Owing to the complexity of the problem, existing thermodynamic or kinetic formulations are too idealized to predict the oxygen-partial-pressure dependence of the termination distribution. Although at sufficiently low oxygen partial pressure the oxygen termination is expected to become thermodynamically unstable relative to the Mg termination, these circumstances may not be not realizable in practice, given the sluggish kinetics.

We address here a more restricted but tractable problem, the relative stability of the alternative terminations at zero temperature and pressure, which sidesteps the complexities of interface thermodynamics. Consider a Born-Haber cycle at 0K by which an O termination is transformed into a Mg termination. The internal energy change

$$\Delta E(\mathrm{O} \rightarrow \mathrm{Mg}) = (W_{\mathrm{O}} - W_{\mathrm{Mg}}) + \ [(U_{\mathrm{evap}}(\mathrm{O};\{111\}) - \frac{1}{2}\Delta H_{\mathrm{assoc}}(\mathrm{O}_2)], \tag{7}$$

where W_i is the work of adhesion of termination i, $U_{evap}(\mathrm{O};\{111\})$ is the heat of evaporation of an O layer from a {222}MgO free surface, and $\Delta H_{assoc}(\mathrm{O}_2)$ is the heat of association (5.09 eV) of diatomic oxygen. This idealized cycle consists of cleaving an oxygen-terminated {222}MgO/Cu interface in vacuum, evaporating the terminating oxygen layer from the free ceramic surface and associating the resultant atoms into diatomic molecules, and finally rejoining the ceramic and metal to form a Mg terminated interface. A positive value of ΔE would indicate a preference for the O termination.

By substituting the works of adhesion calculated for coherent interfaces, we obtain $(W_{\mathrm{O}}-W_{\mathrm{Mg}}) \approx 1$ eV, thus favoring the O termination. This term would most likely remain positive in a more exact treatment. The term in brackets in Eq.(7) involves properties unrelated to interfaces. No estimate of it can be made at this time, owing to the lack of information about $U_{evap}(\mathrm{O};\{111\})$. *Ab initio* calculations of $U_{evap}(\mathrm{O};\{111\})$ are in progress. It would be of interest to evaluate the difference between the termination preference energy, ΔE, for the {222}MgO/Cu interface and the {222}CdO/Ag interface, which exhibits both anion and cation terminations [17]. Both the term in parentheses and that in brackets in eq. (7) are less positive for CdO/Ag than for MgO/Cu.

MISFIT DISLOCATION STRUCTURE

The interface interatomic potential model, eqs.(1-6) enables calculation of the relaxation on the metallic side of the interface. The present formulation treats the ceramic atomic coordinates as frozen, a reasonable approximation in view of the stiffer elastic moduli of MgO relative to those of Cu; in the future we expect to explore generalizations that allow both sides of the interface to be relaxed.

Standoff dislocations

Depending on the circumstances, heterophase interface misfit dislocations may either reside at the interface or "standoff" from it into the metal [18]. Since the parameters in the potential E_1 vary with the density of the terminating Cu layer, separate calculations were performed both for standoff by a single layer, and for the case with dislocations residing in the interface Cu layer. We found that even when employing eq.(6), which favors standoff (bonding per unit area no greater for the semicoherent than for the coherent interface), the network without standoff was energetically preferred [11,15]. Experimentally, the dislocation network of {222}MgO/Cu is known to reside at the interface [5,6], and in fact no standoff effect has been observed for any system with a misfit greater than 0.1; the misfit for MgO/Cu is about 0.15.

Symmetry of misfit dislocation network

The molecular statics calculations [11,15] to determine the relaxed atomic structure of the {222}MgO/Cu interface were performed on periodic unit cells in which the layers parallel to the interface have 7 Cu and 6 O atoms on a side; 7/6 is the commensurate ratio closest to the actual ratio of the lattice constant of MgO to that of Cu. Observation by HREM [3,5,6] and Z-contrast STEM [3] show misfit dislocation networks with periodicity approximately equal to seven Cu atoms. To establish the symmetry of the dislocation network requires a more detailed consideration, since the interface is viewed edge-on in electron-microscopy observation. Two dislocation network symmetries come into consideration for misfitting (111) interfaces, an undissociated hexagonal network and a dissociated trigonal network. Electron microscopy observation alone [3,5,6] has not been able to clearly distinguish between these two symmetries. It would be worthwhile to explore whether the Z-contrast STEM images, in conjunction with image simulations based on atomic coordinates from atomistic simulation [11], are able to identify the network symmetry.

Our molecular statics calculations show a dissociated misfit dislocation network, however, our simulation is biased because the employed interface potential model does not distinguish between the fcc and hcp stacking sequences at the interface: all "hollow" sites are treated as equivalent. If, hypothetically, the energy difference between the two possible stacking sequences were sufficiently large, dissociation of the misfit dislocations would be suppressed, and the network would have hexagonal rather than trigonal symmetry. *Ab initio* calculations with local density functional theory were performed to investigate this interface stacking-fault energy. Within the coherent interface approximation, we find that the fcc stacking at the interface is preferred over the hcp stacking by approximately 0.04 eV/atom (~80 erg/cm^2), a value with considerable uncertainty since it represents a small difference between large numbers. It remains to be determined whether an interface stacking fault energy of this magnitude has a significant effect on the misfit dislocation structure.

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