

## THEORETICAL AND EXPERIMENTAL STUDIES ON Cu METALLIZATION OF $\text{Al}_2\text{O}_3$

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The electronic structure and bonding of Cu to  $\text{Al}_2\text{O}_3$  has been studied both theoretically and experimentally. Ab initio total-energy pseudofunction calculations indicate that Cu initially bonds to surface O atoms instead of surface Al atoms. Ultraviolet photoemission spectra (UPS) for low coverage of Cu on  $\text{Al}_2\text{O}_3$  films support the theory in that good agreement between theory and experiment is only obtained for Cu bonded to surface O.

An  $\alpha$ -alumina is widely used in microelectronic packaging applications. Metallization of this material is therefore an important technological concern. Few fundamental theoretical investigations have been made on the metallization of  $\text{Al}_2\text{O}_3$ . Johnson and Pepper [1] have studied the bonding of Cu to the cluster  $(\text{AlO}_6)^{-9}$  which represents the  $\text{Al}_2\text{O}_3$  surface. They find that a chemical bond is formed between the d-orbital electrons and the nonbonding p electrons of the O anions. They further conclude that an increasing number of occupied metal- $\text{Al}_2\text{O}_3$  antibonding orbitals explains qualitatively the observed decrease of contact shear strength through the series Fe, Ni, Cu, and Ag. Total energy calculations to quantify the trends were not reported by Johnson and Pepper. Most theoretical work for  $\text{Al}_2\text{O}_3$  has been to investigate bulk properties. Ciraci et al. [2] have computed the electronic structure of  $\text{Al}_2\text{O}_3$  non-self consistently. They did not report surface adsorbate results. Tossel [3] and Shangda et al. [4] have reported electronic structure calculations for  $\text{Al}_2\text{O}_3$  using the cluster approach.

Here, we report a joint theoretical and experimental study of Cu adsorption onto  $\text{Al}_2\text{O}_3$  films. This is the first fully self consistent total energy computation of the properties of an infinite  $\text{Al}_2\text{O}_3$  film with metal adsorbates. We find that Cu atoms bond to surface O atoms instead of surface Al atoms. This assignment is based on the lower total energy for Cu–O surface bonds than for Cu–Al bonds. Also, the computed

density of states (DOS) agrees well with our UPS spectra only for Cu–O bonds. Such results are very different from those we recently reported for Cu bonding with an AlN surface [5]. There we found that Cu atoms preferentially bond to surface Al atoms to form Cu–Al bonds. Formation of Cu–N bonds give a higher total energy and a DOS in disagreement with UPS data for low coverages of Cu adsorbed onto AlN.

Experiments reported in this paper concern successive in situ depositions of Cu on “as fabricated”  $\text{Al}_2\text{O}_3$  surfaces. A high-purity polycrystalline aluminum (Johnson Matthey Inc., N.H.) sample was thermally oxidized by exposing to  $10^6$  L-oxygen at  $400^\circ\text{C}$ . This oxidation process has been well documented elsewhere [6]. At each step of Cu deposition, UPS measurements were performed to probe changes in the valence electron distributions with a He-II ( $h\nu = 40.8$  eV) source.

Ab initio total energy calculations were performed for a 10 atom two layer thick film of  $\text{Al}_2\text{O}_3$  with  $(10\bar{1}0)$  symmetry in the rhombohedral notation. The film has all Al atoms five-fold coordinated with O atoms. Only, one O atom bond is missing to form this surface, as bulk Al atoms are six-fold coordinated. Because of the difficulty of our computation, only two configurations were tried for Cu adsorption. The Cu adsorbate atoms are allowed either to bond to the surface Al atom to form a sixth bond as O atoms do in the bulk or to bond to surface O

atoms as Al atoms would attach for further growth of the surface. The total energy is calculated as a function of bond length for these fixed bond angles. The clean surface is non-planar as O atoms stick out above the plane defined by surface Al atoms. Formation of surface Al–Cu bonds makes for a closer packed surface than does O–Cu bonds which has the Cu atoms rather far above the surface Al atoms. Because of these structural considerations based on close packing, it was important to verify that Cu preferentially bonds to surface O atoms. Intuitively, one would probably expect Cu adsorbate atoms to preferentially bond to surface O atoms.

The calculational technique was the pseudofunction (PSF) method [7] with a Hedin–Lundqvist local density potential [8]. Four  $k$  points in the Brillouin zone were used to achieve self-consistency and total energy. The Cu–Cu distance is  $4.75 \text{ \AA}$  thus indicating there is no direct wave function overlap between Cu atoms. Experimentally, the Cu atoms probably would not be deposited mono-dispersed as chosen theoretically. Some Cu–Cu bonds at low coverage could possibly be formed. Such bonds would make the comparison between experiment and theory less reliable. Thus, total energy is an important component of our study in identifying surface bonding. The good agreement between experiment and theory will be taken as evidence that the Cu atoms are deposited approximately uniformly at low coverage.

In fig. 1, the energy bands have been plotted for a Cu–O bond length of  $1.85 \text{ \AA}$  and a Cu–Al bond length of  $2.55 \text{ \AA}$ . These are the bond lengths minimized with total energy. The  $1.85 \text{ \AA}$  bond length is more stable than the  $2.55 \text{ \AA}$  bond length by  $2.5 \text{ eV}$ . Our  $\text{Al}_2\text{O}_3$  substrate has 18 O p-like bands that are labeled from one to seventeen in fig. 1. The Cu d bands are cross hatched as they are very narrow. Clearly, the d-bands overlap the top of the filled O p states. The Fermi energy occurs at a hybridization between the eighteenth O p band and the Cu s orbitals. As most of the O p bands are below the narrow Cu d bands, it would appear that the Cu d bands are in the band gap of the  $\text{Al}_2\text{O}_3$  bulk bands to the first approximate interpretation.

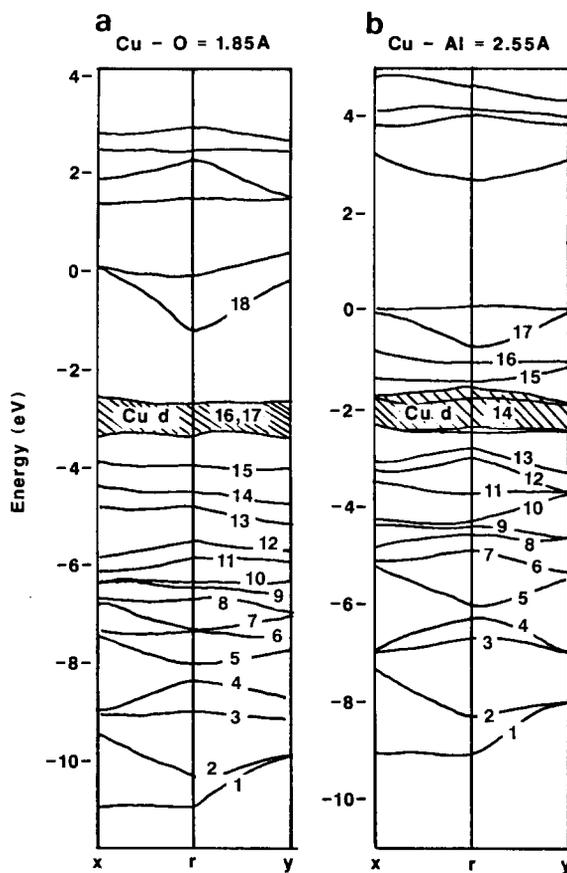


Fig. 1. Energy bands for 0.5 monolayer Cu coverage with (a)  $d(\text{Cu-O}) = 1.85 \text{ \AA}$  and (b)  $d(\text{Cu-Al}) = 2.55 \text{ \AA}$ . The  $\text{Al}_2\text{O}_3$  substrate has 18 filled p states.

The energy bands for the  $2.55 \text{ \AA}$  Cu–Al bonds differ substantially. There are several O p bands which occur above the Cu d bands. Also, the band widths are substantially different for the  $1.85 \text{ \AA}$  and  $2.55 \text{ \AA}$  cases. In fig. 2, a comparison of our density of states for the Cu–O and Cu–Al bonds is made with our UPS data. The spectrometer and theoretical Fermi energies are not the same for several reasons. First, Cu atoms are not expected to absorb uniformly on the  $\text{Al}_2\text{O}_3$  substrate, as is well documented for metals on semiconductors such as GaAs. We can also see this from the shape of the UPS spectrum which looks like metallic Cu in the region near the spectrometer Fermi energy. A monodispersed 50% coverage of Cu atoms would leave the Cu atoms too far apart to form a truly metallic Cu

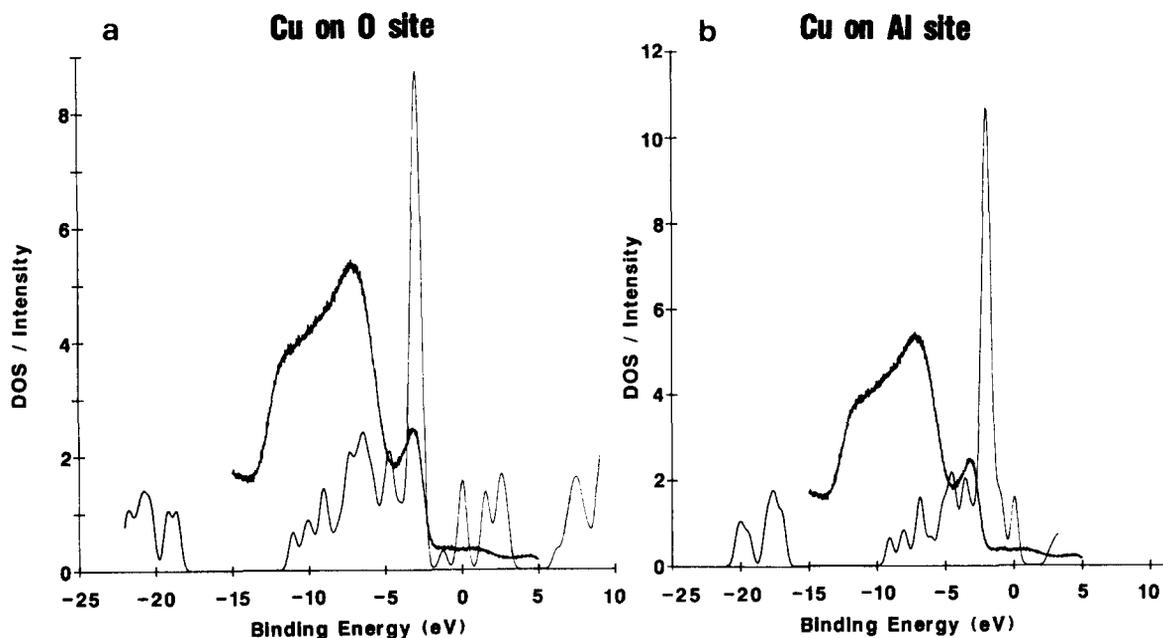


Fig. 2. Comparison of UPS spectrum for 0.5 monolayer Cu coverage on  $\text{Al}_2\text{O}_3$  with DOS for (a) 1.85 Å bond length and (b) 2.55 Å bond length.

Fermi edge. The UPS spectrum in fig. 2 is for 25% Cu coverage. The oxidation of Al films results in primarily  $\gamma\text{-Al}_2\text{O}_3$ . The calculations have been performed for  $\alpha\text{-Al}_2\text{O}_3$ . The UPS spectra were, however, similar for  $\alpha$ - and  $\gamma\text{-Al}_2\text{O}_3$  [8].

The UPS spectra have features characteristic of clean  $\text{Al}_2\text{O}_3$  in the region from  $-5$  to  $-13$  eV. An entirely new peak is observed at about  $-3$  eV. Clearly this peak is due to the d bands. Our calculated 1.85 Å DOS for a four  $k$  point sample is also shown in fig. 2. The d band occurs at  $-3.25$  eV as in the UPS spectrum. The width of the calculated DOS is also very similar to the UPS spectrum. The maximum in the DOS for the p bands occurs near  $-7$  eV as also occurs in the experimental spectrum. Such agreement would be considered excellent and considered to strongly support the view that Cu–O bonds initially form. Such agreement cannot be found for the 2.55 Å case in fig. 2b. The computed DOS is far too narrow. Furthermore, the d bands overlap the primary peak in the O p bands which the UPS data clearly shows to be below the Cu d bands.

In conclusion, our theoretical and experimental work strongly supports the formation of Cu–

O bonds at low coverage for Cu adsorption in  $\text{Al}_2\text{O}_3$ . The resulting structure is thus very non-planar. We would expect that Cu atoms would not deposit uniformly for such bonding. The metallization of the  $\text{Al}_2\text{O}_3$  surface appears to differ fundamentally from that found earlier for AlN surfaces. We would expect the Cu–Al covalent-like bonds on AlN to be much stronger than the partially ionic ones found for Cu on  $\text{Al}_2\text{O}_3$ . Hopefully this can be tested experimentally.

## References

- [1] K.H. Johnson and S.V. Pepper, *J. Appl. Phys.* 53 (1982) 6634.
- [2] S. Ciraci and I.P. Batra, *Phys. Rev. B*, 28 (1983) 982.
- [3] J.A. Tossel, *J. Phys. Chem. Solids* 36 (1975) 1273.
- [4] X. Shangda, G. Chanaxin, L. Libin, D.E. Ellis, *Phys. Rev. B* 35 (1987) 7671.
- [5] R.V. Kasowski and F.S. Ohuchi, *Phys. Rev. B* 35 (1987) 9311.
- [6] W.J. Cignac, P.S. Williams and S.P. Kowalczyk, *Phys. Rev. B* 32 (1985) 1237.
- [7] R.V. Kasowski, M.-H. Tsai, T.N. Rhodin, and D.D. Chambliss, *Phys. Rev. B* 34 (1986) 2656.
- [8] L. Hedin and B.I. Lundqvist, *J. Phys. C* 4 (1971) 2064.
- [9] F.S. Ohuchi and R.H. French, to be published.