Cu deposition on Al₂O₃ and AlN surfaces: Electronic structure and bonding

F. S. Ohuchi, R. H. French, and R. V. Kasowski

E. I. du Pont de Nemours and Co., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

We report a photoelectron spectroscopy study of the interaction of copper with Al₂O₃ and AlN model systems processed under ultrahigh vacuum conditions and compared the intrinsic electronic interactions between the two cases. The evolution of the electronic structure and bonding of Cu to AlN has been further studied using *ab initio* total energy pseudofunction techniques.

I. INTRODUCTION

The metallization behavior of α-Al₂O₃ (an important substrate material for ceramic packages) and AlN (a new substrate material with superior thermal conductivity) are of great importance in packaging applications. In addition, Al₂O₃ and AlN are the end members of a compositional family, including AlON and γ-Al₂O₃. The polycrystalline AlN powders used in ceramic substrates typically contain 1%–2% O, present on the surface or in the bulk, which can effect the thermal conductivity and metallization properties. In studies of the metallization behavior of oxygen contaminated AlN, the intrinsic properties of the interaction between the metal and the substrate may not be observed. Therefore, we have undertaken a comparative study of the bonding of Cu to "pure" Al₂O₃ and AlN, taking care to prepare samples of the intrinsic materials, without the doping or impurities present in substrate samples. This is a study of the room-temperature bonding, and does not consider the effects of eutectic phase formations, alloying, or atomic scale mixing which can occur at elevated processing temperatures. Much previous experimental work has been performed on photoelectron spectroscopy of Cu-Al₂O₃, in addition to cluster-type electronic structure models, to determine the electronic density of states and electronic interaction associated with the bonding in this system. We have extended this work to include both the Cu-Al₂O₃ interaction and photoelectron spectroscopy and self-consistent pseudofunction calculations for Cu-AlN to study the electronic interactions which identify the type of bonding of the metal to the substrate and the atomic configuration of the metal atom on the substrate. The comparison of the bonding of Cu to oxygen-rich surfaces, such as Al₂O₃ or AlN with a high concentration of surface oxygen, to that found in covalent systems, such as surfaces of oxygen-free AlN, may help guide and direct future solutions to metallization problems of AlN and Al₂O₃ substrates.

II. EXPERIMENT

Preparation and characterization of Al₂O₃ and AlN thin films was performed *in situ* in an ion-pumped UHV vacuum system. The system is equipped with a double pass cylindrical mirror analyzer used for AES, XPS, and UPS analyses. The sample was a high-purity polycrystalline aluminum (Johnson Matthey Inc., N. H.). The initial alumi-num surface was cleaned *in situ* by successive argon-ion sputtering and annealing. The Al₂O₃ was formed by thermal oxidation of aluminum [10^6L-oxygen, 400 °C]. This oxidation process has been well documented elsewhere.[1] The AlN surface was created by reacting a N₂⁺ ion beam with the clean aluminum. The conditions for nitridation and characterization of the resulting films have been previously published.[2]

Experiments reported in this paper concern successive *in situ* deposition of copper on these as-fabricated Al₂O₃ and AlN surfaces. At each step of Cu deposition, XPS and UPS measurements were performed to probe changes in the core and the valence-band electron distributions with a MgKα nonmonochromatized x-ray source and a He-II (hv = 40.8 eV) source, respectively. The copper (LMM) Auger signal was measured versus deposition time to identify the growth mode of the overlayer and to determined the coverage.

Ab initio total energy calculations were performed for four layer unrelaxed AlN (110) films with Cu placed on both sides of the film. The calculation technique was the pseudofunction method[3] with a Hedin–Lundquist[4] local density. Computations were made with two different Cu coverage configurations [0.5 monolayer (ML) and 1.0 ML] (Fig. 1). For the 0.5-ML configuration, Cu atoms interact with all surface Al atoms or surface N atoms [Fig. 1(a)]. The bond distance is varied to find the total energy minimum. However, the bond angles are only allowed to assume the tetrahedral value which would be produced with further growth of the film. For the 1.0-ML coverage, additional Cu atoms were placed above the midpoint between adjacent Cu atoms [Fig. 1(b)]. The height was adjusted so as to give a Cu–Cu bond length of 2.60 Å, which is nearly the same as the Cu–Cu bond length found in metallic copper (2.54 Å). This chainlike structure is the simplest configuration for 1-ML coverage which allows us to calculate the density of states with respect to specific bonding sites. Comparison between experiment and theory may not be exact, since the experimental AlN thin films are polycrystalline with unknown surface structure, while the theoretical surfaces are idealized.

III. RESULTS AND DISCUSSION

The experimental UPS valence electron distributions for clean Al₂O₃ and AlN, and after successive Cu deposi-
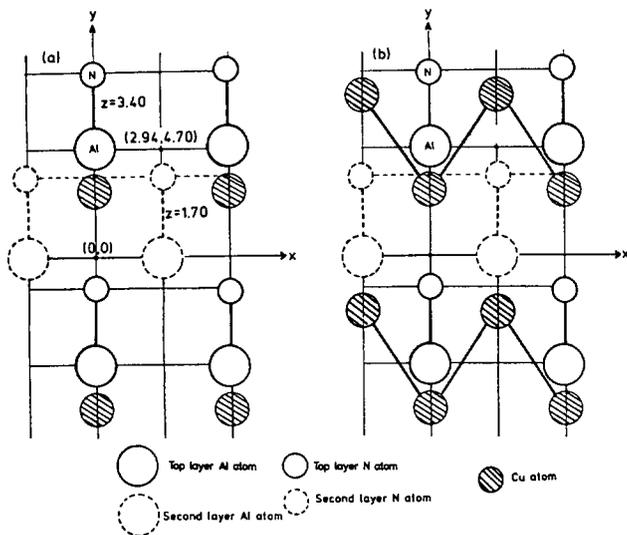
FIG. 1. XYZ coordinates for atom positions of AlN and Cu used in calculation (a) 0.5-ML configuration (Cu on Al site is shown) and (b) 1.0-ML configuration.

FIG. 3. Valence-band photoemission spectra for AlN films with various deposition of Cu.

tions are shown in Figs. 2 and 3, respectively. For Al_2O_3, there are two maxima at 7 and 11 eV below the Fermi level. The 7-eV peak has been assigned to nonbonding oxygen $2p$ lone pair orbitals while the 11-eV peak arises from hybridized oxygen sp^2 orbitals and aluminum sp^3 orbitals.[1] The AlN spectrum is dominated by a band with a maximum at 6 eV [predominantly $N(2p)$ with admixture of Al orbitals[2,5,6]] and a shoulder at 8.5 eV. The valence-band maximum (VBM) for Al_2O_3 and AlN are located at ~ 4 and ~ 2 eV, respectively, below the Fermi edge of the metallic Al.

At copper coverages above one monolayer (1 ML), the $Cu(3d)$ orbital peak, located at 2.5 eV below the Fermi edge, becomes the dominant contribution to the UPS results for both materials. However, for submonolayer coverages, the results are quite different for each substrate material. We will discuss the electronic structure and bonding of Cu at
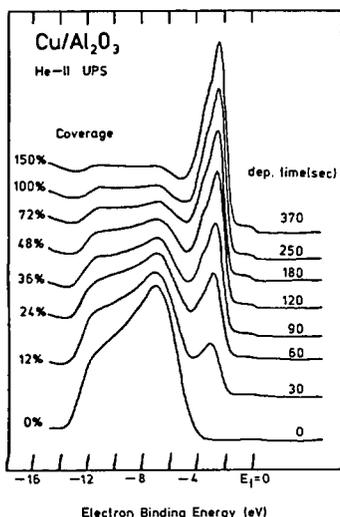

FIG. 2. Valence-band photoemission spectra for Al_2O_3 films with various deposition of Cu.
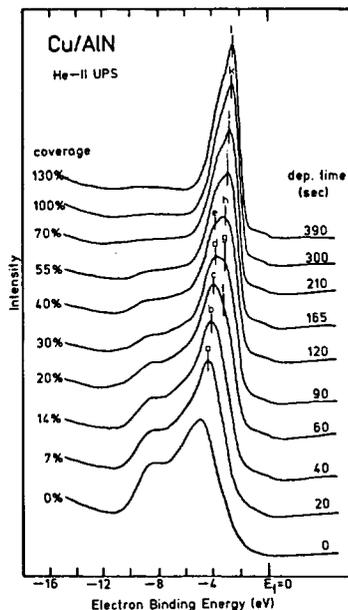
submonolayer coverages on the Al_2O_3 and AlN surfaces in greater detail.

A. Cu-Al$_2$O$_3$

When Cu is deposited on the Al_2O_3 (Fig. 2), the emission from the $Cu(3d)$ band appears initially (12%) at slightly higher binding energy (3 eV) than for metallic copper (2.5 eV). This peak grows and finally approaches that of bulk copper. Compared to bulk copper only a proportional attenuation and small shift was observed. This small shift of the $Cu(3d)$ level indicates that the copper only interacts weakly with the substrate, and the substrate has not changed the character of the $Cu(3d)$ level. Johnson and Pepper[7] have performed self-consistent field, X-α scattered wave, cluster calculations of noble metals on Al_2O_3 surfaces. They found that the electronic interaction between metal d orbitals and nonbonding $O(2p)$ orbital is responsible for bond formation. For Cu on Al_2O_3, it is found that the oxygen $(2p)$ antibonding orbitals are fully occupied while the covalent contribution of the bonding orbitals is canceled with only small residual ionic and van der Waals bonds being formed. The slight shift in binding energy observed for the $Cu(3d)$ band at low coverage presumably indicates this weak bond formation.

Additional support for ionic bond formation between oxygen and copper is given by Mackrodt.[8] He has recently found that, for all but the basal surface, substantial rumpling occurs, leading to surfaces consisting predominantly of oxygen atoms, with the aluminum atoms retracted into surface. Therefore, copper deposited on the surface of Al_2O_3 will primarily interact with the surface oxygen atoms.

These theoretical results serve to explain our observation of the $Cu(3d)$ level at 3 eV, the oxidized copper value. The copper at coverages below one-half monolayer bonds ionically with the outermost oxygen atoms to form copper–oxygen bonds. Above one-half monolayer coverage, this ion-

ic interaction ceases, and we observe the formation of metallic copper [$Cu(3d)$ at 2.5 eV].

B. Cu-AlN

The evolution of the AlN valence-band electron density of states with successive Cu deposition (Fig. 3) is considerably different from that observed for Al_2O_3. At submonolayer coverages, the $Cu(3d)$ derived peak appears at considerably higher binding energy and almost overlaps with $N(2p)$ orbitals (peaks a, b, c, d, and e). As the coverage increases, a second $Cu(3d)$ derived feature appears at approximately 1 eV lower in binding energy (peaks $f, g, h, ...$). While this peak grows in intensity, together with the emission observed in the early stages of coverage, it eventually develops into the metallic $Cu(3d)$ band at higher coverage (peak k and l). The chemical bonding at submonolayer coverage is best resolved by subtracting the contribution of the main AlN photoelectron distribution from the Cu deposited spectrum. It is found that the Cu-derived peak appears at 4.5 eV for a coverage of 7%, which is 2 eV higher in binding energy than that of the bulk $Cu(3d)$ peak. However, development of this peak ceases at a coverage of less than 50%, at which point the metallic $Cu(3d)$ feature (at 2.5 eV) becomes the dominant feature. Therefore, our data suggest the presence of at least two types of bonding for the interaction of Cu on AlN.

In order to elucidate the electronic structure of the Cu-AlN interaction from a more atomistic perspective, and to determine the copper bonding site, we have performed self-consistent *ab initio* band structure and total energy calculations for Cu on AlN. By performing the calculation for 0.5-ML coverage of Cu interacting with Al and N atom sites, it is found that the total energy of the system is 3.1 eV (per surface Cu atom) more stable for Cu on the Al site. Therefore, the calculation suggests that the Cu atoms will interact with the surface Al atoms rather than the surface N atoms initially. The calculated energy bands, for 0.5-ML coverage, for Cu above the Al and N sites are plotted in Fig. 4. We see that $Cu(3d)$ bands overlap the valence band for Cu above the Al site model, while for Cu above the N site the bands lie in the band gap. The Cu on Al site model is more consistent with the data than the Cu–N bonding configuration, since the overlapping of the $Cu(3d)$ band and the valence band is observed experimentally.

For higher coverage of Cu, we have modeled the system by putting Cu atoms on the midpoint between adjacent Cu atoms to form 1-ML coverage. The total density of states and Cu local density of states is shown in Fig. 5. Notice that an additional band (b) develops in the band structure, in addition to the band (a) which overlaps the AlN valence-band density of states. This band (b) primarily consists of the contribution from Cu-Cu interaction and a small contribution from Cu-N interaction. These two bands are separated by approximately 1 eV, consistent with our experimental results which show these two types of bonding.

The binding energy shift and line shape change of the Al core levels also give information about chemical bonding. Figure 6 shows the change of the $Al(2s)$ and development of $Cu(3s)$ core level spectra with increasing Cu coverage. As
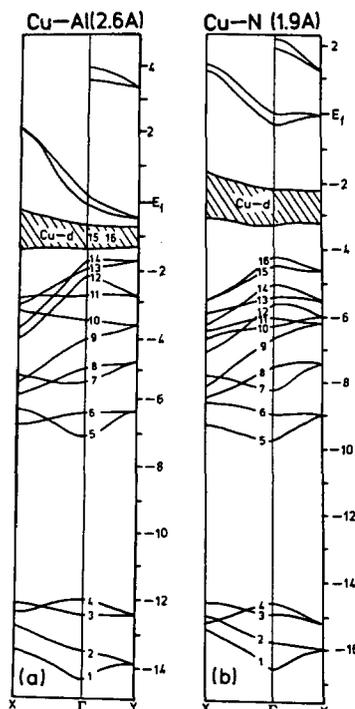

FIG. 4. Energy bands for 0.5-ML Cu coverage with (a) Cu-Al = 2.6 Å and (b) Cu-N = 1.9 Å. The AlN substrate has 16 filled bands.

illustrated in Fig. 6, the $Al(2s)$ level shifts slightly toward lower binding energy with increasing coverage, up to 50% coverage. This is related to band bending as a result of the Fermi level shifting to that of the Cu adsorbate. The $Al(2s)$ level also undergoes peak broadening toward lower binding energy as soon as Cu is deposited, and the lower-energy component of the $Al(2s)$ peak becomes observable because of attenuation of main $Al(2s)$ band. Appearance of this lower binding energy component presumably indicates the formation of some metallic bonding with aluminum. The above experimental and theoretical data consistently suggest Cu–Al bond formation.

IV. CONCLUSION

A study of the electronic structure and bonding of Cu on Al_2O_3 and AlN was performed to elucidate the effect of the
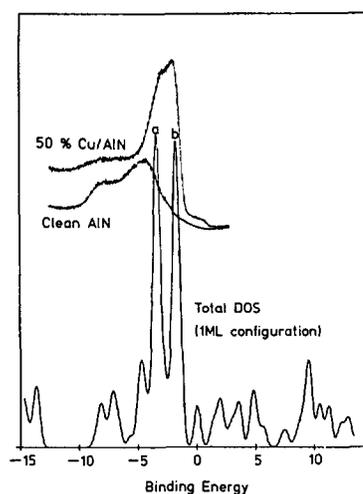

FIG. 5. DOS for 1.0-ML Cu coverage with comparison to valence-band photoemission spectra for clean and 50% Cu covered AlN surfaces.
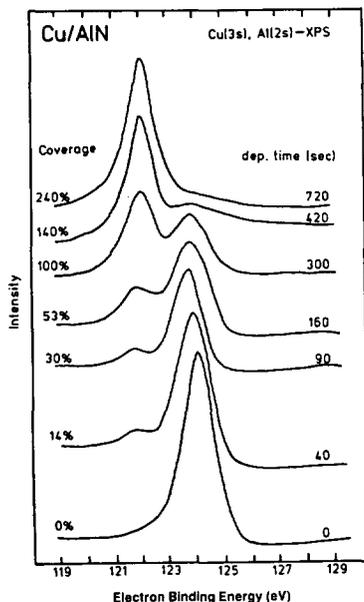
FIG. 6. Al(2s) core level photoemission spectra for AlN with various deposition of Cu.

ionicity or covalency of the material and to determine the metallization behavior of oxygen-free AlN. Cu was deposited *in situ*, up to monolayer coverages, on as-fabricated thin-film surfaces created in UHV. These were then studied using AES, XPS, and UPS, and the case of Cu deposition on AlN was modeled using self-consistent pseudofunction techniques to determine the total energy and band structure of Cu bonded on the Al and N sites. For Al_2O_3 at low coverage (<0.5 ML) only a slight shift of the Cu(3d) derived feature from the copper oxide position was observed. Above 0.5-ML coverage, the Cu(3d) peak appeared at the metallic copper value. This is consistent with reported cluster calculations and demonstrates the initial formation of weak ionic bonds between Cu and O followed by the formation of metallic Cu at higher coverages. For AlN, the Cu(3d) derived feature is strongly shifted and overlaps the AlN valence band. As coverage increases a second Cu(3d) feature appears which develops into the bulk Cu(3d) peak with increasing coverage. Pseudofunction calculations performed with Cu at the Al

and N sites for 0.5 coverages show that the system is more stable for the case where metallic bond formation occurs between Cu and Al atoms. At 1.0-ML coverage the Cu resides in a bridging position between the surface copper atoms, forming Cu–Cu metallic bonds. The calculated electron density of states for the calculations are consistent with the observed appearance of Cu(3d) orbitals in the AlN valence band and the subsequent appearance of separate bands associated with the Cu–Cu bond formation. This analysis is also supported by the observed binding energy shifts and line shape changes of the Al core levels. Therefore, we can see the dramatically different nature of the bonding for the ionic and covalent substrate. The ionic substrate (Al_2O_3) initial bond formation is ionic in nature and forms between the Cu and O atoms, while for the covalent substrate (AlN), initial bond formation is metallic and occurs between Cu and Al atoms. The presence of surface oxygen on contaminated AlN powders may strongly effect the nature of the bonding associated with metallization.

ACKNOWLEDGMENT

[1]W. J. Cignac, P. S. Williams, and S. P. Kowalczyk, Phys. Rev. B 32, 1237 (1985).

[2]J. A. Taylor and J. W. Rabalais, J. Chem. Phys. 75, 1735 (1981).

[3]R. V. Kasowski, M.-H. Tsai, T. N. Rhodin, and D. D. Chambliss, Phys. Rev. B 34, 2656 (1986); R. V. Kasowski, T. N. Rhodin, and M.-T. Tsai, Appl. Phys. A 41, 61 (1986); R. V. Kasowski, M.-H. Tsai, and T. N. Rhodin, Solid State Commun. 59, 57 (1986).

[4]L. Hedin and B. I. Lundquist, J. Phys. C 4, 2064 (1971).

[5]W. Y. Ching and B. N. Harmon, Phys. Rev. B 34, 5305 (1986).

[6]C. G. Olson, J. H. Sexton, D. W. Lynch, A. V. Bevolo, H. R. Shanks, B. N. Harmon, W. Y. Ching, and O. M. Wieliczka, Solid State Commun. 56, 35 (1985).

[7]K. H. Johnson and S. V. Pepper, J. Appl. Phys. 83, 6634 (1982).

[8]W. C. MacKroat, Presented at the Conference on Quantum Theory Applied to Solids, University of Maryland, July 21, 1986 [J. Phys. Chem. Solids (to be published)].