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Electronic structure of Cu overlayers on AlN

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The evolution of the electronic structure and bonding of Cu to AlN has been studied both experimentally and theoretically. *Ab initio* total-energy pseudofunction calculations indicate that the Cu adsorbate initially prefers formation of Cu—Al bonds, not Cu—N bonds. This theoretical finding is supported by good agreement between the density of states (DOS) and ultraviolet photoemission spectra (UPS) for low coverage of Cu on AlN. Cu—N bonds give a DOS in complete disagreement with UPS.

Aluminum nitride (AlN) is emerging as an attractive substrate material in microelectronic packaging applications because of its superior thermal and mechanical properties.[1] Metallization of this material is, therefore, an important technological concern, yet few fundamental investigations have been made in the past. Particularly, there have been no studies of the electronic structure and bonding between a metal and the AlN surface. This is partly because the preparation of oxygen-free AlN is very difficult, so the intrinsic properties of the interaction may not be observable.

The electronic structure of AlN has been studied by several workers both experimentally and theoretically. Gabe, Le Poge, and Mair[2] determined the valence charge density using x-ray diffraction and suggested that the AlN bonding is more ionic than covalent, but some degree of covalency is still present due to the tetrahedral coordination and wurtzite structure. A fully self-consistent electronic structure calculation of AlN has been determined recently by Ching and Harmon[3] and excellent agreement to the photoemission spectra[4] has been observed.

Here, we report the first experimental and theoretical results for the electronic properties of submonolayer to thick film coverage of Cu on AlN. We find that Cu atoms bond preferentially to the surface Al atoms to form metal-metal bonds. This assignment was based on the Al—Cu bonds having lower total energy than the Cu—N bonds. Also, the computed density of states (DOS) agrees well with our experimental ultraviolet photoemission spectrum (UPS) only for the Cu—Al bonds. The Cu—N bonds give an electronic DOS in total disagreement with the experiment.

Experiments reported in this paper concern successive *in situ* deposition of copper on "as-fabricated" AlN surfaces. At each step of Cu deposition, x-ray photoemission spectroscopy (XPS) and UPS measurements were performed to probe changes in the valence and core-level electron distributions with a Mg $K\alpha$ nonmonochromatized x-ray source and the He II ($h\nu=40.8$ eV) ultraviolet photoelectron source, respectively. Copper (LMM) Auger signal versus deposition time was measured and used to determine the coverage. To fabricate an AlN surface, a high-purity polycrystalline aluminum was first cleaned by successive argon sputtering (Ar^+, 1 keV) and annealing at 450 °C and then bombarded *in situ* by a 3-keV N_2^+-ion beam with a beam intensity of 18 μA/cm^2 for 300 sec at room temperature. The estimated range of nitride layer is in the order of 100 Å according to the Lindhart-Scharff-Schiott (LSS) theory.[5] The conditions for nitridation and characterization of the resulting films have been previously published.[6] An oxygen-free stoichiometric AlN surface is obtained and identified by Auger-electron spectroscopy (AES), XPS, and UPS. With the thin nitride layer underlying the metallic substrate, no charging effect was observed during analyses.

Ab initio total-energy calculations were performed for four-layer unrelaxed AlN($11\bar{2}0$) films with Cu placed on both sides of the films. The calculation technique was the pseudofunction (PSF) method[7] with a Hedin-Lundqvist[8] local density potential. Computations were made with two different Cu coverage configurations [0.5 and 1.0 monolayers (ML)]. For the 0.5 ML configuration, Cu atoms interact with all surface Al atoms or surface N atoms. 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 at the midpoint between

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adjacent Cu atoms forming a plane of Cu parallel to the surface. The positions were adjusted so as to give a Cu—Cu bond length of 2.6 Å, which is nearly the same distance as metallic Cu (2.54 Å). This chainlike structure is the simplest configuration of 1 ML that allows us to calculate the total energy and DOS with specific bonding sites. Comparison between experiment and theory may not be exact since the AlN thin film is polycrystalline and the surface structure is unknown. Therefore, the most reasonable estimate of the surface structure for calculation should be the most stable surface, AlN(11$\bar{2}$0). Furthermore, recent theoretical calculations[9] for AlN indicate that the surface Al—N bond on the (11$\bar{2}$0) surface rotates by only 2°, so that the surface reconstruction is very small.

The UPS spectra for an AlN film with successive depositions of Cu are shown in Fig. 1. The clean AlN spectrum consists of two maxima at 5 and 8.5 eV below the Fermi edge, as determined by the clean Al substrate before nitridation. It is shown that the electron density near the Fermi edge has totally vanished and is polarized into the nitrogen $2p$ level observed at 5 eV. A very similar clean AlN spectrum[4] has been previously obtained with excellent agreement to the calculated DOS.[3] When Cu is deposited onto the AlN surface, we observe the Cu($3d$)-derived peak overlapping the N($2p$) peak at submonolayer coverages (peaks a, b, c, d, and e). As the coverage increases, a second Cu($3d$) feature appears at approximately 1 eV lower in binding energy (peak $f,g,h,\ldots$). While this peak grows in intensity, together with the emission observed in the early states of coverage, peak f,g,h 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 spectrum from the Cu deposited one. 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. Development of this peak, however, ceases at coverage of less than 50%, at which point the metallic Cu($3d$) feature becomes the dominant contribution. Therefore, our data suggest the presence of at least two types of bonding for the interaction of Cu on AlN.

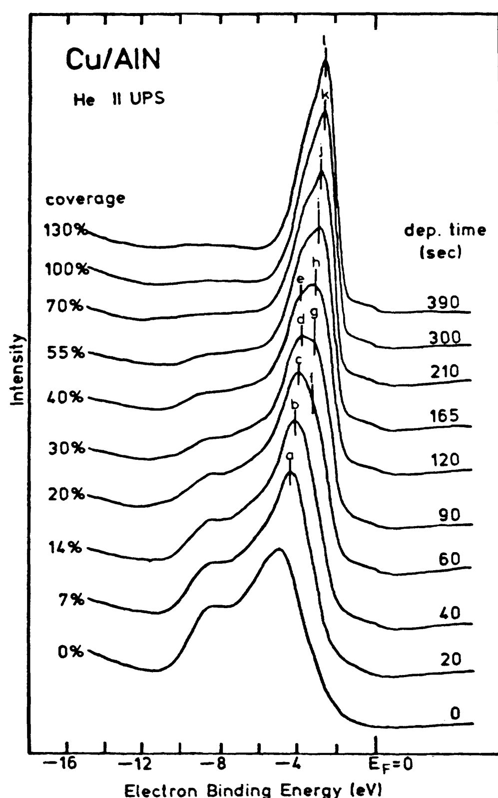

FIG. 1. UPS spectra for AlN films with various deposition of Cu.

We now show that the above data can be explained by the formation of Cu—Al metal-metal bonds. First, we performed total-energy calculations for Cu bonding only to Al atoms or only to N atoms. For this 0.5-ML coverage, the adatoms are in a tetrahedral site. The minimized bond lengths are found to be 2.63 and 1.90 Å for Cu—Al and Cu—N bonds, respectively. The total energy of the Cu-Al configuration is found to be 3.1 eV per surface Cu atom more stable than that of the Cu-N configuration. Therefore, the Cu atoms will interact with the surface Al atoms rather than the surface N atoms, initially. This assignment is supported by comparison to the UPS data. The energy bands for 0.5 ML of Cu bonded to Al atoms or N atoms of the AlN surface are plotted in Fig. 2. The $3d$ bands overlay the valence band for Cu—Al bonding [Fig. 2(a)], while the bands lie in the band gap for Cu—N bonding. Therefore, the Cu on Al site model is more consistent with the UPS data.

In an effort to see how the electronic structure is altered at higher coverages of Cu, we formed a 1.0-ML Cu coverage on the AlN surface. Our guideline is to form a planar Cu coverage which does not have strong Cu—N bonds, which we previously found to drive the d bands into the band gap. Thus, a reasonable surface structure is to place Cu atoms between the surface Cu atoms to form a zigzag pattern of 2.60-Å Cu—Cu bonds in a direction and perpendicular to surface Al—N bonds. This configuration has Cu—N bonds of 2.9 Å. The resultant density of states, with comparison to UPS spectra of the clean AlN and 50% coverage of Cu, is shown in Fig. 3. Two $3d$ bands are indicated by (a) and (b). Notice that the peak (b) develops in the band gap, in addition to the band (a) which overlaps the AlN valence band DOS. This band (b) primarily consists of the contributions from Cu-Cu interactions and a small contribution from Cu-N interactions. These two bands are separated by approximately 1 eV, consistent with our experimental results which show these two types of bondings.

The spectrometer Fermi energy and the theoretical Fermi energy are not identical for experiment and theory in Fig. 3. It is expected that Cu atoms do not adsorb uniformly on the AlN 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 very much like metallic Cu in the region near Fermi energy. A monodispersed 50% coverage of Cu atoms on AlN would

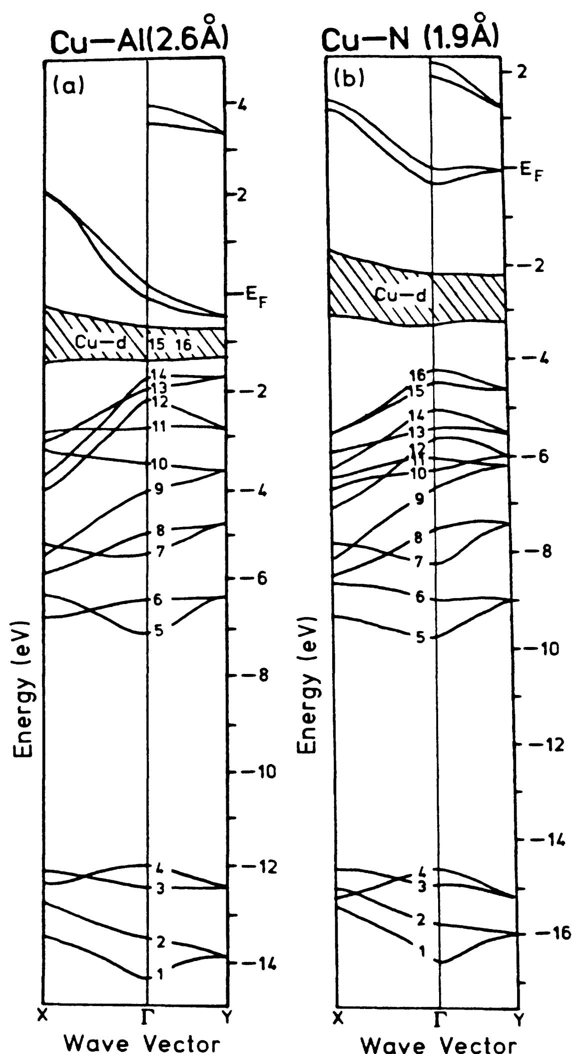

FIG. 2. Energy bands for 0.5-ML Cu coverage with (a) d(Cu—Al) = 2.6 Å and (b) d(Cu—N) = 1.9 Å. The AlN substrate has 16 filled bands.

leave the Cu atoms too far apart to form a truly metallic Cu Fermi edge. Thus, we have tried to match the bottom of the UPS spectra near 10 eV with the bottom of the calculated valence band stated near Fermi energy. The features 5 to 10 eV below Fermi energy do not appear very sensitive to Cu deposition and thus serve as a reasonable guide to aligning the theoretical and experimental Fermi energy.

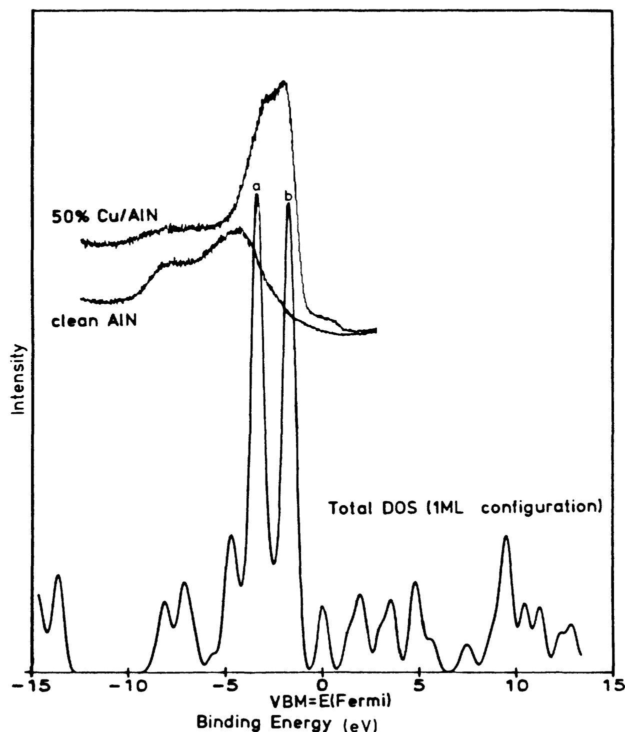

FIG. 3. DOS for 1.0-ML Cu coverage with comparison to UPS for clean and 50% Cu coverage. VBM denotes valence-band maximum.

The binding-energy shift and line shape change of the Al core levels obtained from XPS measurement also give information about chemical bonding. Two things are noted in the observation: (1) The Al(2s) level shifts toward higher binding energy by 0.7 eV with increasing coverage up to 50%. The shift is related to band bending as a result of the Fermi level shift to that of the Cu adsorbate. (2) The Al(2s) level undergoes peak broadening with appearance of a low-energy component of Al(2s), which is presumably assigned to a metallic Al component at the surface. Appearance of a metallic Al component is consistent with the theoretical computation.

In summary, we have presented an experimental and theoretical investigation of the electronic structure of a Cu overlayer on AlN. It appears that metal adsorbates prefer to form metal–metal bonds.

[1]G. R. Kline and K. M. Lakin, Appl. Phys. Lett. **43**, 750 (1983); Y. Kurokawa, K. Utsumi, H. Takamizawa, T. Kamata, and S. Noguchi, IEEE Trans. Compon. Hybrids Manuf. Technol. **8**, 247 (1985).

[2]E. Gabe, Y. LePoge, and S. L. Mair, Phys. Rev. B **24**, 5634 (1981).

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

[4]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).

[5]J. P. Biersack and J. F. Ziegler, in *Ion Implantation Technique,* Springer Series in Electric Physics, Vol. 10, edited by H. Rys-sel and H. Lawisching (Springer, Berlin, 1982), pp. 122 and 157.

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

[7]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. **41**, 61 (1986); R. V. Kasowski, M.-H. Tsi, and T. N. Rhodin, Solid State Commun. **59**, 57 (1986).

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

[9]R. V. Kasowski, M.-H. Tsai, and J. Dow (unpublished).