Summary Abstract: A study of roomtemperature Cu–Al2O3 and Cu–AlN interfacial reactions

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temperature. Mass scans (beam energy = 325 eV) were taken at various temperatures during heating and cooling. The area of the \( H^+ \) peak in the mass spectrum is plotted as a function of temperature in Fig. 2(a). The \( H^+ \) yield increases at temperatures slightly above room temperature and then decreases gradually to about 450 °C, above which a background level remains. Such a background level is to be expected, since it has been shown that hydrogen will diffuse from the bulk to the LiF surface, particularly under photon \(^+\) or electron \(^-\) bombardment. Upon cooling, no significant readsorption of hydrogen or hydrogen-containing species occurs until temperatures below 300 °C. The initial increase in \( H^+ \) yield immediately above room temperature is very likely due to diffusion of impurities from the near-surface region to the surface as the \( H^+ \) increase is correlated with \( Li^+ \) and \( F^- \) decreases immediately above room temperature [Figs. 2(b) and 2(c), respectively]. The behavior of the \( F^- \) and \( Li^+ \) yields as a function of temperature cannot be completely understood from the data presented, as it has been shown above that the \( Li^+ \) and \( F^- \) yields cannot be directly related to surface species concentration.

One conclusion of this work is that the LiF surface structure greatly influences the interaction of the surface with \( H_2O \), as undissociated water was observed at the surfaces of evaporated thin films, but not single crystals. A second conclusion is that sample heating reduces surface contamination, as evidenced by the reduction of contaminant peaks [Fig. 2(b)] and the behavior of the \( H^+ \) yield with temperature. However, the \( Li^+ /F^- \) ratio is also significantly affected, though the exact relationship of this behavior to actual surface stoichiometry can only be established by analytical techniques less potentially sensitive to defect or minority sites, such as XPS or Auger spectroscopy.

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Summary Abstract: A study of room-temperature Cu–\( Al_2O_3 \) and Cu–\( AlN \) interfacial reactions

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Aluminum oxide (\( Al_2O_3 \)) and aluminum nitride (\( AlN \)) are two of the most important ceramic materials in microelectronic packaging because of their superior physical and chemical properties. Metallization of these materials is an important technological concern in these applications. Therefore understanding of the electronic interaction and bonding of metals with these materials is of great fundamental and technological importance.

In spite of the many previous studies of metallization of \( Al_2O_3 \), there have only been a few papers discussing metallization of \( AlN \). This is because the properties of \( Al_2O_3 \) have been the subject of intense study for the last three decades due to its many ceramic and optical applications, while \( AlN \) is a relatively new material in these fields. In addition, experimentally, the preparation of oxygen-free \( AlN \) is very difficult, so it is difficult to study the intrinsic \( Cu/AlN \) interaction. A comparative study of \( Cu/Al_2O_3 \) and \( Cu/AlN \) is especially interesting because of the dramatic differences in the chemical bonding of the two substrate materials, \( Al_2O_3 \) is an ionic material while \( AlN \) is covalently bonded. Therefore we may expect that this difference in chemical bonding will lead to changes in the metallization behavior of the two systems. In view of these facts, we have undertaken to study the interaction of copper with \( AlN \) and \( Al_2O_3 \) on model systems processed under UHV conditions.

The \( Al_2O_3 \) was obtained by thermally oxidizing a clean aluminum surface (10\(^{-6}\) L oxygen at 400 °C \( in situ \)). The \( AlN \) samples were created by reacting a \( N_2^+ \) ion beam with a clean aluminum surface. The conditions for nitridation and characterization of the resulting films have been previously published. Experiments were carried out \( in situ \) by depositing copper onto these “as-fabricated” \( Al_2O_3 \) and \( AlN \) sur-

faces. At each step of Cu deposition, x-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) measurements were performed to probe changes in the valence and the core level electron distribution with He II ($h\nu = 40.8$ eV) and Mg K\alpha nonmonochromatized x-ray sources, respectively. The valence electron distributions for successive room-temperature Cu deposition on Al$_2$O$_3$ and AIN are shown in Figs. 1 and 2, respectively. Clean Al$_2$O$_3$ has a maximum in the electron distribution at $\sim 7$ eV with a shoulder at $\sim 11$ eV, which have been assigned as the O(2p) orbital and the Al-O hybridized orbital, respectively. The AIN spectrum is dominated by a broad band with a maximum at $\sim 6$ eV (predominantly N(2p) with admixture of Al orbitals) and a shoulder at $\sim 8.5$ eV. The valence-band maximum (VBM) is located at $\sim 2$ eV below the Fermi edge of the metallic Al.

For Cu coverage above one monolayer, 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, due to the relatively high cross section for photoionization of the Cu(3d). However for submonolayer coverage the results are very different for each substrate material.

For Cu/Al$_2$O$_3$, the Cu derived emission initially (at 12% coverage) appeared at slightly higher binding energy (\sim 3 eV) than for metallic copper (\sim 2.5 eV). While this Cu peak grows and finally approaches that of bulk copper, only a proportional attenuation, but no shift in binding energy of the Al$_2$O$_3$ peaks was observed. These data, therefore, indicate that the copper interacts only weakly with the substrate. Johnson and Pepper, using cluster electronic structure models, have suggested the formation of an ionic bond between the Cu(3d) orbital electrons and the nonbonding oxygen 2p orbital electrons on the Al$_2$O$_3$ surface. In addition Mackrodt, using atomistic lattice simulations has found that for all but the basal surface substantial rumpling occurs leading to surfaces consisting predominantly of oxygen atoms with aluminum atoms retraced into surface. This result supports the idea that copper deposited will interact initially with oxygen. 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 ionic interaction ceases and we observe the formation of metallic copper [Cu(3d) at 2.5 eV].

Considerably different photoemission features are observed during deposition of Cu on the AIN surface. At submonolayer coverages, the Cu(3d) derived peak appears at considerably higher binding energy than is the case for Al$_2$O$_3$ and overlaps with the N(2p) orbital at submonolayer coverages (peaks a–c in Fig. 2). Development of this peak, however, ceases at a coverage of less than 50%. The chemical bonding at submonolayer coverage is best resolved by subtracting the contribution of the main AIN photoelectron distribution from the Cu deposited spectrum. The subtracted peak position in binding energy is plotted as a function of Cu coverage in Fig. 3. It is found that the Cu derived peak appears at \sim 4.5 eV [2 eV higher in binding energy than the bulk Cu(3d) peak] for a coverage of 7% and a progressive shift in the binding energy along with the increase in the intensity are observed for increasing coverage up to one-half monolayer.