An x-ray spectromicroscopic study of electromigration in patterned Al(Cu) lines

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We studied the surface properties of patterned Al(Cu) lines related to the electromigration phenomena using photoemission spectromicroscopy techniques. We stressed the lines for electromigration *in situ* in the ultrahigh vacuum microscope chamber and observed the changes on the line surface. Our results show surface precipitation of Cu beneath the Al_2O_3 layer on the line surface as well as on side walls. Enrichment of grain boundaries in Cu due to electromigration flux was observed in areas downstream of voids with respect to the electron flow. © *1999 American Institute of Physics.* [S0003-6951(99)01801-X]

Electromigration in Al(Cu) interconnect lines has been studied extensively as an important reliability problem in microelectronic circuits. In particular the role of Cu in improving resistance to electromigration damage has drawn much attention.[1,2] Cu is usually swept away from an area by electromigration before fast Al diffusion leads to appreciable damage in the line.[3] Dominant paths for electromigration flux of atoms are believed to be along grain boundaries and interfaces. Cu has very low solubility in Al at operation temperatures and has been shown to segregate into θ phase Al_2Cu precipitates[4] as well as to grain boundaries and interfaces.[3,5] In electron microprobe measurements grain boundaries were shown to become rich in Cu depending on the prior thermal treatment of the film.[2,3] Cu must be effective in reducing the electromigration flux along these dominant paths to produce the observed improvement. Because of its critical role in the electromigration process, it is essential to obtain information on the distribution and chemical state of Cu in the grain boundaries, interfaces, precipitates, and grains during operation and test conditions.

Photoemission spectroscopy is a powerful method used in studying physical and chemical properties of solid surfaces. However, the sampling area is ordinarily too large to obtain spatially resolved information on the scale that is necessary for analysis of microscopic changes associated with the electromigration process in interconnect lines. This limitation is overcome in MAXIMUM (installed at the Advanced Light Source of Lawrence Berkeley National Laboratory), a scanning photoemission spectromicroscope with a spatial resolution better than 0.1 μm and an energy resolution of 300 meV.[6] In this study we used a number of contrast mechanisms afforded by this microscope including elemental and chemical sensitivity, and beam induced charging to investigate this problem.

For this experiment a 600 nm thick Al 4 wt % Cu alloy was dc magnetron sputter deposited on Si wafers with 200 nm thermally grown SiO_2. The wafers were not heated during the deposition and the base pressure of the deposition system was better than 1.3×10^{-5} Pa. Single and parallel lines were patterned using conventional photolithography techniques and wet etching. Samples were later annealed at 450 °C for 30 min in forming gas and quenched. No passivation was deposited on the patterned wafers. Patterned lines were 270 μm long and had widths between 2 and 10 μm. Lines had four contacts for electrical testing.

Sets of parallel lines containing 16 lines each were tested in a separate ultrahigh vacuum (UHV) chamber for electromigration under 330 °C and 1×10^6 A/cm^2 to obtain statistical and morphological information on the failure characteristics. The Al–Cu binary phase diagram shows that the solubility of Cu in Al at this temperature ($<$1%) is significantly lower than the concentration present in our samples (4%). This allowed us to use a slightly higher test temperature than is usual for samples with lower Cu concentrations. Log-normal *time to failure* distributions were obtained in these tests which were useful in determining the suitable acceleration conditions for the *in situ* experiments as well as to confirm that failures were due to typical electromigration damage mechanisms.

For *in situ* experiments a special sample stage and holder were made to stress the samples by passing an electrical current at temperatures up to 350 °C in the UHV chamber of the microscope while performing observations. Some samples were slightly etched as described by Colgan *et al.*[1] to expose the Cu rich precipitates. After introduction into the microscope chamber, the samples were imaged by scanning the sample while the electron energy analyzer was tuned to accept the photoelectrons in the spectral region of interest. Micro energy distribution curves (EDCs) were acquired from spatial features of interest as well. The samples were subsequently stressed under accelerated conditions until an open circuit failure was obtained, which took between 2 and 5 h for the 5 μm wide lines. Samples were again characterized to observe the changes that have occurred due to the electromigration process. Performing the tests in the UHV environment ensured protection of the fresh surfaces created during the testing from contamination. Tested lines were later examined with scanning electron microscope (SEM) and energy dispersive spectra (EDS) techniques for comparison with spectromicroscopy findings.

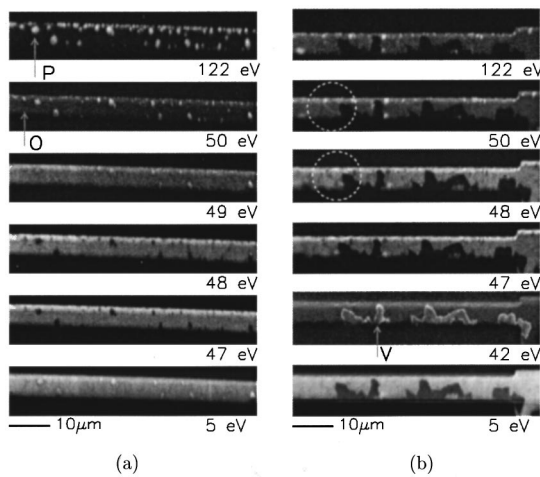[a]Electronic mail: solak@xraylith.wisc.edu

FIG. 1. Micrographs of a 5 μm wide Al(Cu) line: (a) before and (b) after electromigration testing at indicated photoelectron energies.

Images of a 5 μm wide line taken at six different photoelectron energies before electromigration testing are shown in Fig. 1(a). This sample was etched as noted before for exposing the Cu rich precipitates. In order to interpret the features that appear in varying contrasts in those images we refer to the micro EDCs shown in Fig. 2 ($h\nu = 130$ eV for all photoemission data presented). Figure 2(a) shows two micro EDCs acquired at points O and P that are marked in Fig. 1(a). The EDC acquired at point P has a peak due to Cu_{3d} emission at 121.8 eV which is absent at point O. Because of that, areas with higher Cu concentration appear brighter in the 122 eV image in Fig. 1(a), which we will refer to as Cu rich surface precipitates. There is a number of large precipitates seen on the top surface of the line and many small ones
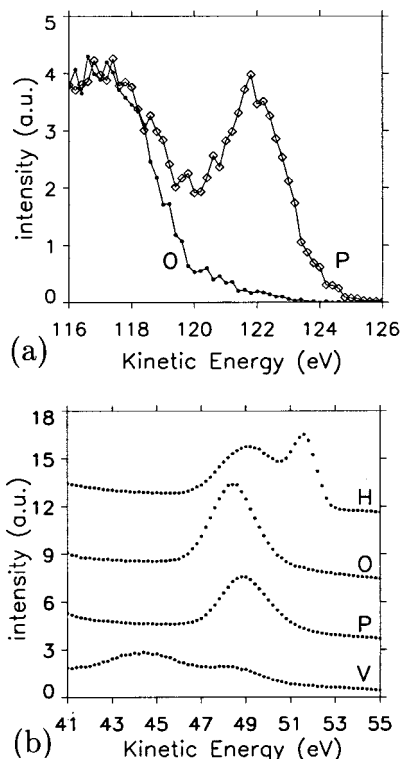

FIG. 2. Micro EDCs of (a) Cu_{3d} and (b) Al_{2p} core levels acquired at positions H, O, P, and V marked with arrows in Figs. 1 and 3 ($h\nu = 130$ eV).

along one edge. This apparent asymmetry is an artifact of our electron collection geometry and it is evident that both edges of the line have a large number of small precipitates. The binding energy of the Cu_{3d} in the surface precipitates, measured as 3.1 eV, is close to our measured values for UHV deposited metallic Cu film (2.75 eV) and the published value of 3.0 eV for Cu_2O.[7] Binding energies for $\theta-Al_2Cu$ and CuO phases are reported as 4.3[8] and 2.0,[7] respectively, and we rule those phases out on that basis.

EDCs of the Al_{2p} core level taken at points O and P are shown in Fig. 2(b). Analysis of these two peaks after background removal showed that the line shapes are very similar except for a 0.4 eV shift towards higher kinetic energy on the precipitate P and an intensity ratio of $P/O = 0.65$. This ratio is consistent with what would be expected between Al and Al_2Cu stochiometries. 76.0 eV binding energy measured for the Al_{2p} core level at the precipitate locations represents a shift of 2.8 eV towards higher binding energy with respect to the metallic Al found in the hillocks. This shift is consistent with the Al^{+3} state in the $\alpha-Al_2O_3$.[9] On the other hand the Al_{2p} binding energy found at 76.4 eV at point O is shifted by 3.2 eV towards higher binding energy with respect to metallic Al. It was proposed that the presence of Cu promotes cracking of the oxide layer or induces an intrinsic loss of electrical resistance in the oxide layer itself.[10] Therefore we conclude that this 0.4 eV shift is due to beam induced surface charging; with the precipitate surface charging less than other areas on the Al(Cu) film. Al in both locations is in the Al_2O_3 state while Cu found on the precipitate surfaces is in either the metallic or Cu_2O state. The charging induced shift as well as the intensity difference of the Al_{2p} level between precipitates and the film surface makes the precipitates appear bright in the 50 eV and dark in the 47 and 48 eV images in Fig. 1(a).

When the etching step was omitted, the top surface was completely covered with Al_2O_3 and the precipitates were not detectable with photoemission. The main effect of the etching was removing the native Al_2O_3 layer and exposing the Cu rich precipitates since our measurements showed no appreciable thickness loss due to the etching process. SEM and EDS examination of some of these samples revealed that some of these precipitates extended into the bulk while some were confined to the surface. Our results agree well with the recent studies showing segregation of Cu to the Al/Al_2O_3 interface,[3,11] and further shows that this segregation is in the form of surface precipitation. Smith *et al.* have also witnessed surface segregation of Cu that showed grain to grain variability.[11] On the other hand SEM and EDS images showed precipitates in the *bulk* of the film which were not detected in the more surface sensitive photoemission images.

Figure 1(b) shows micrographs of the cathode end of the same line after it had failed due to electromigration damage. Extensive voiding is apparent in those images as dark areas except for the one taken at 42 eV. A one to one comparison of the 122 eV images taken before and after the electromigration stressing showed that Cu rich surface precipitates have largely remained in place except for those that were in the void areas. The void and the hillock locations show no clear relation to the surface precipitate locations before or after the testing.
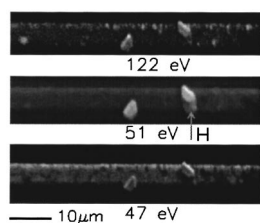
FIG. 3. Micrographs of a 5 μm wide Al(Cu) line after electromigration testing at indicated photoelectron energies showing crystalline shaped hillocks.

A remarkable difference between the *before* and *after* electromigration images is in the grain boundary areas. 47, 48, and 50 eV micrographs in Fig. 1(b) clearly show grain boundaries that were not visible before the testing. We rule out topographical changes for this effect because of the inverse contrast of the grain boundaries at 48 and 51 eV images shown in the encircled area in Fig. 1(b). Instead, this contrast [i.e., bright at 50 eV and dark at 47 and 48 eV] is the same as the charging induced one related to the Cu presence as we discussed for the surface precipitates. However we did not find an appreciable increase in Cu_{3d} emission from the grain boundary areas as can be noticed in the 122 eV micrograph in Fig. 1(b). This may be due to the narrow width of the grain boundaries that did not include a sufficient amount of Cu to be detected in the Cu_{3d} level. However small amounts of Cu in the grain boundary and the surface interface can modify the conductivity around the grain boundary sufficiently to alter the level of surface charging. Therefore we propose that the Cu presence in those grain boundaries was the cause for the contrast between 47, 48, and 50 eV micrographs. Interestingly, grain boundaries became enriched in Cu mostly in the downstream direction of the voids and the undamaged portions of the line did not show the same contrast.

Void areas appear dark at all photoelectron energies except for the 42 eV one in Fig. 1(b). The micro EDC labeled *V* in Fig. 2(b) was acquired on a void surface at point *V* marked in Fig. 1(b). It shows an Al_{2p} core level component shifted to higher binding energy by more than 4 eV with respect to the oxidized Al_{2p} level. This shift is due to the charging of the Al_2O_3 ''skin'' left over the void areas. We later confirmed the presence of the Al_2O_3 skin by depositing a thin film of Au on the sample and examining it with SEM. With this charging related contrast we can image voids between the Al_2O_3 and Al film that can be as thin as several monolayers, but that are too thin to be detected with other

techniques such as SEM or transmission electron microscopy (TEM).

Material carried away from the void areas appears as faceted hillocks in the downstream direction as shown in Fig. 3. The micro EDC labeled *H* in Fig. 2(b) is acquired on such a hillock marked *H* in Fig. 3. The strong peak at 51.6 eV is due to the freshly created metallic Al surface. We did not observe metallic Al anywhere else on the line other than on the hillocks themselves, indicating that electromigration proceeded strictly under the Al_2O_3 layer.

In summary we have used unique sensitivities of photoemission spectromicroscopy to observe chemical and structural changes that occur on surfaces of patterned Al(Cu) thin film lines. We found evidence of Cu segregation to the Al_2O_3 interface in the form of surface precipitates. Side walls of the lines had smaller Cu rich precipitates in higher numbers. The charging induced shift of the Al_{2p} core level was smaller for the Cu rich precipitates than the uniform Al film surface which provided a useful contrast mechanism for detection of the presence of Cu. Grain boundaries on the downstream side of the voids with respect to the electron flow became rich in Cu while no change was observed in other areas. Voids were imaged using the beam induced charging of the surface layer that remained over them. Metallic Al was observed only in hillocks and the surface of the line remained covered with oxide elsewhere.

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