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ANODICALLY ENHANCED DIFFUSION IN CU/AG THIN FILM COUPLES

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ABSTRACT

Thin, 100-nm films of first silver and then copper were deposited consecutively onto pure single-crystal (111) silicon substrates by magnetron sputter deposition. Controlled anodic current density was applied at room temperature to dissolve the outer copper film to varying depths approaching the copper/silver interface. Profiles of copper and silver concentration vs. depth below the anodically dissolved surfaces were subsequently obtained by argon ion sputtering and simultaneous Auger Electron Spectroscopy. Despite some intrinsic mixing during the profile analysis, there is clear evidence that diffusion of copper and silver into one another is enhanced by anodic currents at the outer copper surface. Our preliminary interpretation leads us to believe that the effect is caused by surface formation of vacancies during anodic dissolution. The anodically generated vacancies can migrate as divacancies to the copper/silver interface where they enhance diffusion by the usual vacancy exchange mechanism.

Vacancies may be formed during anodic dissolution and corrosion. Forty (1) originally suggested that vacancies produced by dezincification may interact with dislocations to produce stress corrosion cracking in brass. Subsequently, Pickering and Wagner (2) further implicated corrosion-generated vacancies (Figure 1) as the cause of dealloying in brasses. Revie and Uhlig (3) postulated anodically generated vacancies to explain enhanced creep (Figure 2) during anodic dissolution of Cu. One of the present authors (4) proposed that the process(es) causing increased creep, perhaps anodic generation of vacancies, may also play a role in the mechanism of stress corrosion cracking (Figure 3) and corrosion fatigue. More recently, Melitis (5) suggests that corrosion-generated vacancies produce dislocation locks and consequent embrittlement by stress corrosion.

Thus, subsurface vacancies injected by anodic dissolution may have significant effects on dealloying and environmental embrittlement. However, the presence of vacancies is rather speculative in all the references listed above. The purpose of this note is to report preliminary results showing more direct experimental evidence of anodically generated vacancies. The critical experimental is described conceptually in Figure 4. Anodic dissolution of a 100-nm Cu layer on a Ag substrate presumably generates near-surface vacancies which migrate as divacancies to the Cu/Ag interface, where Ag and Cu can then more readily diffuse into one another than they would otherwise. A profile of Cu concentration with distance across the interface in Figure 4 shows a simple step function for an undissolved diffusion couple. One which is anodically dissolved for some time at the Cu surface would be expected to show an enhanced diffusion profile, as indicated, if vacancies are indeed generated at the dissolving surface.

EXPERIMENTAL PROCEDURES

Cu/Ag diffusion couples were prepared using magnetron sputter deposition on polished Si wafers which served only to provide a convenient reproducible substrate for deposition and had no further role in subsequent processes and experiments. In the evacuated deposition chamber, vertical Si wafers were rotated past 0.999 pure Ag and Cu magnetron sources located at a minimum horizontal distance of 9-cm. The Cu and Ag sources operated separately in the dc mode at discharge voltages of 290 and 550 Volt, respectively, creating a horizontal flux to the specimen surfaces. This procedure ensured that layer thicknesses were uniform over each sample surface and from sample to sample.

A 100-nm base layer of Ag was sputter deposited first on each Si-wafer substrate, followed by a second 100-nm Cu layer on the Ag base layer. X-ray diffraction characterization indicated that the Cu and Ag films grew epitaxially in a (111) orientation on the Si substrate. Characterization by Rutherford back scattering (RBS) showed a compositionally discrete interface between the Cu and Ag layers.

Each of the 5-cm diameter wafers was cut into several specimens of approximately 1.3 x 2-cm. Each specimen was in turn coated with an air curing lacquer (fingernail polish), leaving a 1-cm square area unexposed on the flat (111) outer Cu film surface near one end. About 2-mm on the other end was also left unexposed for electrical contact. The configuration of the coated specimen is shown schematically in Figure 5. No effort was made to measure coating thickness, which was adequate to protect the coated surfaces for the relatively short electrolyte exposure times during subsequent anodic processing.

Each specimen was partially immersed in 1N sulfuric acid to a depth indicated in Figure 5, thus exposing the 1-cm² uncoated area while leaving the upper uncoated end above the solution. Constant anodic current was applied to the exposed surface of separate coated specimens for times calculated to dissolve increasing fractions of the 100-nm Cu outer layer of the Cu/Ag couple. Concentration profiles of Cu and Ag vs. depth below the anodically dissolved Cu surface were then measured for each of the specimens by argon sputtering and simultaneous AES.

RESULTS AND DISCUSSION

Figure 6 shows Cu and Ag concentration vs. sputter time for an as-fabricated specimen and two others in which 12.5 and 25.0-nm had been anodically dissolved from the surface at 0.225 mA cm⁻². The as-fabricated specimen unfortunately does not display the ideal step function of composition vs. sputtering time (depth below the surface), due to intrinsic mixing inherent in the sputtering process. Nevertheless, diffusional processes superimposed on the base-line concentration profile of the as-fabricated specimen seem clearly present in the specimens subject to anodic current. Our present interpretation of this behavior is that indeed vacancies are generated at the anodically dissolving surface and migrate probably as divacancies to the Cu/Ag interface where they affect diffusion.

In Figure 6, Ag concentration generally increases and Cu concentration decreases in the concentration profiles for anodically treated specimens, as compared to the profile for the untreated, as-fabricated specimen. That is, the interface becomes "sharper"; absolute values of Cu and Ag concentration slopes have increased as a result of exposure to anodic current. This suggests that the Ag is diffusing into the Cu more rapidly than the Cu into the Ag. The lower atomic diameter of Cu (1.28 Å) than Ag (1.44 Å) would predict the reverse. However, increased presence of vacancies in this experiment may initially stimulate diffusion on the Cu side of the Cu/Ag interface. For longer time under anodic current (Figure 7), the slopes become lower, suggesting that vacancies have migrated across the Cu/Ag interface allowing the normally expected higher diffusion of Cu into Ag.

The transition from preferential diffusion of Cu over to preferential diffusion of Ag is much less apparent at higher anodic current densities. The Cu/Ag interface generally becomes more diffuse with increasing time, i.e. the concentration slopes become lower at the interface, for higher anodic currents. Thus, it appears that more vacancies, generated at higher current, are able to more readily migrate across the Cu/Ag interface and again allow the expected faster diffusion of Cu into Ag. However, the diffusion effects at higher current seem to be much lower for the same amount of Cu removed, because of the shorter times that the currents were applied.

Unfortunately, the concentration profiles presented in this paper can be regarded as only qualitative. Sputtering efficiency varies for different metals and their mixtures, and a quantitative relationship between sputter time and depth is difficult to determine. Thus, the relative positions of the concentration profiles in Figures 6 and 7 seem to be self consistent but are subject to interpretation. Although AES analysis is reasonably good at intermediate compositions, it is not very accurate for determining trace levels. For example, in Figures 6 and 7, we know that the composition of Cu on the Ag side of the interface is very low, near zero, but the low sensitivity of the instrument for Cu at low levels causes spuriously high values probably from background noise, and the corresponding concentrations of Ag are reduced below the true 100 % value. Nevertheless, we feel confident of the trends shown at intermediate concentrations around the Cu/Ag interface.

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Figure 1. Mechanism for generation of surface vacancies by anodic dissolution and/or corrosion (2).

Figure 2. Anodically enhanced creep in Cu wire (3).

Figure 3. Mechanism for SCC caused by anodically generated vacancies at the plastically constrained crack tip (4).

Figure 4. Schematic diffusion experiment to show evidence of anodically generated vacancies.

Figure 5. Coated specimen for anodic dissolution of exposed Cu from a Cu/Ag diffusion couple deposited on a Si substrate wafer (not to scale).

Figure 6. AES concentration profiles for Cu and Ag after anodic dissolution for 0, 1.25, and 2.50 min. at 0.225 mA cm^{-2} , indicating preferential diffusion of Ag into Cu.

Figure 7. AES concentration profiles for Cu and Ag after anodic dissolution for 2.50, 5.00, and, 10.00 min. at 0.225 mA cm^{-2} , indicating preferential diffusion of Cu into Ag.

Figure 1

FIG 2

STEPS in SCC MECHANISM

1. Film rupture by mechanical stress
2. Retarded repassivation by competitive adsorption of critical species, e.g. Cl^-
3. Anodic dissolution by coupling to surrounding passive surfaces
4. Vacancy formation from rapid dissolution
5. Divacancy formation and migration
6. Crack initiation (Omitted from diagram)
7. Crack propagation by cleavage due to accumulation of divacancies on prismatic planes, e.g. $\{100\}$

Figure 3

FIG 5

FIG. 6

FIG. 7