Novel Surface Segregation Phenomena at the Plasma/Copper–Silver Alloy Interface

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Exposure of clean 29% Cu–71% Ag eutectic alloy surfaces to a variety of nonisothermal glow discharges (O_2, H_2, and N_2) have been studied by X-ray photoelectron spectroscopy (XPS), Ar^+ ion depth profiling, and scanning electron microscopy (SEM). Preferential build-up of either metallic component at the substrate surface can be induced by selecting the appropriate feed gas.

Introduction

Low-temperature glow discharges are an attractive means for engineering solid surfaces; this can occur via either chemical or physical processes. Applications are widespread and can be as diverse as the molecular rearrangement of polymers,[1] plasma polymerization,[2] deposition of thin inorganic coating,[3] and the hardening of metals by nitriding.[4] A whole variety of plasma/solid interactions are believed to be present in these systems, including the interaction of radicals, atoms, and electronically excited molecules with the surface, neutralization, secondary electron emission, sputtering, ion-induced chemistry, electron-induced chemical reactions, and photochemistry.[5] The major attribute of nonisothermal plasmas is that they are capable of generating a very reactive medium at room temperature, whereas high temperatures (typically 10 000's K) are necessary to achieve the same types of species via thermal ionization. Investigations related to the glow discharge treatment of metals are widespread in the literature.[6,7] However, there have been very few studies dedicated to nonisothermal plasma modification of binary alloy surfaces, in fact the first ever report concerning the plasma oxidation of a binary metal alloy system (Cu–Al) has only recently been published.[8]

In this article, a detailed account of the influence of various glow discharges (O_2, H_2, and N_2) on Cu–Ag eutectic alloy substrates is presented. Cu–Ag alloys are potential candidates for electrical switching applications, and therefore it is desirable to devise protective finishes.[9] The microstructure and chemical nature of the resulting surfaces have been evaluated by scanning electron microscopy, X-ray photoelectron spectroscopy, Ar^+ ion depth profiling, and plasma emission spectroscopy.

Experimental Section

For each experiment, a new piece of eutectic copper–silver alloy (29% Cu–71% Ag, Goodfellows, 0.05 mm thick) was mechanically polished and subsequently rinsed in isopropyl alcohol. The high proportion of silver in the binary alloy gave it a silvery appearance. A small strip of this material was placed in an electrodeless flow reactor, which is similar in construction to that described in a previous article.[10] It was fitted with a gas inlet, a Pirani gauge, a two-stage rotary pump with a liquid nitrogen cold trap, and a matching network for inductive coupling of a 13.56-MHz radio-frequency (rf) source. All joints were grease-free. The RF coils were positioned over a quartz substrate holder. First, the system was pumped down to 4×10^{-3} Torr pressure, and the walls of the chamber were allowed to outgas. Each surface modification experiment comprised of flushing the reactor with 2×10^{-1} Torr of reactant gas at a flow rate of 1.9 $cm^3 min^{-1}$ for 10 min, this was then followed by the appropriate plasma treatment for 5 min, and finally the feed gas was allowed to continue purging through the reactor for a further 10 min. Bulk sample heating due to the rf field was tested by measuring the substrate temperature immediately after extinguishing the glow discharge, this was never found to be greater than 40 °C (however surface temperatures may be much higher).

XPS measurements of the plasma treated alloys were performed in a Kratos ES200 spectrometer, and Ar^+ ion depth profiling studies were performed in a VG ESCALAB instrument. Magnesium Kα radiation was used as the excitation source with electron detection in the fixed analyzer transmission (FAT, 65-eV pass energy), and constant analyzer energy (CAE, 50-eV pass energy) modes, respectively. An IBM PC computer was used for data accumulation and component peak analysis with linear background removal. All binding energies were calibrated with respect to adventitious hydrocarbon at 285.0 eV.[11] Peak area ratios were normalized relative to the data obtained from the VG CLAM 100 spherical sector electron analyzer; sensitivity factors have not been taken into consideration. A cold cathode ion gun (VG AG21) was used for depth profiling studies (3-kV beam energy, 1.7-μA Ar^+ ion current).

SEM and EDAX analysis of the treated alloy surfaces was carried out on a Hitachi S 2400 electron microscope.

A home-built UV emission spectrometer which included a Czerny-Turner type monochromator was used for plasma glow analysis. A computer was used to rotate the grating via a stepping motor and also to accumulate the counts from a photomultiplier tube detector. This instrument could scan continuously from 180 to 500 nm at 0.5-nm resolution.

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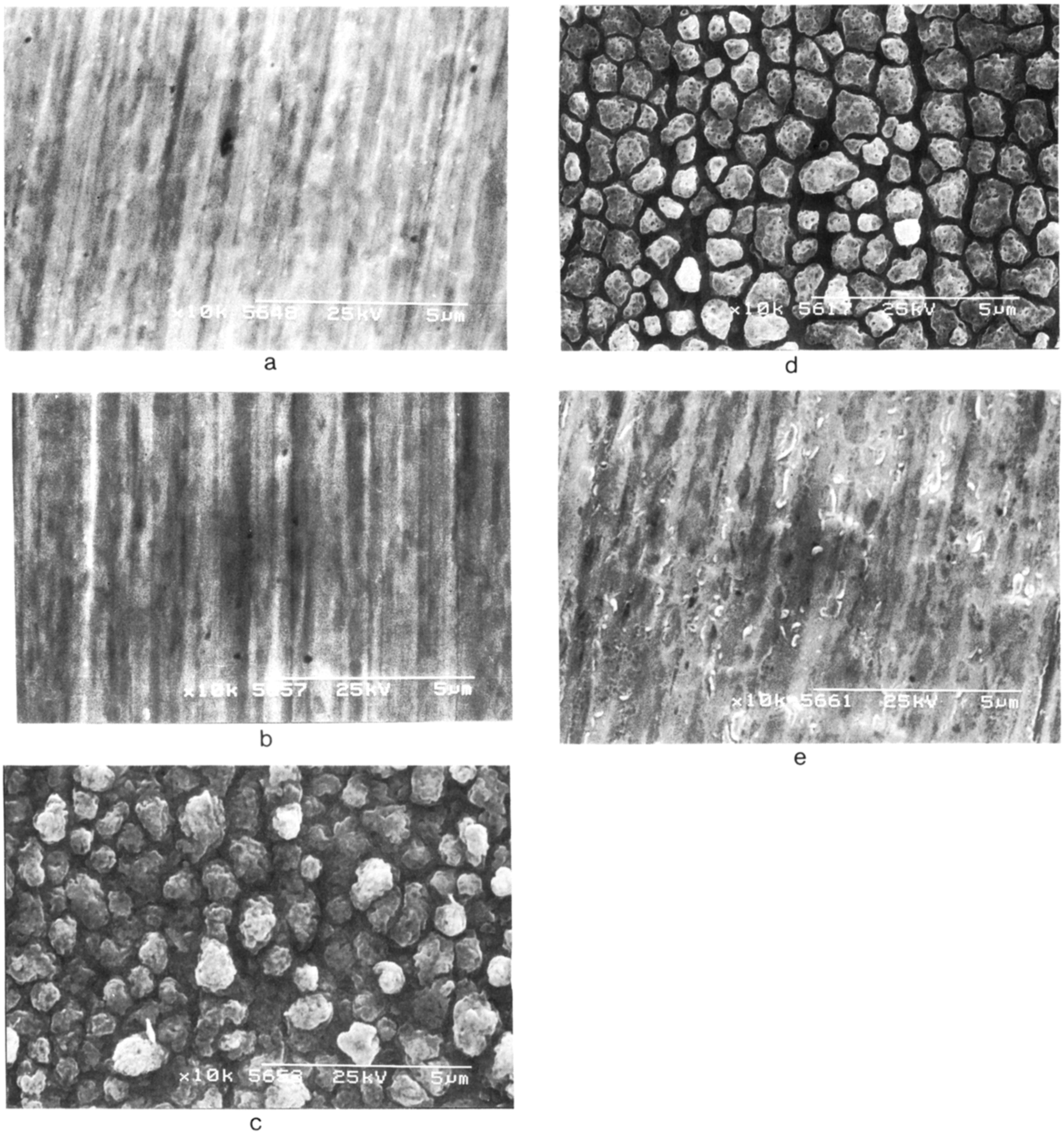

Figure 1. SEM image of (a) clean eutectic, (b) H_2 plasma exposure (20 W, 5 min), (c) O_2 plasma exposure (20 W, 5 min), (d) O_2 plasma exposure (20 W, 5 min) followed by H_2 plasma treatment (20 W, 5 min), and (e) N_2 plasma exposure (20 W, 5 min).

Table I. Cu($2p_{3/2}$) and Ag($3d_{5/2}$) XPS Binding Energies

treatment	Cu($2p_{3/2}$) ● 0.1 eV	Ag($3d_{5/2}$) ± 0.1 eV
clean Cu foil	932.9	
clean Ag foil		368.6
clean Cu–Ag eutectic	932.3	368.5
O_2 plasma/Cu–Ag eutectic	933.8	368.5
H_2 plasma/Cu–Ag eutectic	932.3	368.5
H_2 plasma/O_2 plasma/ Cu–Ag eutectic	932.7	368.6
N_2 plasma/Cu–Ag eutectic	variable (see Figure 6)	368.7

Results

A summary of the variations in Cu($2p_{3/2}$) and Ag($3d_{5/2}$) binding energies with plasma treatment is given in Table I.

Clean Cu and Ag Reference Materials. XPS characterization of clean copper and silver foils yielded Cu($2p_{3/2}$) and Ag($3d_{5/2}$) binding energy values which are in good agreement with previous literature reports.[12]

Clean Cu–Ag Eutectic. A significant difference is apparent between the Cu($2p_{3/2}$) binding energy value for the alloy and that recorded for pure copper foil. Copper has a greater electron work function (4.65 eV) than silver (4.26 eV).[13] Since the alloy is Ag-rich overall, then one would expect some degree of charge donation from silver to copper; in turn this should lead to a lower Cu($2p_{3/2}$) binding energy compared to pure copper. The presence of intermetallic bonding within the Cu-rich and Ag-rich eutectic phases may also influence the electronic envi-

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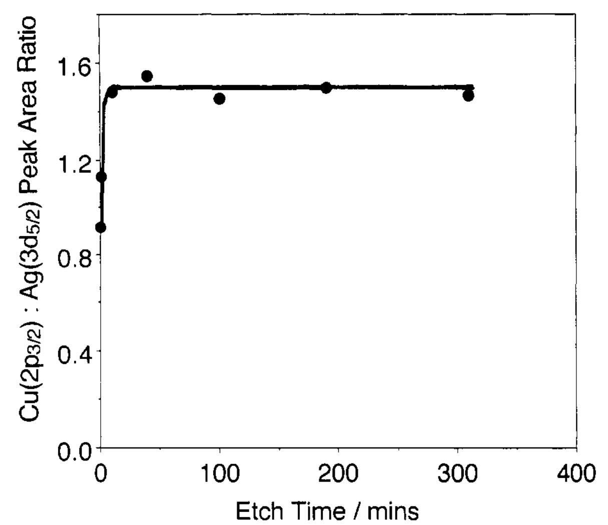

Figure 2. Ar^+ ion depth profile of clean eutectic.

ronments of the constituent metal atoms. A Cu($2p_{3/2}$):Ag($3d_{5/2}$) ratio of 0.89 ± 0.03 (as determined from peak area measurements) was found to be characteristic of a clean surface. Small amounts of adventitious oxygen and carbon were always detected at the substrate surface, typical concentrations for these were 0.03 for O(1s):[Cu($2p_{3/2}$) + Ag($3d_{5/2}$)], and 0.04 for C(1s):[Cu($2p_{3/2}$) + Ag($3d_{5/2}$)]. It was found that very mild Ar^+ ion sputtering was sufficient to remove these surface contaminants.

SEM analysis of the clean surface just shows the scratches imparted to the substrate during mechanical polishing (Figure 1a).

Ar^+ ion depth profiling experiments gave a strong indication of there being a slight surface enrichment of silver with respect to the bulk composition of the binary alloy (Figure 2). There are two possible explanations for these results: first, surface segregation of silver has been previously reported for silver rich Cu–Ag alloys;[14] alternatively, this may be a manifestation of the greater sputtering yield associated with silver[15] which will result in a build-up of copper at the alloy surface during Ar^+ ion depth profiling. However, it is clearly evident that the Cu($2p_{3/2}$):Ag($3d_{5/2}$) ratio quickly reaches a steady value of 1.50 ± 0.05 during Ar^+ ion sputtering of the cleaned eutectic substrate. This value will be taken as a reference point for the Ar^+ ion depth profiling experiments reported below.

H_2 Plasma/Cu–Ag Eutectic. Exposure of clean eutectic surfaces to a hydrogen glow discharge caused negligible variation in Cu($2p_{3/2}$) and Ag($3d_{5/2}$) binding energy values: also there was no change in physical appearance to the naked eye, or in the SEM analysis, Figure 1b.

A slight increase in the surface concentration of Cu^0 was detected for low-power plasma exposures (Figure 3). Copper has been reported to produce a hydride of the type CuH.[16] This could be a plausible explanation for the migration of copper towards the H_2 glow discharge/alloy interface. Alternatively this effect may be attributed to a small amount of preferential sputtering of silver from the eutectic surface.

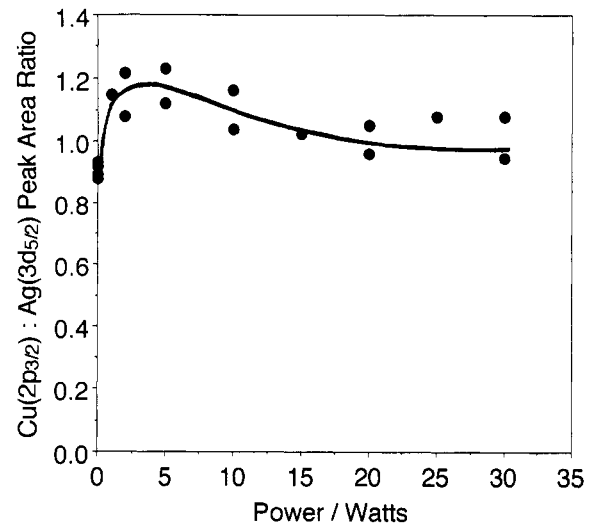

Figure 3. Variation of Cu($2p_{3/2}$):Ag($3d_{5/2}$) peak area ratio as a function of H_2 plasma power.

O_2 Plasma/Cu–Ag Eutectic. Both the Cu($2p_{3/2}$) and Ag($3d_{5/2}$) peak energies were found to be independent of glow discharge power: a +1.5-eV shift in binding energy with respect to the clean alloy was measured for the former, whereas no change in value was detected for the latter. A strong shake-up satellite at ~942 eV in the Cu($2p_{3/2}$) region was also observed; this can be taken as being representative of Cu^{2+}, i.e., CuO.[17,18] It should be noted that previous studies have reported a negligible variation in the Ag($3d_{5/2}$) binding energy value between metallic and oxidized silver surfaces.[12]

A marked decrease in Cu($2p_{3/2}$):Ag($3d_{5/2}$) ratio with increasing glow discharge power was noted (Figure 4a). This was accompanied by the formation of a black layer. The limiting O(1s):[Cu($2p_{3/2}$) + Ag($3d_{5/2}$)] value for these treatments was 0.31 ± 0.03. By taking all of these observations into consideration, it can be concluded that there is a strong localization of silver oxide moieties at the surface (Ag_2O and AgO are black[19]), these are interdispersed amongst a small amount of CuO species.

SEM and EDAX characterization of the plasma treated eutectic reveals a very rough surface comprising of silver oxide globules of 1.0-μm average diameter (Figure 1c).

XPS measurements made during Ar^+ ion depth profiling of the plasma oxidized alloy are summarized in Figure 4b, this demonstrates that the silver moieties have preferentially segregated at the glow discharge/eutectic interface, and copper species have been left behind. The presence of a Cu($2p_{3/2}$) shake-up feature in the subsurface region implies that CuO is present beneath the AgO_x overlayer.

UV emission diagnostics of the oxygen glow discharge were consistent with the depth profiling experiments in that there was no indication of any metal containing species being evolved into the plasma phase.

H_2 Plasma/O_2 Plasma/Cu–Ag Eutectic. Exposure of a plasma oxidized alloy (20 W) surface to a hydrogen glow discharge (20 W) created a dramatic transformation in appearance of the substrate from black to bright silver. Both the Cu($2p_{3/2}$) and Ag($3d_{5/2}$) binding energy values were comparable to those measured for the pure parent

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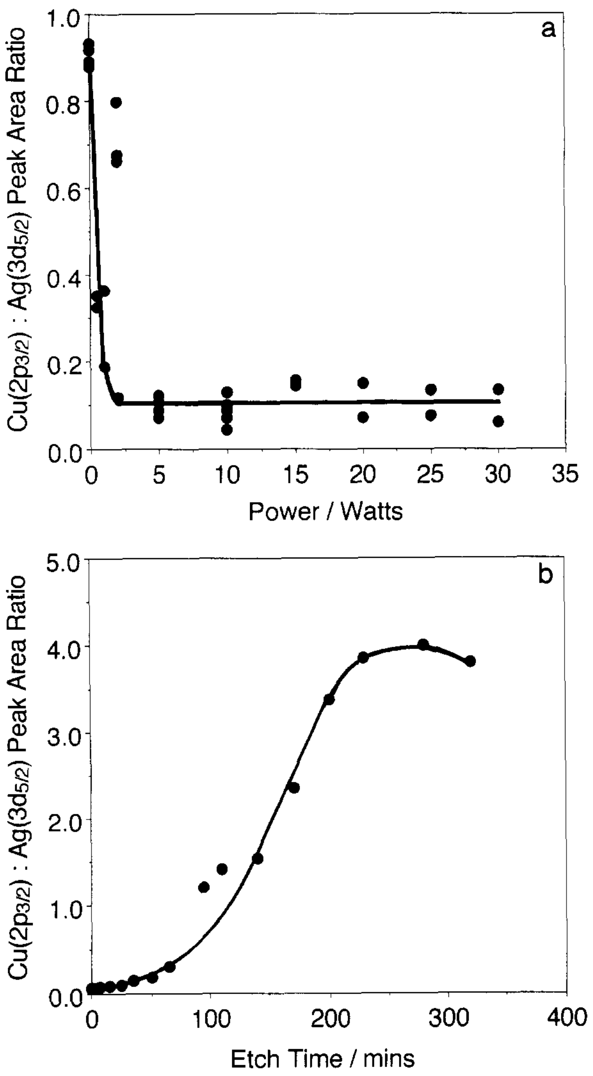

Figure 4. (a) Variation of $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ peak area ratio as a function of O_2 plasma power. (b) Ar^+ ion depth profile of plasma oxidized (20 W, 5 mins) eutectic.

metals rather than being similar to those observed for either the clean or plasma oxidized eutectic foil. Also the $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ peak area ratio increased slightly with respect to the value obtained following plasma oxidation (the $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ ratio equals 0.20 for a 20 W H_2/ 20 W O_2 treatment). From these experiments, it can be concluded that a hydrogen plasma is a very efficient medium for reducing oxide layers to their constituent metals.

XPS depth profiling studies are in agreement with the aforementioned interpretation, in that silver is leached out of the eutectic by the oxygen plasma to create a silver oxide top layer, subsequent exposure to a hydrogen glow discharge reduces the silver oxide to metallic silver, Figure 5. The copper constituent of the eutectic mixture is left behind in the subsurface region. No $Cu(2p_{3/2})$ shake-up satellite or O(1s) signal were measured during deeper ion etching, therefore the underlying copper oxide must also have undergone reduction to metallic copper during exposure to the hydrogen plasma.

SEM images of the surface following plasma reduction clearly show that the overlying silver oxide moieties have undergone a slight degree of shrinkage to an average size of 0.8 μm, (Figure 1d). This is consistent with the observed rise in $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ peak area ratio. EDAX analysis confirmed that the large globules are silver rich, whereas copper is concentrated in the interglobular regions.

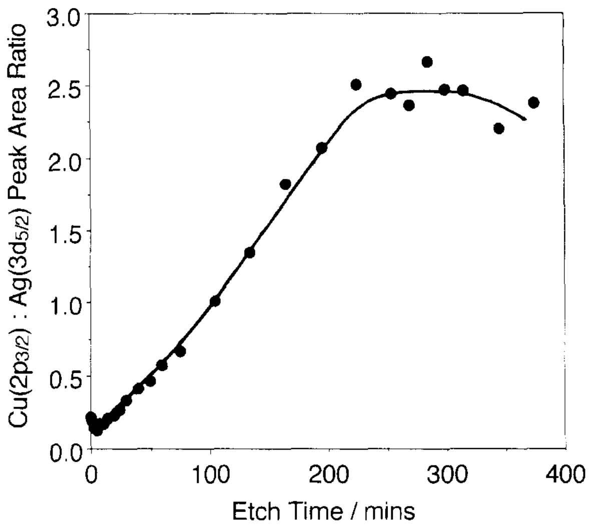

Figure 5. Ar^+ ion depth of O_2 plasma exposure (20 W, 5 min) followed by H_2 plasma treatment (20 W, 5 min).

N_2 Plasma/Cu–Ag Eutectic. Nitrogen plasma treatment of the Cu–Ag eutectic surface caused a slight increase in the $Ag(3d_{5/2})$ binding energy relative to the clean alloy; however a considerably greater shift is observed for the $Cu(2p_{3/2})$ binding energy (Figure 6a). Furthermore, a pronounced $Cu(2p_{3/2})$ shake-up satellite was observed, which can be taken as being characteristic of Cu^{2+} (d^9) species.[17,20] A weak N(1s) peak was centred at 398.3 ± 0.1 eV, this is representative of anionic nitrogen species.[21] A significant rise in $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ ratio with increasing glow discharge power was found for these experiments (Figure 7a). This was accompanied by a change in appearance of the surface to a light brown colour. Figure 6b shows that the N(1s):$Cu(2p_{3/2})$ peak area ratio is independent of plasma power (except at 0 W), and therefore it must be the copper component of the alloy which forms the nitride.

Ar^+ ion depth profiling studies show that there is a much greater concentration of copper at the surface following nitrogen plasma treatment than that typically found for samples of the clean alloy (Figure 7b). On probing into the bulk, the $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ ratio approaches the value characteristic of Ar^+-sputtered clean eutectic, and concomitantly the $Cu(2p_{3/2})$ shake-up satellite is attenuated. This is indicative of silver having been removed from the substrate into the plasma, rather than preferential segregation of copper toward the surface. Furthermore, it can be deduced from the XPS depth profiling studies that the nitride is a lot thinner than the corresponding oxide layers formed during plasma oxidation. Glow emission analysis of the nitrogen plasma was inconclusive, since the rate of surface segregation was found to be much faster than the scan time of the UV emission spectrometer used in these experiments.

SEM characterization of the nitrided surface revealed some roughening in surface microstructure, however these changes in topography where not as dramatic as those observed for the plasma oxidation treatments.

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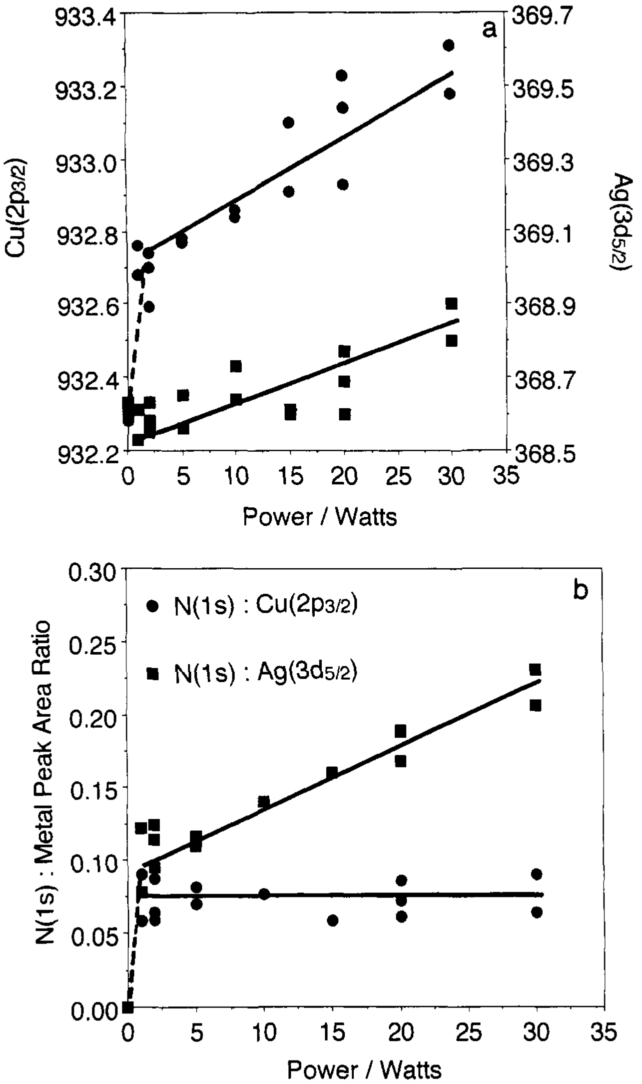

Figure 6. (a) Variation of $Cu(2p_{3/2})$ and $Ag(3d_{5/2})$ binding energies as a function of N_2 plasma power. (b) Variation of $N(1s)$:$Cu(2p_{3/2})$ and $N(1s)$:$Ag(3d_{5/2})$ peak area ratios as a function of N_2 plasma power.

Discussion

Copper and silver are virtually immiscible in the bulk state at room temperature.[22] The equilibrium eutectic structure of the copper–silver system consists of small copper-rich particles dispersed throughout a continuous silver-rich matrix.

The high degree of surface modification observed in these glow discharge experiments can be attributed to the reaction of ions, radicals, atoms and excited molecular species with the alloy surface.[6] Such treatments can only be attained at very high temperatures by more conventional methods. For instance, oxidation of the Cu–Ag eutectic occurs quite readily in the presence of a nonisothermal oxygen glow discharge, whereas this reaction is orders of magnitude slower on exposure to just molecular oxygen at room temperature. Furthermore, copper and silver oxides can be easily converted back to the constituent metals at low temperature by a hydrogen plasma, whereas thermal reduction in a H_2 atmosphere requires far greater temperatures.[23]

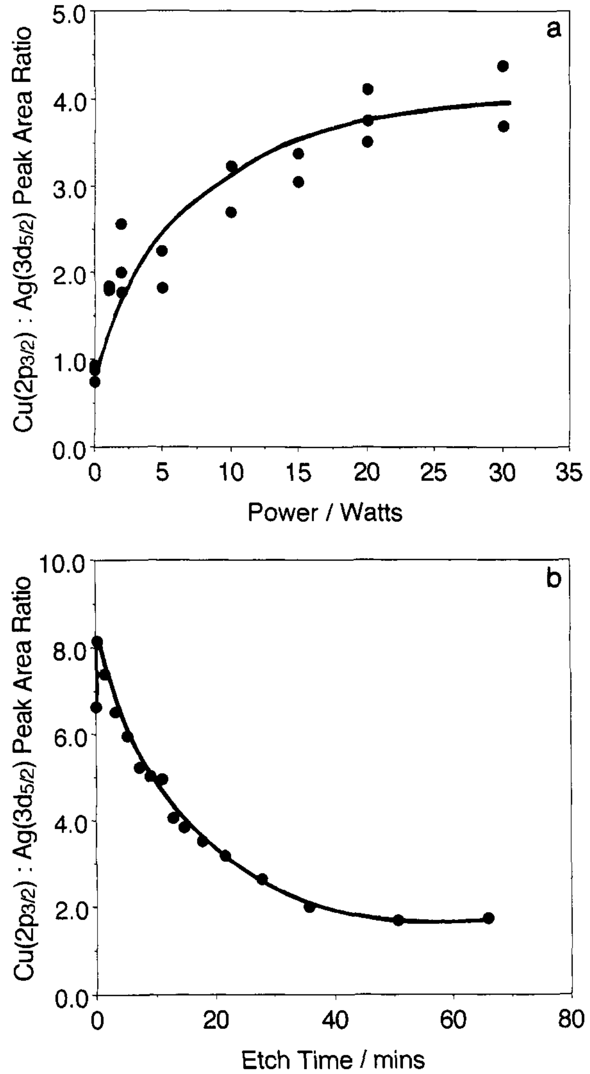

Figure 7. (a) Variation of $Cu(2p_{3/2})$:$Ag(3d_{5/2})$ peak area ratio as a function of N_2 plasma power. (b) Ar^+ ion depth profile of plasma nitrided (20 W, 5 min) eutectic.

Depth profiling studies have demonstrated that preferential segregation of either eutectic component can be successfully achieved by selecting the appropriate glow discharge treatment. An oxygen plasma favors the leaching out of silver from the subsurface, and a copper-rich underlayer accompanies this phenomenon. Whereas a nitrogen glow discharge results in a CuN_x surface layer, however, there is no corresponding silver-rich subsurface phase in this case, which means that silver must have been ablated or preferentially desorbed during the glow discharge exposure.

It is useful to compare this study with related work done on a 20% Cu–80% Ag alloy.[24] In the latter case, no significant degree of silver oxide build-up at the substrate surface was observed during plasma oxidation. Presumably this may be attributed to its hypoeutectic structure: the presence of large regions of silver-rich phase and a heterogeneous distribution of eutectic structure into the subsurface would be expected to result in markedly different oxidation kinetics at the plasma/substrate interface.

Generally, solid-state segregation processes observed in metal alloys at elevated temperatures can be interpreted

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in terms of atom currents/vacancy winds if vacancy concentration gradients are significant.[25] Segregation in Ag–Cu alloys due to the formation of vacancy gradients during sintering has been studied by Kuczynski et al.[26] Although cold plasmas can generate vacancy gradients in solids, it seems unlikely that these gradients alone can set up sufficient atom currents so as to account for the degree of segregation encountered in our experiments (unless the surface temperatures are much greater than the measurable bulk temperatures).

Conclusions

It has been demonstrated that low-temperature plasma processing of multicomponent alloys offers significant benefits and novel characteristics compared to conventional surface treatments. Oxygen glow discharge exposure yields a virtually copper-free silver oxide surface with an underlying copper oxide layer. Reduction of this sandwich oxide structure by a hydrogen plasma generates metallic silver and copper without disturbing their relative spatial distributions. On the contrary, nitrogen glow discharge modification of clean Cu–Ag eutectic results in a build-up of copper nitride species at the alloy surface; however, in this case there is no corresponding silver underlayer. This account is only one of a handful of studies that have been carried out on binary metal alloy systems so far, and no doubt further work in this field will unveil many more fascinating aspects concerning the interactions of non-equilibrium plasmas with multicomponent substrates.

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