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The effect of microstructure on interphase interaction in layered polycrystalline films of silver-nickel and silver-copper-nickel

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The purpose of this research work was to study how the microstructure of individual phases influences the interphase interaction in the Ni-Ag and Ni-Cu-Ag layered structures at elevated temperatures. The paper presents the depth distributions of each element in the Ni-Ag and Ni-Cu-Ag layered structures, before and after annealing. The depth distributions were obtained by Auger Electron Spectroscopy (AES). These AES studies are an extension of previous research. It has been discovered that microstructure will critically affect interphase boundary formation, when copper is introduced into the Ag-Ni interfacial region. Copper mainly diffuses into nickel and less into silver. The shape of the copper concentration profile is dependent on which type of diffusion is dominant, grain boundary or volume. The diffusion-type interphase boundary has not been observed in the silver-nickel binary system. © *2000 Kluwer Academic Publishers*

1. Introduction

Silver-Nickel (Ag-Ni) composite material is widely used for contacts in electrical industry. Ag-Ni material consists of two metals which form a virtually immiscible system, with no reported solubility of silver (Ag) in nickel (Ni) and with solid solubility of Ni in Ag as low as 0.1 at % at 750 °C [1].

Copper (Cu) can be used to enhance the interaction between the individual components of the Ag-Ni system because it is mutually soluble in both silver and nickel [2, 3]. Previous research [4] has shown that copper introduced into the silver-nickel interfacial region facilitates the formation of the interfacial joints that are created during manufacturing of Ag-Ni contact material.

Polycrystalline films of Ni and Ag interact by growing grains of separate phases [5, 6]. Previous examinations [6] of the Ni-Ag and Ni-Cu-Ag structures, prepared by magnetron D.C. sputter deposition of 500 nm Ni or 100 nm Cu/500 nm Ni on a high purity Ag substrate, demonstrated that introducing Cu at grain boundaries had the effect of stabilizing the grain size of the nickel and allowed the migration of silver atoms to the nickel surface.

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2. Experimental procedure

2.1. Preparation of specimens

Four types of layered specimens were prepared:

a) Ni-Ag
b) Ni-Cu-Ag
c) Ag-Ni
d) Ag-Cu-Ni

The substrate symbol is underlined.

The Ni-Ag and Ni-Cu-Ag samples were prepared by D.C. sputter deposition of 450 nm Ni or A.C. sputter deposition of 100 nm Cu and D.C. sputter deposition of 450 nm Ni on high-purity Ag substrate. Before deposition, the Ag samples were mechanically polished to a mean surface roughness of 20 nm and then subjected to annealing in argon at 850 °C for 1 hour. This procedure was used to stabilize the Ag grain size.

The Ag-Ni and Ag-Cu-Ni samples were prepared by A.C. sputter deposition of 450 nm Ag or 100 nm Cu/450 nm Ag on a high-purity Ni substrate. Before deposition, the Ni samples were mechanically polished to a mean surface roughness of 34 nm and then annealed in dry hydrogen at a temperature of 1100 °C for 1 hour to stabilize the Ni grain size. The layered samples were annealed in dry hydrogen at temperatures of 650 °C and 750 °C for 1 hour. 750 °C is close to the manufacturing temperature for Ag-Ni contact materials.

2.2. Chemical composition analysis and morphology examinations

Depth distributions of the elements involved were determined using Auger Electron Spectroscopy (AES). This analysis was made by VARIAN Auger spectrometer, model 981-2000. After the specimens were placed in a vacuum chamber, the chamber was evacuated to a pressure of 1×10^{-8} Pa. Then argon was introduced to the chamber, which increased the pressure to 7×10^{-3} Pa. The primary electron beam energy was 3 keV. Argon ion sputtering with energy of 2 keV was used to make depth profiles of the chemical composition. The differential Auger electrons' energy spectrum was registered in the energy range of 0–1000 eV.

Quantitative analysis of the chemical composition was performed using the elemental sensitivity coefficients given by Davis *et al.* [7]. In the quantitative analysis of Ni and Cu the peaks at 848 eV and 920 eV were used respectively. The superposition of the secondary peak at 840–849 eV for Cu and the primary peak at 848 eV for Ni made the direct determination of Ni in the analyzed specimens impossible. Therefore it was assumed that the ratio of the corresponding peaks for Cu (in the range of 840–849 eV as well as at 920 eV) is constant (equal to 0.35) and did not depend on the concentration of Cu in the specimen. The real value of the 848 eV peak for Ni was calculated by substracting the value corresponding to the peak 840–848 eV for Cu from the registered common peak (for Cu and Ni at 848 eV).

Scanning electron microscopy (SEM) was used to examine the morphology of the external Ni surface of Ni-Ag and Ni-Cu-Ag samples.

3. Results

Fig. 1 shows AES depth profiles of Ag, Ni and O atoms from the as-deposited Ag-Ni sample and from the sample annealed at 750 °C for 1 hour. A significant interpenetration of Ag and Ni as compared with the initial interface can be seen in this figure (the interface has become blurred). A small quantity of Ag in the Ni substrate of the as-deposited sample is apparent and results from sputtering-induced degradation of the depth resolution. A similar observation, referring to the Ag profile in the annealed sample, may be attributed also to this phenomenon.

The interface is shifted towards longer etching times in the sample annealed as compared with the as-deposited sample. This effect must have been caused by the different rates at which the Ag layer underwent ion etching before and after the annealing. Previous investigations of Ni-Ag [6] are in agreement with this assumption.

Fig. 2 shows AES concentration profiles for Ni-Ag samples. The significant interpenetration of Ni and Ag relative to their initial interface is similar to that in the Ag-Ni samples. Previous investigations [6] revealed that the apparent shift of the interface to the surface could be attributed to different etching rates of the as-deposited and annealed Ni layer.

There was more oxygen at the interface in the Ni-Ag and Ni-Cu-Ag than in the Ag-Ni samples and Ag-Cu-Ni samples. This existance of oxygen may result from the silver oxide film covering the substrate, which was not removed before depositing the Ni or Cu layer.

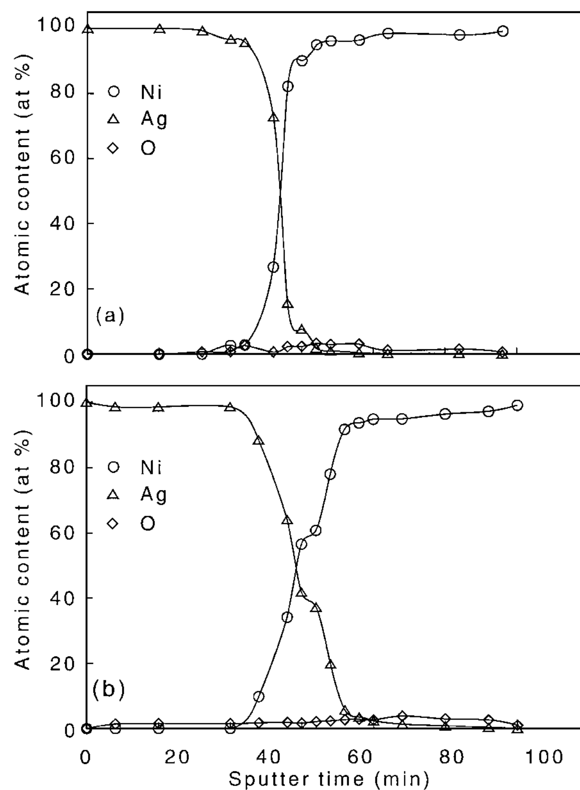

Figure 1 Profiles of Ni, Ag and O from Ag-Ni: (a) as-deposited and (b) annealed at 750 °C for 1 hour.

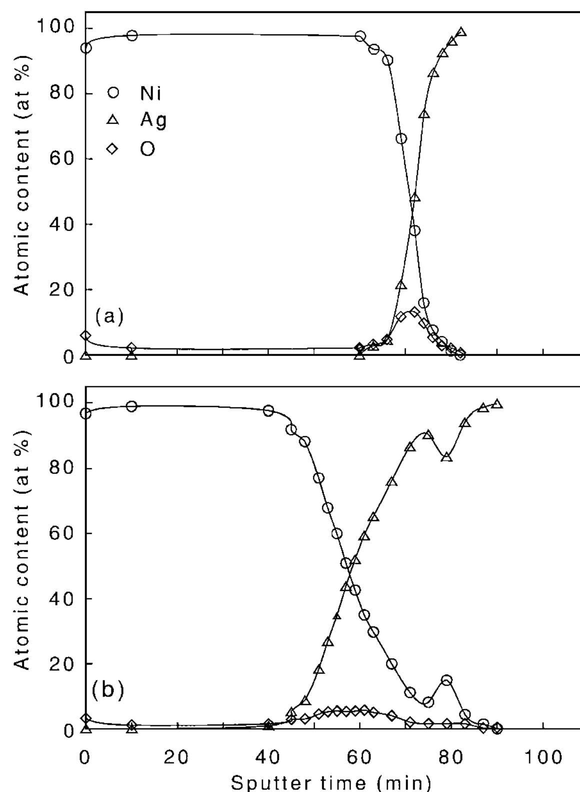

Figure 2 Profiles of Ni, Ag and O from Ni-Ag: (a) as-deposited and (b) annealed at 750 °C for 1 hour.

AES concentration profiles for Ag-Cu-Ni and Ni-Cu-Ag samples are shown in Figs 3 and 4,

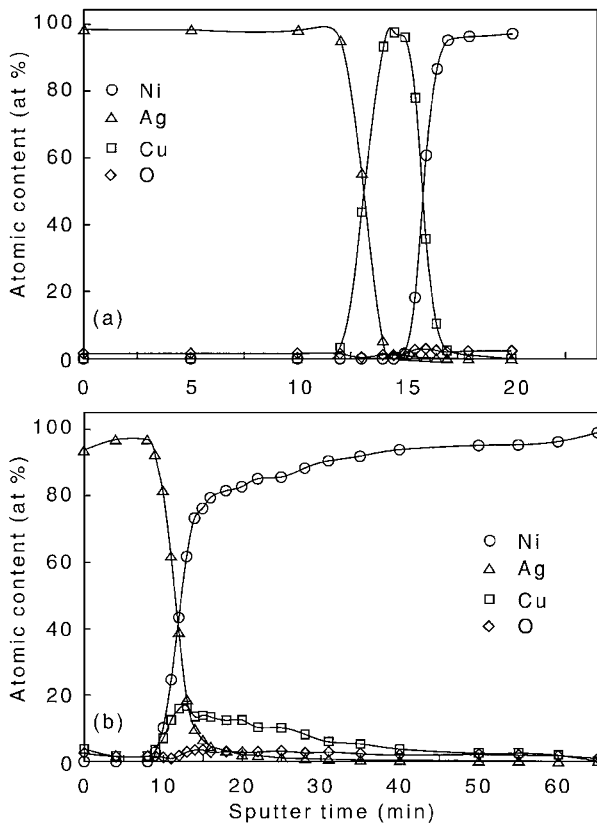

Figure 3 Profiles of Ni, Ag, Cu and O from Ag-Cu-Ni: (a) as-deposited and (b) annealed at 750 °C for 1 hour.

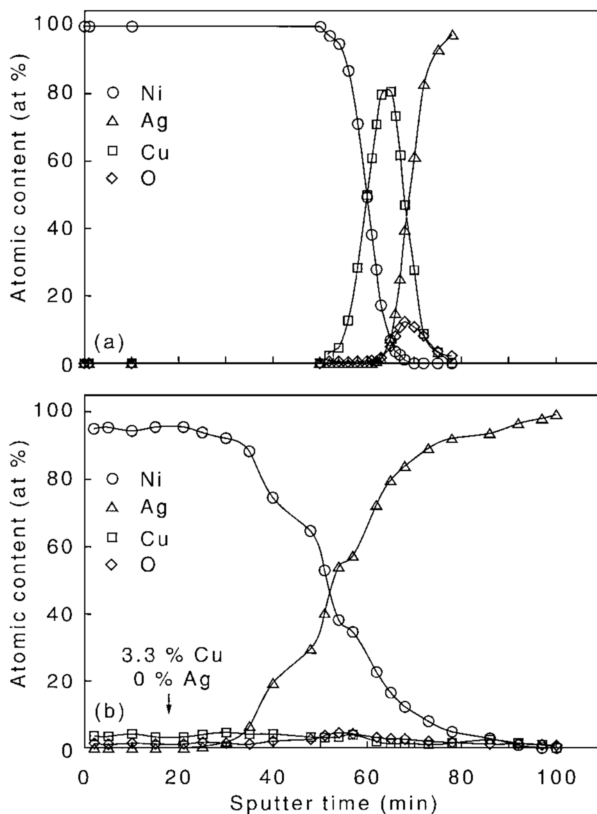

Figure 4 Profiles of Ni, Ag, Cu and O from Ni-Cu-Ag: (a) as-deposited and (b) annealed at 750 °C for 1 hour.

respectively. Fig. 5 shows some of the AES spectra from Ag-Cu-Ni sample annealed at 750 °C, which were used to determined the depth distributions of the elements involved.

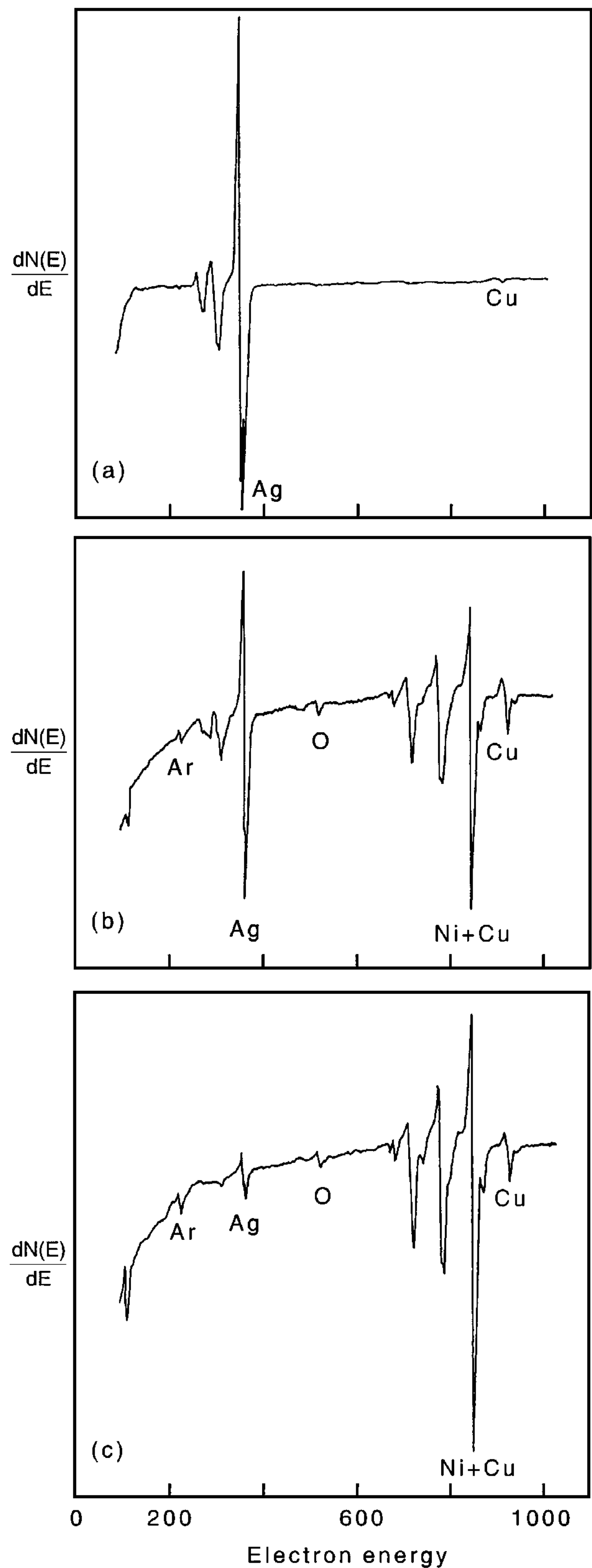

Figure 5 AES spectra from Ag-Cu-Ni annealed at 750 °C after ion sputtering for: (a) 8 min, (b) 13 min and (c) 20 min.

Annealing the Ag-Cu-Ni sample at a temperature of 750 °C caused the Cu atoms to migrate into the Ag layer and the Ni substrate. This migration is shown in Fig. 3. The Cu level in the Ag layer in the flat portion of the profile is 1.6 at %. The maximum Cu content, registered after 13 min of ion etching, is 16.8 at %. Taking into account that the time needed to etch the silver and nickel layers of the same thickness is dissimilar (about

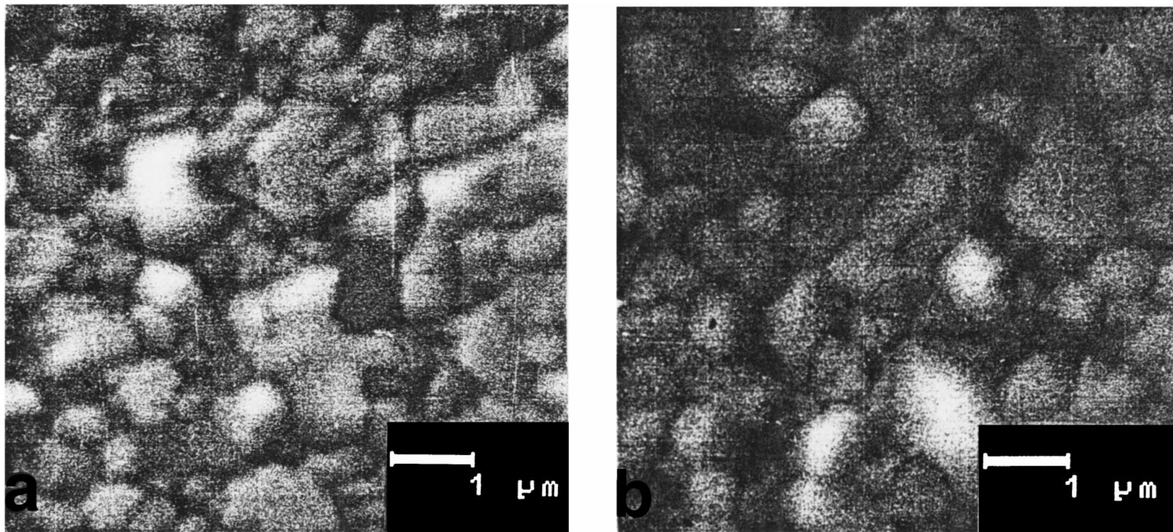

Figure 6 Plane views of scannnig electron micrographs of the Ni surface films for: (a) Ni-Ag and (b) Ni-Cu-Ag samples annealed at 750 °C.

4.5 times shorter for silver) it was observed that more copper diffused into the nickel than into the silver.

Cu atoms in the Ni-Cu-Ag sample migrate into the Ni layer and Ag substrate. The Cu profile in the Ni layer, shown in Fig. 4, is roughly flat with a Cu level of 3.3 at %. The flat Cu profile occured in all cases, except for the Cu concentration profile in the Ni substrate. It is characteristic that the shapes of the Cu profiles in the Ni layer and in the Ni substrate are dissimilar to each other.

Although the reliance upon the Ag profile in the Ni substrate shown in Fig. 3 is decreased by the sputtering-induced degradation of the depth resolution, the Ag profiles from Ag-Ni and Ag-Cu-Ni samples still suggest that the diffusion of Cu into the Ni substrate in the annealed Ag-Cu-Ni sample was accompanied by Ag diffusion. Neither Ag in the near-surface volume of the Ni layer of Ni-Ag or Ni-Cu-Ag sample nor Ni in the near-surface volume of the Ag layer of Ag-Ni or Ag-Cu-Ni sample was observed.

SEM examinations of the surface morphology of the Ni-Ag and Ni-Cu-Ag samples annealed at 650 °C and 750 °C revealed that the grains of surface layer grow during annealing and the growth is more intensive at higher temperature. Fig. 6 contains the plane views of scanning electron micrographs of the Ni surface films for the Ni-Ag and Ni-Cu-Ag samples annealed at 750 °C. The mean grain size of the Ni surface layer in these samples is about 1000 times less than that of Ni substrate in Ag-Ni and Ag-Cu-Ni samples. It should be noted that grains were difficult or impossible to observe in annealed sputter-deposited Ag films of Ag-Ni and Ag-Cu-Ni samples using SEM method.

4. Discussion

It should be noted that copper mainly diffuses into nickel and not into silver, when copper is introduced into the Ag-Ni interfacial region, Figs 3 and 4. Moreover, the amount of Cu in Ni layer of the Ni-Cu-Ag sample (3.3 at %) is about 2 times higher than in Ag layer of the Ag-Cu-Ni sample. The observation that a greater amount of copper diffuses into the Ni phase may be explained in terms of unlimited solubility of Cu in Ni in contrast to the relativly poor solubility of Cu in Ag. The solubility of Cu in Ag at the temperature of 750 °C is 12 at % [2].

It is interesting that the shapes of Cu concentration profiles from the samples Ag-Cu-Ni and Ni-Cu-Ag annealed at 750 °C are different. The experiments have shown that the Cu can easier outdiffuse from the previously continuous layer into neighbouring phases in the Ni-Cu-Ag layered structure than in the Ag-Cu-Ni sample, Figs 4 and 3, which must result from the differences in microstructures of the nickel phase. The samples examined contain silver and nickel phases of different microstructures. The grain size of the substrate is about 1000 times bigger than that of the surface layer. Therefore, the content of grain boundaries in the volume of the material is much higher for the surface layer than for the substrate. The microstructure of Ni in Ni-Cu-Ag is fine-grained, which promotes grain boundary diffusion. Grain boundary diffusion dominates bulk diffusion for the temperatures of experiments that are covered by the range from 0.5 to 0.6 of the melting point of nickel. This is an explanation of the apparent influence of the nickel's grain size on the shape of the copper concentration profile.

There are two possible reasons for the flat shape of the copper concentration profile in the silver substrate. The participation of grain boundary diffusion in mass transport of copper in silver is much lower than in nickel within the temperature range involved. This statement is in accordance with the results obtained by Murakami and de Fontain for the diffusion in the Ag-Cu system [8]. Another reason for the flat shape of copper profile in silver substrate is that Cu outdiffuses preferentially into the Ni phase.

The previous observations that introducing Cu at grain boundaries had the effect of stopping the growth of the nickel's grain size and allowed the migration of silver atoms to the nickel surface [6] were not confirmed in these experiments. The level of Cu in the Ni layer of the Ni-Cu-Ag sample (3.3 at %) is lower than in the

previous experiments (4.5 at % of Cu in Ni) [6] and the Ni layer is 0.05 μm thinner in these experiments. Therefore the amount of Cu that diffused into the Ni layer was smaller in these experiments. Moreover, the existance of Ag in the Ni layer was not detected during this research work. The smaller diffusion of Cu into the Ni layer and the lack of silver in the nickel phase might be attributed to the differences in Ni microstructure in as-deposited state and/or the differences in Ni purity. In this case the purity of Ni, equal to 99.9 weight %, was higher.

When copper is introduced into the Ag-Ni interfacial region, the grain boundary of diffusion type is created in the system. It should be noted that microstructure will critically affect the interphase boundary formation.

5. Conclusions

—The copper concentration profile is dependent on which type of diffusion is dominant, grain boundary or volume. The shape of the copper concentration profile is influenced by nickel's grain size.

—Microstructure will critically affect interphase boundary formation, when copper is introduced into the Ag-Ni interfacial region.

—Copper mainly diffuses into nickel and less into silver, when copper is introduced into the Ag-Ni interfacial region.

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