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Sputtering of two-phase Ag_xCu_y alloys

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Elemental sputtering yields from two phase AgCu alloys were measured for 20, 40 and 50 at % Ag. Argon ion bombardment energies were in the range 35–55 keV and the ion dose was 1×10^{19} ions cm^{-2}. The sputtering yield for silver was found to be considerably below what was expected by simple selective sputtering of a two component alloy. Analysis by electron probe X-ray microanalysis and scanning electron microscopy of the eroded surface indicated that surface diffusion of copper from copper rich grains and geometrical constraints in the dense cone forest on Cu/Ag eutectic regions combine to reduce the sputtering yield for silver.

1. Introduction

The sputtering of multicomponent targets such as alloys and compounds has become a subject for study within the last 20 years. The main effect in the sputtering of multicomponent targets is that the different components are generally not sputtered in proportion to their areal concentration on the surface [1–3]. This phenomenon is called preferential sputtering.

In analysis of preferential sputtering of multicomponent materials a difference between alloys forming a solid solution or an intermetallic compound and those forming multiphase structures is observed [2]. Single-phase systems have been investigated much more experimentally and theoretically. For these systems steady state conditions are reached quickly after removal of a layer comparable to the range of the incident ions. Multiphase materials are heterogenous consisting of different crystallites which represent different phases with different composition and sometimes different crystal structure. Compared with preferential sputtering of single-phase systems, sputtering of multiphase systems is called selective sputtering and represents selective erosion of different grains. For low ion doses, when the amount of sputtered material is of the order of a few monolayers, sputtering can be considered as a simple superposition of processes taking place in a mixture of different single-phase crystals. With the increase of ion dose, medium and high doses, a pronounced topography is developed at the surface [6–8]. As a result of selective sputtering, the development of surface topography, and surface diffusion, a certain equilibrium (perhaps dynamic) may be reached.

In our experiment we have studied the sputtering of two-phase Ag_xCu_y alloys, after bombardment with argon ions. The sputtering yields of alloy components were determined for the ion energies of 35–55 keV. The ion dose in all cases was 1×10^{19} ions cm^{-2}. The effects of ion dose on topography have been described in an earlier paper [6].

2. Experimental procedure

The surfaces of the Ag_xCu_y alloy samples were mechanically polished with a fine diamond paste prior to bombardment. Alloy composition was 20, 40 and 50 at % Ag.

Samples were bombarded in the collector region of an electromagnetic isotope separator with normally incident Ar^+ ions. The collector chamber was evacuated differentially from the isotope separator and the pressure was 5×10^{-7} mbar or better. The ion beam current density was between 30 and 150 $\mu A\,cm^{-2}$, but was kept constant during each experiment. Measurement of sputtering yield was performed for energies of 35, 45 and 55 keV and an ion dose of 1×10^{19} ions cm^{-2}. Sputtering yields were determined from spectrophotometric composition measurement of sputter deposited films on hemispherical glass collectors. The changes of surface topography and composition of different phases of the alloys were analysed by Scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EMPA).

3. Results

The measured sputtering yields S for (a) silver, (b) copper and (c) their sum, as a function of silver volume concentration in the alloy, are plotted in Fig. 1. Sputtering yields for silver (1 to 4 atoms per ion) are considerably lower than for pure silver, although they increase slightly at higher concentrations of silver in the alloy. The sputtering rate of copper reduces at high concentrations of silver, although the values remain close to those for pure copper. Sputtering coefficients of copper for the alloys with 20 at % Ag are in the

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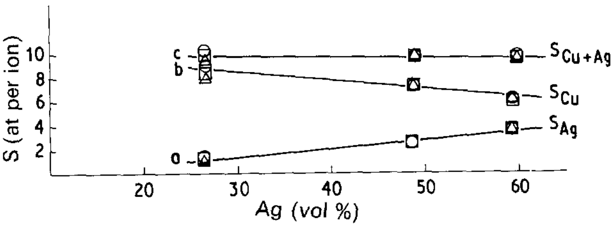

Figure 1 Experimentally obtained sputtering yields of (a) silver (b) copper and (c) their sum. (Argon ion energies (△) 35, (□) 45 and (○) 55 keV, ions dose 1×10^{19} ions cm^{-2})

interval from 7.8 to 8.9 atoms per ion, slightly higher than the value for pure copper of 7 atoms per ion. In the alloys with 40 at % Ag, the sputtering coefficient values of copper reduce to 7.3 atoms per ion. The alloys with the highest concentration of silver (50 at % Ag) yield a sputtering coefficient of copper of around 6 atoms per ion, lower than for pure copper targets. The sum of the sputtering yield of copper and silver does not vary appreciably with the composition of the alloy, the values being in the interval 9 to 10.5 atoms per ion. These values are somewhat lower than the sputtering coefficient of pure silver.

Experimental yield values for Cu, Ag and their sum, as a function of the incident ion energy and alloy composition are presented in Table I. The results show that, for the small energy interval used, the sputtering coefficients are insensitive to ion energy. This is in agreement with the behaviour of the pure components of the alloy (Cu and Ag), and is the reason why the energy interval 35–55 keV was chosen. However the alloys with 20 at % Ag, do show a slight increase of the sputtering yield for copper with increasing ion energy.

The specimen topography was investigated using a scanning electron microscope (SEM). The micrographs show that the topography of the bombarded alloys is characterized by large grains distributed in a eutectic mixture. The distribution of components and composition of the two different phases were analysed by EPMA. The X-ray image of Cu in Fig. 2a, clearly shows that the large grains represent a copper rich phase. The presence of two different phases and an inhomogeneous distribution of the alloy components in the eutectic mixture regions is also illustrated by the compositional (backscattered electron) image in Fig. 2b. The SEM micrograph in Fig. 3 shows the development of cones in the regions of eutectic mixture. The cones always occur in the eutectic mixture regions of copper and silver crystallites after bombardment with ion dose of 1×10^{19} ions cm^{-2}. The difference in sputtering yield of copper crystallites relative to that of silver results in masking by copper clusters, differential erosion, then formation of columns which evolve into maximum sputtering yield cones [6, 7].

The results of our earlier investigations [6] show that the surface topography, which is developed during sputtering, changes with respect to the alloy composition. Namely, with the increase of silver concentration in the alloy, the regions of eutectic mixture of copper and silver crystallites increase, with a corresponding

TABLE I Measured and calculated sputtering yields for argon bombarded AgCu alloys.

Yield component (atoms/ion)	Alloy composition (at % Ag) 20	40	50	Ar^+ ion energy (keV)
S_{Cu}	7.84	7.37	6.01	35
S_{Ag}	1.22	2.42	3.60	35
S_{Cu+Ag}	9.06	9.79	9.61	35
S_T	7.51	8.08	8.40	35
S_{Cu}	8.67	7.42	5.73	45
S_{Ag}	1.31	2.45	3.48	45
S_{Cu+Ag}	9.98	9.87	9.21	45
S_T	7.50	8.12	8.46	45
S_{Cu}	8.98	7.32	6.14	55
S_{Ag}	1.52	2.51	3.56	55
S_{Cu+Ag}	10.50	9.83	9.70	55
S_T	7.45	8.11	8.48	55

S_{Cu} measured sputtering yield for copper.
S_{Ag} measured sputtering yield for silver.
S_{Cu+Ag} sum of measured sputtering yields.
S_T calculated total sputtering yield.

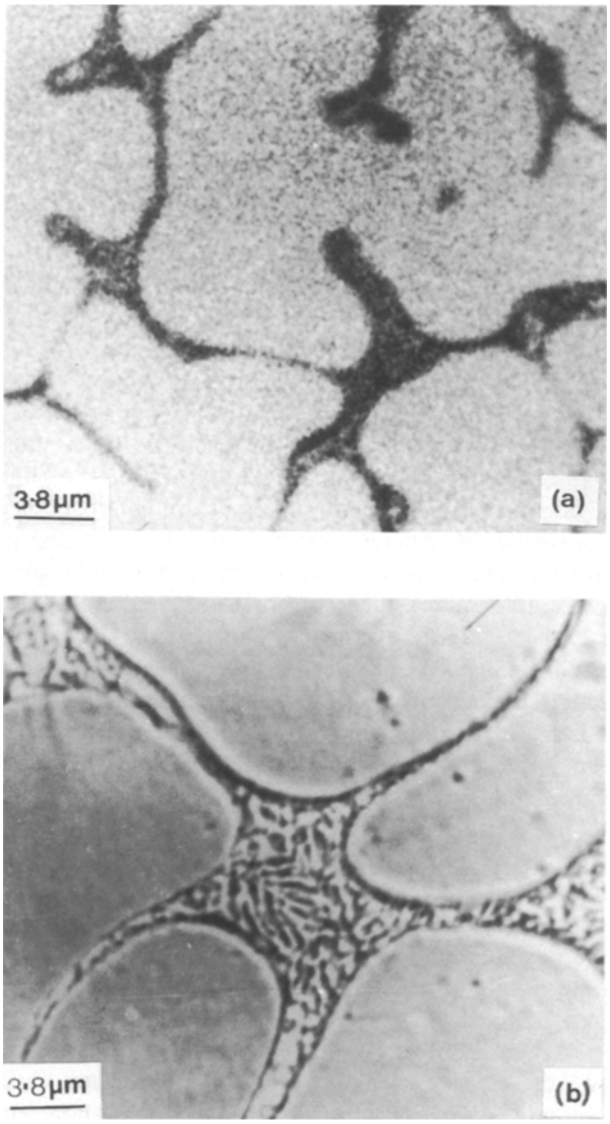

Figure 2 EPMA images of a 20 at % Ag alloy specimen. (a) X-ray image showing distribution of Cu (b) Backscattered electron image (compositional). Ion dose 1×10^{19} ions cm^{-2}, incident ion energy 55 keV.

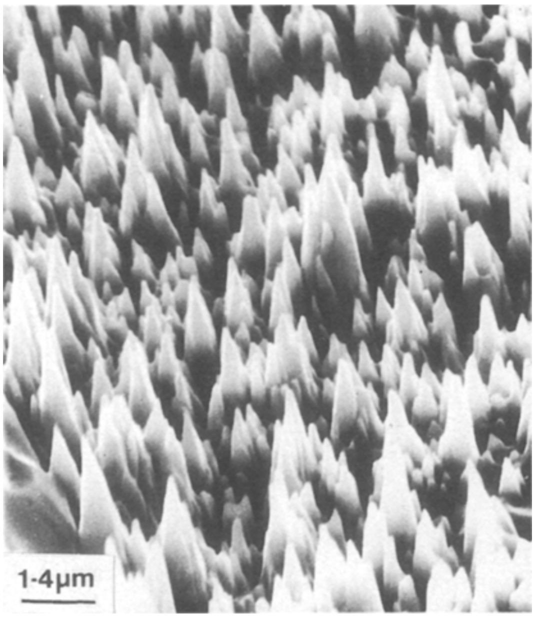

Figure 3 SEM micrograph of cone development in the regions of eutectic mixture. Ion dose 1×10^{19} ions cm^{-2}, ion energy 45 keV, composition 50 at % Ag.

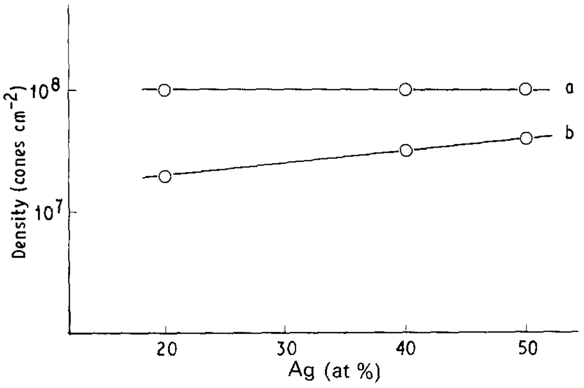

Figure 4 The areal density of cones (a) in the regions of eutectic mixture and (b) the mean areal cone density for the whole surface.

decrease in the size of the copper grains. The average density of cones in the regions of eutectic mixture of copper and silver crystallites, which was determined by the counting of cones from the micrograph is of the order 10^8 cm^{-2}, and is insensitive to alloy composition as shown in Fig. 4a. The dependence of the mean areal cone density on the silver concentration is shown in Fig. 4b. This is based on the assumption that the areal density of silver is equivalent to the volume concentration. As the silver concentration increases the large copper rich grains shrink and the regions of eutectic mixture, and therefore the coverage by cones, grows. The mean areal density of cones increases from 0.3 to 0.6×10^8 cm^{-2} as the silver concentration increases from 20 to 50 at %.

4. Discussion

By applying the method for calculation of the average sputtering coefficient of an alloy, S, we can estimate the contribution of the pure components to the total sputtering yield of the alloy [4]. For example the sputtering coefficient of pure silver (10.5 atoms per ion) and the volume concentration of silver (for 50 at %) $V = 59.2\%$ gives $S_{Ag} = 6.2$ atoms per ion (a factor of two higher than the experimental value). On the other hand, the experimental value for copper (6.01 atoms per ion) is a factor of two higher than that calculated by the average method (2.8 atoms per ion). The difference in the predicted and experimentally obtained results can be explained by the surface atom migration and the coverage of the eutectic mixture regions (silver rich phase) by copper atoms, moving from the large copper grains.

The number of sputtered atom N_1 and N_2 from the two different phases can be expressed as

$$N_1 = S_1 C_{s1} J^+ t \qquad (1)$$

and

$$N_2 = S_2 C_{s2} J^+ t \qquad (2)$$

where S_1, S_2 and C_{s1}, C_{s2} are sputtering coefficients of pure elements and fractional surface areas of each component. The ion dose is expressed by J^+t (J^+ is the constant current density on the target and t the bombarding time). For steady state conditions

$$N_1/N_2 = C_1/C_2 = S_1 C_{s1}/S_2 C_{s2} \qquad (3)$$

where C_1 and C_2 are the atomic bulk concentrations of the two components. The total sputtering coefficient S_T of a two-phase alloy is then

$$S_T = 1/(C_1/S_1 + C_2/S_2) \qquad (4)$$

taking into account only pure selective sputtering, without the contribution of surface atom migration and the development of surface topography [2].

The calculated yield values, shown in Table I, are lower than the sum of the sputtering coefficients for silver and copper which were determined experimentally. The total sputtering yields calculated by the Equation 1 are close to the measured values of copper for alloys with 20 at % Ag. This indicates that coverage of the Ag rich phase with copper atoms and the topography effects are more important than pure selective sputtering.

Our results show that the values of sputtering yield can be influenced by the ion beam induced enhanced mobility of copper atoms and by the development of surface topography. During initial sputtering the copper grains are eroding at a lower rate compared to the regions of eutectic mixture, so the migration of copper atoms from the large grains is probably one of the reasons for the lower sputtering yield of silver. The SEM results have shown that the ion dose of 1×10^{19} ions cm^{-2} which was used for the measurement of sputtering yield, always induces formation of cones in the region of eutectic mixture. As the density of cones is rather high (10^8 cm^{-2}) it can be assumed that an appreciable fraction of the atoms which are sputtered within the eutectic mixture are captured again at slopes of the cones, resulting in a reduction in the sputtering yield for silver. This means that the surface topography which is developed during ion bombardment, and particularly the formation of cones in the regions of eutectic mixture, can have the strongest influence on the sputtering yields of a two-phase Ag_xCu_y alloy. The prevention of sputtered atoms from escaping the target by geometrical constraints on a cone covered surface was reported in the experiment of Ashida *et al.* [5]. It was found that the Ag concentration of the deposited films was considerably reduced by the growth of cones on Ag plates during bombardment of target consisting of a small Ag plate placed on a Si wafer.

5. Conclusions

Our results show that the sputtering yield for silver in AgCu two phase alloys is considerably below what was expected from simple selective sputtering of a two component alloy, the yield for copper is greatly enhanced. We conclude that the low values of the sputtering yield for silver are a consequence of a higher surface mobility of copper atoms induced by the ion beam and of the development of surface topography. Copper atoms migrate from the large grains and cover the region of the eutectic mixture and thus causing a lower sputtering rate for silver and an enhanced copper yield. The influence of surface topography is in the capture of sputtered atoms at the slopes of the cones in the regions of eutectic mixture. This contributes to a reduced sputtering yield for silver.

The density of cones in the region of eutectic mixture was determined to be 10^8 cm^{-2}. Coverage of the bombarded surface by the eutectic mixture and therefore by cones increases with the concentration of silver in the alloy.

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