Electrodeposition of supersaturated CuAg alloys in pyrophosphate-iodide electrolytes

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A novel electrolyte based on CuSO4 complexed by K4P2O7 and AgNO3 complexed by KI is studied for the deposition of CuAg alloys having a range of Ag compositions between 3 %at. and 16 %at. The deposition occurred in non stirred conditions at 50°C. A characterization of the coatings is presented with a focus on the properties of the supersaturated alloy and the demonstration of its metastable behavior. The electrochemical characterization of the solution is also reported.

Introduction

The use of electrodeposited copper for the manufacturing of electrical contacts in microelectronic is nowadays widespread and the processes used are well implemented in the industry. The high conductivity of the metal, the simple use of the electrolytes used for its deposition and the good productivity make this metal the most suitable to achieve high performances. However, also copper presents some problems, especially for uses that require high mechanical properties as the connections used in probing technology. Another problem can be found in electromigration, a phenomenon that is significant in structures of reduced section where a high current flows (1). To improve these two aspects a possibility can be the adding of an alloying element at the electrodeposited copper, and among the possible metals, silver can be an attractive option for its high conductivity (2). Silver is known to form in particular manufacturing conditions a supersaturated solid solution (3,4) with copper. The Ag-Cu phase diagram (4) clearly shows that at room temperature the solid solutions between Cu and Ag are not stable and the two metals are completely immiscible. This instability is obviously related to the positive heat of mixing between the metals, and for this reason is possible to have only metastable solid solutions at room temperature on the whole range of compositions. The thermodinamical properties of CuAg have been extensively studied in previous works (3,4), as well as the optical and electrical ones (5,6). Other couples of metals that behave in a similar way have been characterized too, including AgFe (7), FeCu (8-13), CoCu (14-16), CuW (17), CuV (18) and CuTa (19,20). Since such systems are unstable, a high enough temperature or other influences can easily lead to the decomposition in the two separated components. The methods used to get these alloys are based on the overcoming of the cited positive heat of mixing and include electrodeposition (21,22), mechanical alloying (1) and sputtering (5). In particular, for the technique used in the present work, the presence of an underpotential deposition leads to the fast inglobation of silver atoms inside the crystal lattice of copper. The adatoms are not able for this reason to reach their equilibrium sites and they stay in interstitial positions between copper atoms. By adding such interstitial silver atoms a stretching of the crystal lattice and a significant increase in mechanical properties is induced. In addition silver can decrease the electromigration tendency without affecting the conductivity.

The literature on the plating of CuAg is poor and it focus mainly on the deposition of alloys from cyanide electrolytes (21,22). To have acceptable mechanical properties and keep the cost at an affordable level the Ag percentage in the deposit should not exceed 8%, and articles on the deposition of 1-4% Ag alloys are also available but the processes described are not reliable for the deposition of high thickness coatings or the electroforming of parts (2).

The aim of the work presented here is to look for a new solution suitable for low and high thickness deposits, with good surface quality and a silver content in between 1-10 %. In particular the high thickness is of great interest due to the possibility of using the solution in electroforming processes.

Experimental

All the chemicals used were purchased from SIGMA ALDRICH, and they were used as received. The solution used for the electrodeposition experiments was: 50 g/l $CuSO_4 \cdot 5H_2O$, 150 g/l $K_4P_2O_7$, 150 g/l KI and 75 ml/l solution 0.1M $AgNO_3$. Electroplating was done in non-stirred conditions at 50°C, deposition time was in the range 10-150 minutes. The electrochemical cell used was constituted by a pure copper plate as anode and electrodeposited nickel as cathode. Such nickel was plated on steel samples using an industrial solution of nickel sulfamate. For the X-Ray Fluorescence XRF measurements a FISCHERSCOPE X-RAY XAN was used, while all the X-Ray Diffraction XRD data were acquired by mean of a PHILIPS 1830 system. The cyclic voltammetries were obtained using an EG&G potentiostat-galvanostat model 273. Microhardness was measured with FISCHERSCOPE HCU microindenter, while the SEM images with a ZEISS EVO 50. Finally, the evaluation of the cathodic efficiency was performed comparing the weight of the alloy deposited with the theoretical amount to be deposited (calculated balancing the relative amounts of the two metals with the XRF measures).

Results and discussion

Voltammetric tests have been used to understand the behaviour of the solution. Figure 1 represents the result obtained.

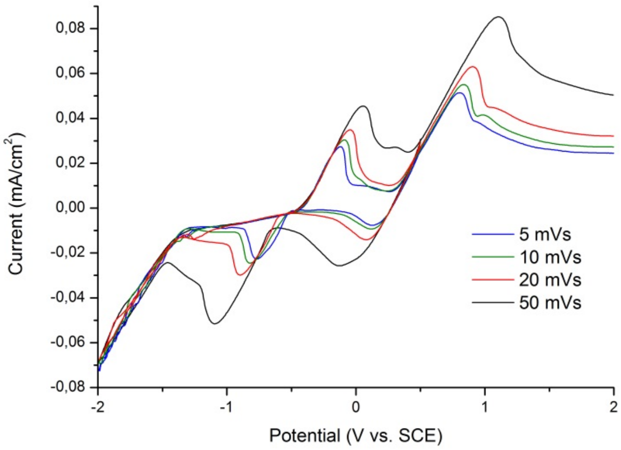

Figure 1: voltammograms in non-stirred condition of the CuAg solution.

It is evident from the picture that the reduction peaks of interest are covered by other features connected to the presence of the two complexing agents. Two different solutions were prepared, the first one with the base formulation minus $CuSO_4$/pyrophosphate and the other with the base formulation minus $AgNO_3$/KI. These two new electrolytes were analysed separately; voltammetries for the one with $AgNO_3$/KI is reported in figure 2.

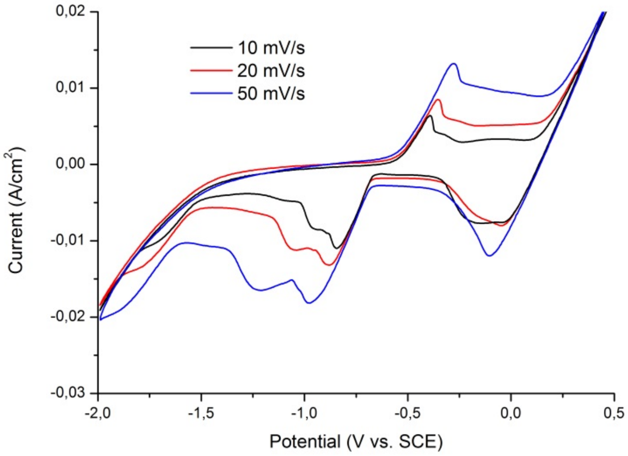

Figure 2: voltammograms in non-stirred condition of the base solution without copper complex: 150 g/l KI and 75 ml/l solution 0.1M $AgNO_3$.

The interpretation of the results is helped by the huge literature present on the iodide solutions. It appears clear that the first reduction peak located around 0 V is actually the result of two contributions: the $Ag^+ + e^- \rightarrow Ag^0$ part around -0.2 V (24) and the $I_3^- + 2e^- \rightarrow 3I^-$ part close to 0 V (25,26). This is evident in particular at the lowest scanning speed (10 mV/s). The double peak in correspondence of the zone around 1 V is linked to the absorption of iodide ions on the silver surface created during the Ag^+ reduction step and the subsequent electroreduction of the formed AgI layer (27,28) to Ag^0 according to:

$$AgI_{(adb)} + e^- \rightarrow Ag^0 + I^-$$

The anodic peak at -0.4 V represent the corresponding oxidation reaction ($Ag^0 + I^- \rightarrow AgI_{(adb)} + e^-$).

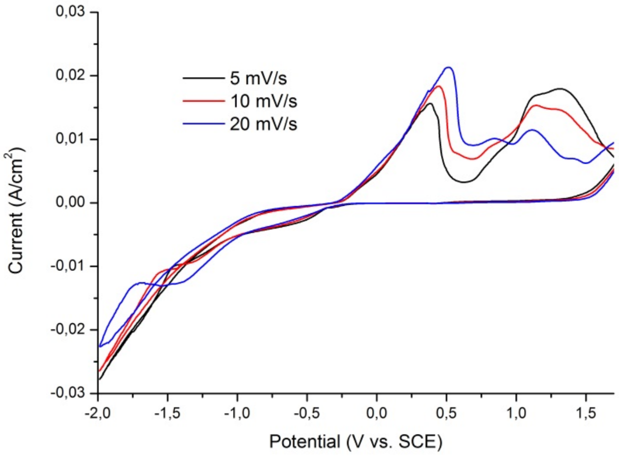

Figure 3: voltammograms in non-stirred condition of the base solution without silver complex: 50 g/l $CuSO_4 \cdot 5H_2O$, 150 g/l $K_4P_2O_7$.

The curve obtained from the copper sulphate complexed by potassium pyrophosphate (figure 3) is correspondent to various references that is possible to find in the literature. The slope change visible around -0.4 V is representative of the following reactions (29) giving elemental copper:

$$Cu(P_2O_7)_2^{6-} \rightarrow Cu(P_2O_7)^{2-} + Cu(P_2O_7)^{4-}$$

$$Cu(P_2O_7)^{2-} + 2e^- \rightarrow Cu(s) + Cu(P_2O_7)^{4-}$$

The oxidation peak for $Cu^0 \rightarrow Cu^{2+} + 2e^-$ is at 0.4 V, while the complex series of features visible between 0.75 V and 1.5 V is caused by the presence of the pyrophosphate (30,31).

The pyrophosphate-iodide solution was used to deposit CuAg coatings at various current densities, changing the deposition time in relation to have constant theoretical thickness. The coatings obtained at the various current densities have thicknesses between 5 µm and 7 µm. As easily predictable, the main effect of increasing the current density is the reduction of the Ag content. Despite the absence of stirring in the solution, XRF measurements in different zones of the coated surface show a good uniformity in terms of thickness and composition. Figure 4 shows the change in the mean silver atomic percentage acquired from 5 points of the layer.

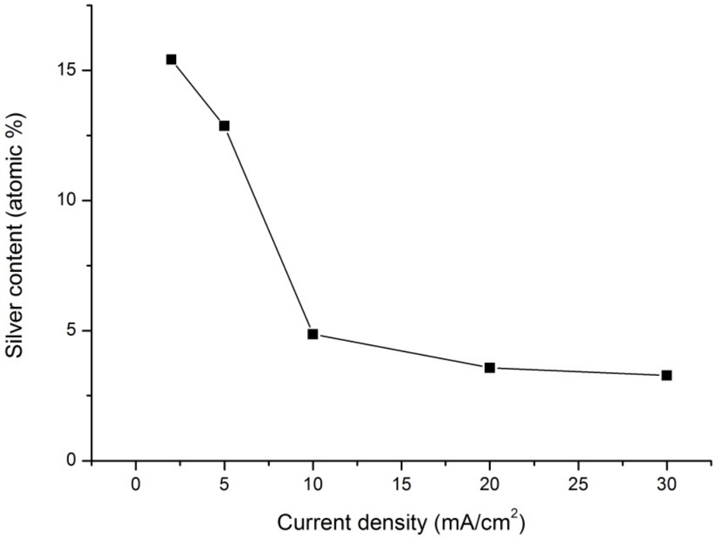

Figure 4: silver content as a function of deposition current density.

The cathodic efficiency was studied as well, and as visible in figure 5 it is near 100% only at low current densities. The change in efficiency explains the non homogeneity of the thicknesses measured with XRF. High currents give lower values mainly due to the reduced copper ions concentration, significantly lower than commercial pyrophosphate solutions, and the presence of the iodides.

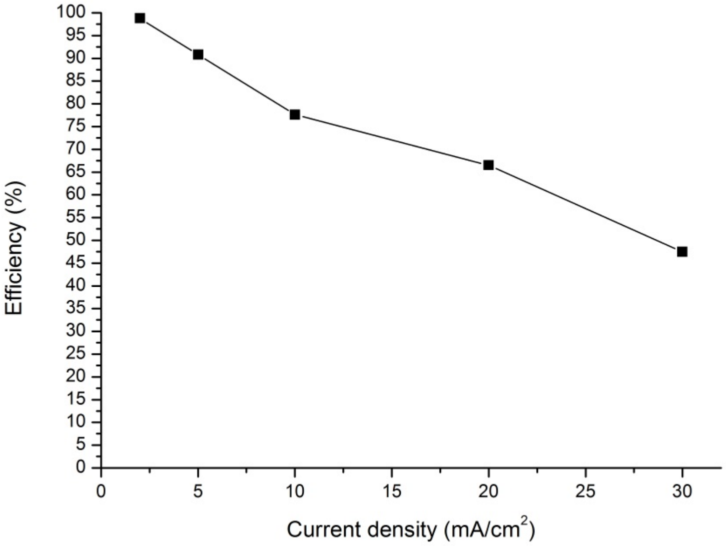

Figure 5: cathodic efficiency as a function of the increasing current densities.

To prove the metastable behaviour, the samples produced were studied with XRD. The graphs of different coatings at various deposition rates are reported in figure 6, where is represented also the behaviour of pure copper deposited with a standard pyrophosphate solution. This was chosen for its similarity with the copper complexing system used in the new electrolyte.

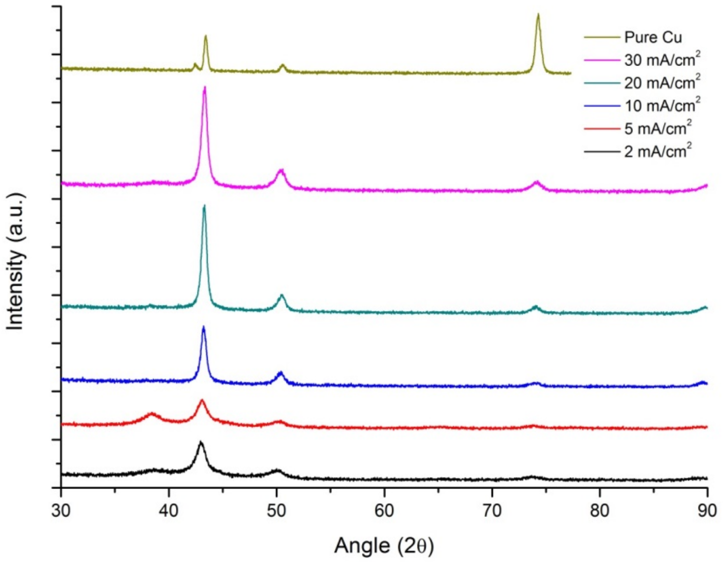

Figure 6: XRD spectra of different CuAg samples at various plating conditions.

The most evident feature in the graph is the presence of all the copper standard peaks in the silver containing samples at all the current densities: Cu (111) around 43°, Cu (200) at 50° and Cu (220) near 74°. The absence of the complete set of Ag peaks is in fact consistent with the interstitial position of silver in the supersaturated solid solution, even if for the two samples at lower current density (higher silver content) also one silver peak appears: Ag (111) at 38°. This can indicate the presence, at high silver percentages, of some silver not in solution in the metastable alloy. Silver domains are probably present in the two samples at 2 and 5 mA/cm^2.

Another aspect that is useful to point out is the different crystallographic orientation of the CuAg alloy with respect to copper from pyrophosphate. Observing the XRD of this one, is clear that the dominant orientation in the deposit is the (220), while in all the other samples it is (111) like the Cu powder case. From this point of view the solution behave more like a copper sulphate solution rather than a pyrophosphate one. The most interesting alteration induced by the presence of silver is the peaks position. As the percentage of the metal increase the features are shifted to the right of the graph to lower angles. To underline this effect the measured values of 2θ for peak (111) were used to calculate the corresponding values of mean interplanar distance. Then the difference with the lattice parameter for peak (111) of pure copper was calculated. Table 1 report the results.

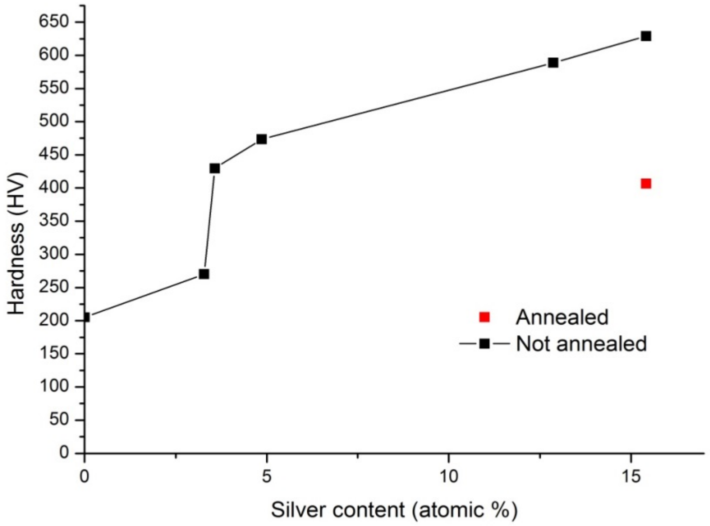

Figure 7: microhardness with Vickers microindenter at 5 mN load on AgCu samples and pure copper.

As evident from figure 7, hardness measured by microindentation with a Vickers indenter does not increase in a linear way with the silver content. The first part of the graph shows a slightly exponential growth, while the zone at high silver contents is more linear.

Table 1: calculation of Δd as $d_{alloy} - d_{Cu}$ lattice parameters.

Current density	Ag %	Peak position (2θ)	d-spacing (Ȧ)	Δd (Ȧ)
2 mA/cm^2	15.42	42.973	2.1030	0.0203
5 mA/cm^2	12.87	43.056	2.0991	0.0164
10 mA/cm^2	4.86	43.170	2.0938	0.0112
20 mA/cm^2	3.57	43.271	2.0892	0.0065
30 mA/cm^2	3.27	43.336	2.0862	0.0035
(pure copper)	0	43.413	2.0827	0

Conclusions

The electrodeposition of solid solution of silver and copper from novel electrolyte has been studied. XRD spectra were obtained from the samples produced and their analysis clarified the behaviour of the plated coatings as metastable solid solutions. In particular the good accordance with Vegard's law is representative of the linear lattice deformation induced by interstitial silver atoms. The present study opens new possibilities for the electrodeposition of electromigration resistant coatings having also good mechanical properties for the use in the electronic industry.

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