

Electrodeposition of supersaturated CuAg alloys in pyrophosphate-iodide electrolytes

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The application of electrodeposited copper to the manufacturing of electrical contacts in microelectronics is nowadays widespread. However, the use of this metal presents problems when high mechanical properties are required. Another problem can be found in electromigration, a phenomenon that is significant in structures of reduced section. To improve these two aspects a possibility can be the addition of an alloying element to the electrodeposited copper, and among the possible metals, silver can be an attractive option for its high conductivity. This metal, normally immiscible with copper at room temperature, forms a supersaturated alloy when electrodeposited. The main aim of this work is to understand the behaviour of this resulting system.

In the sample preparation phase a novel electrolyte based on CuSO_4 complexed by $\text{K}_4\text{P}_2\text{O}_7$ and AgNO_3 complexed by KI was used for the deposition of CuAg having a range of compositions between 3% and 16% (atomic). The deposition occurred in non stirred conditions and at 50°C on nickel plated steel. Figure 1 shows the change in silver content with the increasing current density measured using XRF.

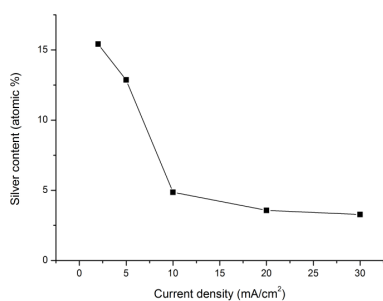


Figure 1: composition-current density correlation for deposition in non stirred conditions.

The XRD analysis of the samples shows a slightly linear shift in the position of the visible peaks, as showed in figure 2 for CuAg (111).

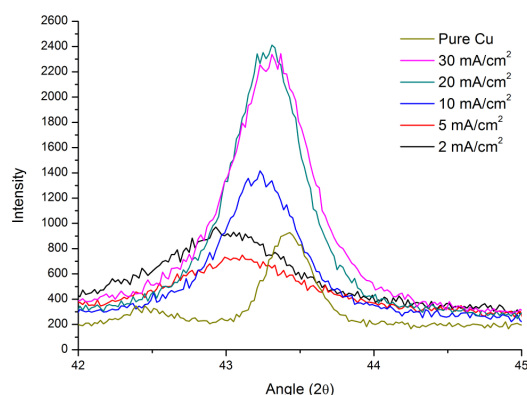


Figure 2: focus on the (111) XRD peak of the alloy for various Ag concentrations.

The recorded linear shift is correlated to a constant

deformation of the lattice induced by the increasing interstitial silver atoms. This can be visualized representing the difference between the mean (111) interplanar distance of pure copper and the one of the alloys. Annealing the CuAg layer at 400°C led to the complete separation of the two metals, as predicted by the phase diagram and visualized by XRD. Another effect of the presence of interstitial Ag is the substantial increase in hardness, as pointed out in figure 3 (also the annealed case is reported for comparison).

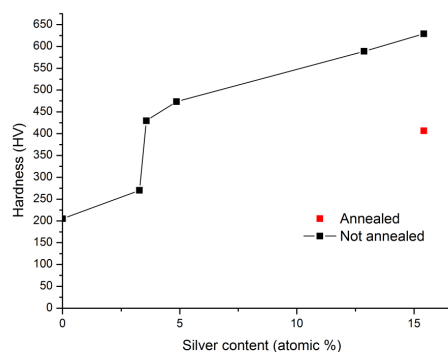


Figure 3: mean hardness (according to UNI EN 6507, load 5 mN) with respect to Ag content.

The low hardness performance of the sample at 30 mA/cm^2 is probably related to the current density being too high for the solution and leading to poor quality of the layer more than to the Ag content. Figure 4 represent the typical surface morphology of a sample, showing a nodular conformation.

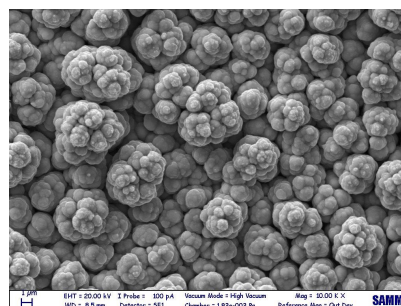


Figure 4: SEM image of the 5 mA/cm^2 sample.

Experimental data will be discussed on the basis of a new modelling frame for electrochemical systems.