

# Low-Temperature Cu Segregation and Oxidation in Microwaved Ag-Cu Alloys

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## **Abstract:**

Samples of a silver-copper (Ag-Cu) alloy of 13% Cu were annealed in a microwave cavity for up to 200 seconds, with a maximum temperature of 80°C. Rutherford backscattering spectrometry (RBS) indicated copper segregation to the surface. Oxygen resonance analysis and x-ray diffraction (XRD) showed that a thin copper oxide layer began forming on the surface at 40 seconds and completed at 80 seconds. Four-point probe measurements showed a decrease in the sheet resistance and XRD suggested that subsequent annealing resulted only in additional Ag grain growth.

## **Introduction:**

Microwave processing has gained, and is gaining, much attention regarding materials processing due to its ability to process materials at low temperatures, and its efficiency in respect to time and energy savings, which lead to monetary savings [1]. Silver is a great conductor and has a high electromigration resistance [2], however, silver particles tend to cluster at high temperatures and oxidize in certain environments. To control these downsides, it is vital that an encapsulation layer be formed, in a sense, to protect the silver.

In this paper, it is noted that the copper will diffuse out of the alloy and react with ambient oxygen to form a copper oxide layer, which will act as an encapsulation layer protecting the silver from agglomeration and oxidation [3].

## **Experimental Procedure:**

An Ag(Cu) alloy was fabricated by co-sputtering pure, 99.99%, Ag and Cu targets onto a silicon (Si) substrate with a previously deposited 100 nm thick silicon nitride ( $\text{SiN}_x$ ) layer. The  $\text{SiN}_x$  layer ensured that the silver did not diffuse into, or agglomerate on, the Si substrate. The alloy structures were heated in a

2.45 GHz microwave cavity for up to 200 seconds. The temperatures of the samples were recorded using a Raytek low-temperature pyrometer. The resistivity of the samples, taken before and after the heating, was measured using a four point probe. RBS measurements using the RUMP simulation program determined the thickness and composition of the alloy. Glancing angle x-ray diffraction (XRD) measurements confirmed the phases of the alloy.

## **Results and Conclusions:**

Glancing angle x-ray diffraction, using Cu  $K\alpha$  particle radiation, at a wavelength of 1.54Å, rendered the preferential orientation for the alloy. An asymmetrical omega-two-theta scan was performed on the as-deposited and the 200 second annealed samples. JCPDS x-ray card number 04-0783 confirmed the defined Ag  $\langle 111 \rangle$  and  $\langle 220 \rangle$  peaks for both samples. Figure 1 shows that the Ag  $\langle 111 \rangle$  and  $\langle 220 \rangle$  peaks became narrow after annealing, suggesting that the alloy gained a better crystalline structure. We contributed the narrowing of the peak to be evident of the grain growth of the underlying silver layer.

RBS spectra, portrayed in Figure 2, showed an oxygen peak for the annealed sample only. RBS measurements showed that as the heating continued, the oxygen peak increased, indicating the formation of a thicker oxide layer. Figure 3 shows that as the heating time increased, the copper segregated to the surface of the alloy; also the front edge of the silver layer moved back, providing evidence that copper oxide formed on the surface of the alloy. By simulating the data using the RUMP program, we were able to determine how much copper remained in the alloy after annealing. Initially at 13% in the as-deposited sample, the copper decreased to 3% after 200 seconds of annealing. A more detailed analysis of the percent of residual copper per anneal time is detailed in Table 1.

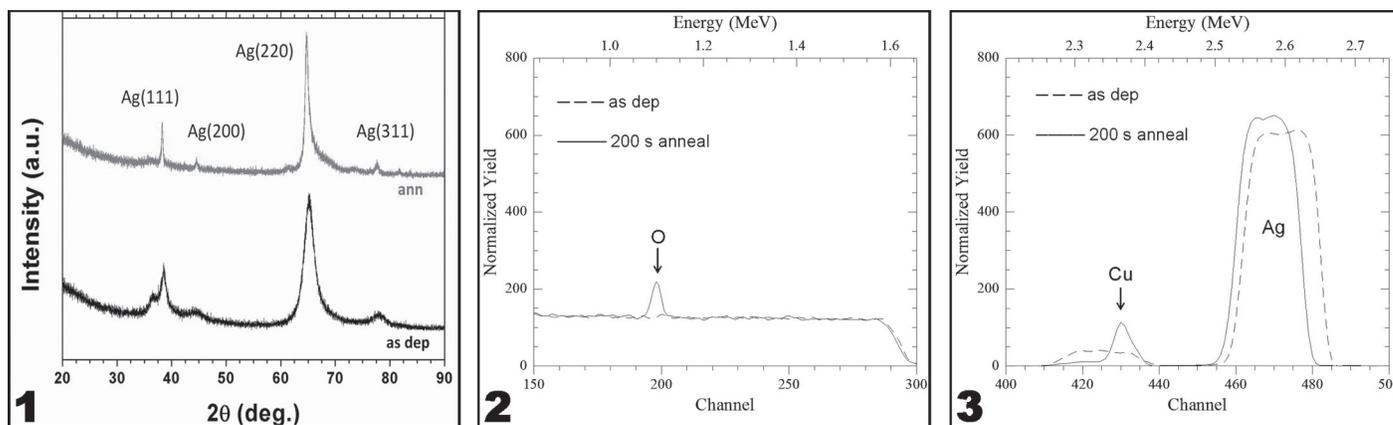


Figure 1, left: Glancing angle XRD measurements suggests the alloy's preferential orientation.

Figure 2, center: The RBS spectra for the as deposited and 200 second annealed samples highlighting the oxygen peak.

Figure 3, right: The RBS spectra for the as deposited and 200 second annealed samples highlighting the copper and silver peaks.

A four-point-probe was employed to measure the sheet resistance of the samples before and after heating. The sheet resistance decreased as the annealing time increased. Combined with the thickness measurements from RBS and RUMP simulations, the resistivity of each sample was approximated. The resistivity measurements, with respect to various anneal times is also described in Table 1. Since the newly formed copper oxide layer was considered to be an insulator, this decrease in resistivity can be attributed to the grain growth of the underlying silver layer. The grain size of both the as-deposited sample and the heated sample for 200 seconds were approximated using the Debye Scherrer Equation. It approximated that the grain size of the silver layer did increase from 39 nm to 111 nm.

Microwave annealing proved to be a sufficient method for annealing thin metal films. It promotes a processing technique that provides short processing times and efficiency. Ag(Cu) alloy structures at 13% percent copper, annealed at temperatures below 80°C for times ranging between zero to two minutes did prove to have enhanced electrical properties.

**Future Work:**

X-ray photoelectron spectroscopy measurements will determine whether a copper (I) oxide or copper (II) oxide formed on the surface of the alloy.

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**References:**

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Microwave Processing Time	Resistivity	% of Residual Cu
0 s	5.63 μΩ cm	13%
40 s	3.60 μΩ cm	9%
80 s	3.32 μΩ cm	6%
120 s	3.37 μΩ cm	3%
200 s	3.21 μΩ cm	3%

Table 1: As the heating time increases, the resistivity and the percent of residual copper decreases.