High Strength/ High Conductivity Copper Fabricated by Pulsed Electrodeposition

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Introduction

The most commonly used form of wiring in our current society is Copper wiring. The reason for this fact is that Copper is a metal that manages high conductivity at a fraction of the price of other metals such as silver. Because of the low resistivity of Copper, its application has spread to other processes that require high conductivity with a moderate amount of strength. The strength of Copper can also be increased by such methods as rolling and cold working which work defects into the material making it more resistant to plastic deformation but also creating blockage for conducting electrons. It is in this manner that strength is achieved at the expense of conductivity in the material. The challenge is then to find optimal conditions to maximize the strength of the material, while minimizing the effect on the conductivity. Using pulsed electrodeposition, several samples were produced under varying parameters and then measured for resistivity and hardness. Using the data collected, a conclusion can be made about which deposition parameters strike the best balance between the two properties and also be able to skew the material to be either highly conductive or high in strength.

Lattice defects introduced into a material can occur in several forms such as grain boundaries, point defects, dislocations, and twin boundaries. Both twin and grain

boundaries strengthen the material by effectively blocking and preventing the multiplication of dislocations throughout the material which lead to plastic deformation. While producing the same effect in terms of effective blockage of dislocations, the two types of defects differ in their effect on conducting electrons. Twin boundaries (or twins) have an electrical resistivity one order of magnitude lower than that of conventional Grain Boundaries[1]. Therefore, to produce a material that minimizes the tradeoff between strength and conductivity, the material must contain a high number of twin boundaries and a low number of grain boundaries.

Experimental Setup

While the mechanism of twin formation is not entirely understood, it has been shown that samples with a high density of twin defects were produced using the high deposition rates of pulsed electrodeposition. It is presumed that because of the unusually high deposition rates that can be achieved with a pulsed deposition, amplified by short on times and long off times, that a high density of twin boundaries form so as to lower the total interfacial energy[2]. It was using this approach that we hoped to produce pure Copper samples that have a high density of twin boundaries, increasing the strength of our material while having minimal effect on the resistivity.

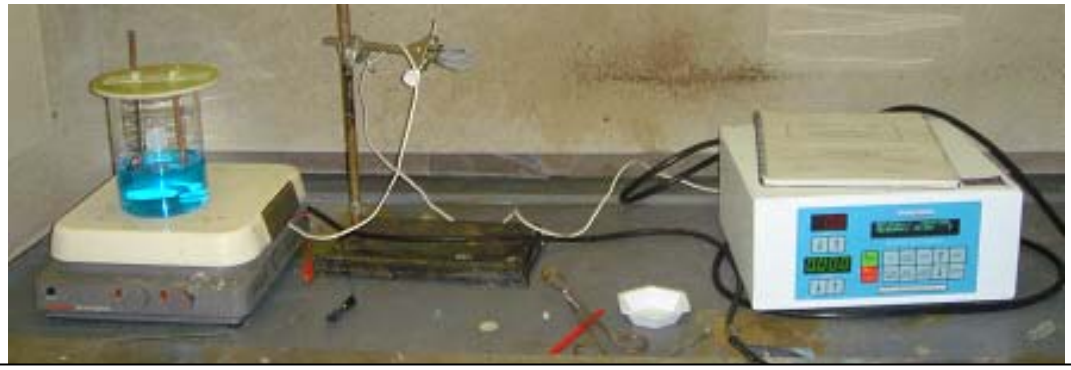


Figure 1- Experimental setup with power supply on right and electrolyte on stir plate

The method that we used to produce these samples was pulsed electrodeposition. This method differs from standard DC deposition in that the user can control specific ON and OFF times to periodically run the current. The method is usually used with very short ON times and long OFF times in order to allow for very high deposition rates during the short ON times[3]. Additionally, the user can control the current density for the ON time and thus control the deposition rate of the Copper onto the substrate. By using pulsed electrodeposition we attempted to optimize the strength and resistivity of the electrodeposited Copper.

To determine the effect of several factors on the deposition, 8 distinct samples were produced (See Table 1). The samples were identified using 3 parameters; electrolyte concentration, current density, and cathode substrate. The samples were all produced in varying concentrations of a Cupric Sulfate solution. The cathode and anode were spaced 30mm apart on a dish and connected to the power supply using Copper wiring. All samples were deposited for a total of 24 hrs and were submerged either 5 or 10 mm into the electrolyte solution for deposition. The prepared samples were then peeled off the substrates using a

Table 1

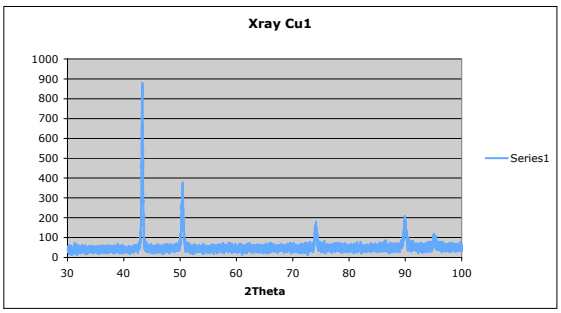
Sample #	Solution Conc.	Current	Substrate
1*	5 g/L	0.5 A/cm^2	Steel
2	28 g/L	0.5 A/cm^2	Steel
3	50 g/L	0.5 A/cm^2	Steel
4	28 g/L	1.0 A/cm^2	Steel
5	28 g/L	0.5 A/cm^2	Alloy
6	28 g/L	2.0 A/cm^2	Alloy
7	28 g/L	2.0 A/cm^2	Steel
8*	5 g/L	0.5 A/cm^2	Steel
9	28 g/L	1.5 A/cm^2	Steel

*Samples 1 and 8 are the same conditions

razor blade and washed in acetone for 15 min before being placed in a vacuum to prevent oxidation.

Sample Analysis

To determine the true composition of the deposited Cu samples, all of the samples underwent X-ray diffraction to see if they were in fact pure Copper. The results of the x-ray analysis could be visually grouped into two categories, showing a clear distinction between Copper deposited on steel vs. Copper deposited on the Co-Ni Alloy. The samples deposited on the steel showed a predominant peak at around 43 degrees (See figure 2) while the Copper deposited on the alloy exhibited a strong peak at around 73 degrees (see figure 3). The difference in peaks is indicative of the texture that was formed on the samples deposited on the Co-Ni alloy. The Copper deposited onto the alloy was stacked in the (110) direction as opposed to the Copper on steel, which was deposited in the (111) plane. All peaks exhibited in the samples were indicative of pure Copper samples and thus we deduced that the Copper produced was in fact pure Copper.



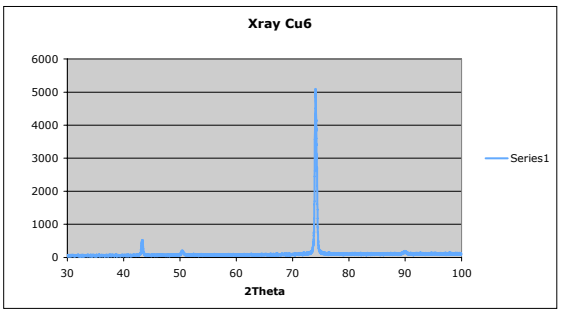


Figure 2- X-ray Analysis (Steel/ 5g/L / .5 A/cm^2) **Figure 3- X-ray Analysis (Alloy/ 5g/L / 2.0 A/cm^2)**

The hardness of the Copper produced was measured using the Vickers hardness measurement, which is determined by applying a square shaped diamond into the

material with an applied force of 120 kg and then measuring the area of the indentation, left by the diamond. By substituting the area of the indentation into the formula,

$$HV = 1.854\frac{F}{A}$$

Where F is the applied load and A is the area of the indentation, we can find the Vickers hardness.

The hardnesses of our samples ranged from 82.6 HV to 115.5 HV. (See Table 2) The hardness measurements represented an increase from regular annealed Copper that is generally measured at around 77 HV. The Copper samples produced on the Co-Ni alloy had consistently higher hardness values than similar samples deposited on the steel. The samples deposited on the alloy yielded hardness values of 102.8 and 115.8, whereas their steel counterparts yielded hardness values of 83 and 91.3 respectively. The samples

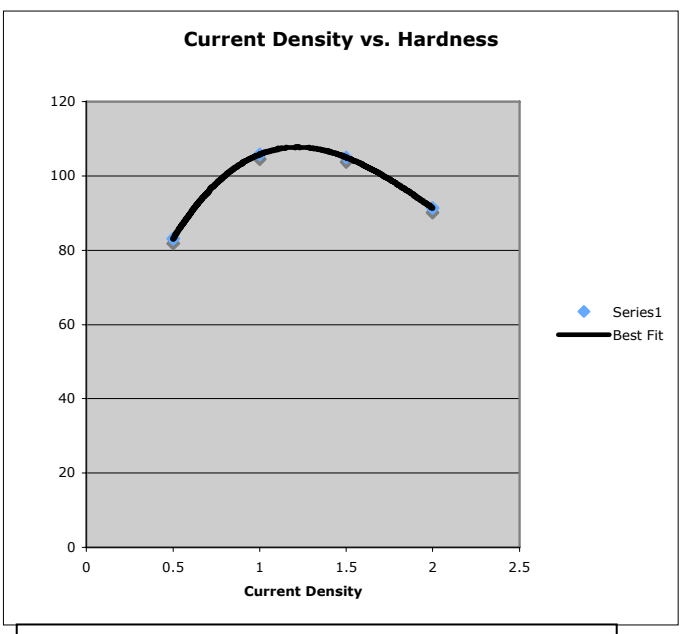


Figure 3- Plot showing Hardness vs. Current Density with a curve of best fit

Table 2

Sample #	Hardness (HV)
1	82.6
2	83
3	111.4
4	105.8
5	102.8
6	115.5
7	91.3
8	*
9	105

25%

harder than their steel counterparts which

corresponds well to the fact that the Co-Ni alloys were stronger than the steel to begin with. The substrate onto which the Copper was deposited had a noticeable effect on the mechanical properties of the Copper. Further work should be done on other types of substrates to better understand the relationship between substrate and Copper properties.

The resistance measurements for the samples were conducted using a 4 point setup on 3mm by 30mm strips of the Copper. The strips had two current wires attached on the ends and then two Ag coated Copper needles made contact in the middle of the sample. Then using 10 measurements taken from each sample, a line of best fit was graphed of Current vs. Voltage and the slope was used as the resistance and subsequently used to calculate the resistivity of the sample.

The resistivities of our samples ranged anywhere from 9.87×10^{-9} Ω ·m to 2.14×10^{-8} Ω ·m. There were two samples with measured resistivites below the Copper standard of 1.72×10^{-8} Ω ·m, however all other resistivities ranged between 1.81×10^{-8} Ω ·m and 2.14×10^{-8} Ω ·m, which more closely match predicted offsets from the standard resistivity for Copper (See Table 3). The samples were all measured at least twice using different lengths between the needles and on different areas of the sample producing similar results across the board. As table 3 shows, the least

Table 3

Sample #	Resistivity (Ω ·m)	% Offset*
2	1.8842×10^{-8}	16.42
3	2.0075×10^{-8}	28.75
4	2.1474×10^{-8}	42.74
5	2.0222×10^{-8}	30.22
6	9.9590×10^{-9}	-72.41
7	1.9540×10^{-8}	23.4
8	1.8178×10^{-8}	9.78
9	1.2517×10^{-8}	-46.83

*Based on copper standard of 1.72×10^{-8} Ω ·m [4]

amount of offset from standard Copper was about 10% (disregarding the two lower values) with a hardness of approximately 82.6 HV. In order to determine the tradeoff between hardness and resistivity, we created a ratio to account for unit hardness per Ω ·m.

Table 4

Sample #	Resistivity (Ω ·m)	Hardness (HV)	HV/(Res*10E7)
2	1.88E-08	83	44.05
3	2.01E-08	111.4	55.49
4	2.15E-08	105.8	49.27
5	2.02E-08	102.8	50.84
6	9.96E-09	115.5	115.98*
7	1.95E-08	91.3	46.72
8	1.82E-08	82.6	45.44
9	1.25E-08	105	83.89*

*Excluded pending further tests

We then defined this ratio as $R = \frac{HV}{\rho \times 10^7}$. Using the values calculated we found that sample 3 (Steel, 50 g/L, .5 A/cm^2) struck the best tradeoff balance hardness and conductivity (See Table 4). From this we can conclude that it is roughly somewhere around that deposition rate that the most hardness can be achieved while limiting the impact to resistivity.

Conclusions

Copper produced by pulsed electrodeposition yields higher hardness values than annealed Copper as well as minimal offset from the standard resistivity of Copper. While no work was done to determine the density of twin defects in the sample, it can be safely

assumed that twins did, to some extent form in the samples. Examining the rough curves created by the data, it can also be shown that there is an optimum deposition rate to maximize hardness and conductivity. Preliminary results using steel and a Co-Ni alloy hint at an effect that the substrate has on the strength and conductivity properties of the deposited Copper. Further work using different substrates is necessary in order to confirm a direct correlation between substrate and the properties of the deposited Copper. Visual examination of the samples using TEM will yield more specific information regarding the actually density of twin boundaries produced. In addition while hardness is a measure of strength, there are many other tensile tests that could be performed to provide a better idea of the true mechanical properties of the deposited Copper. Only then can a definite conclusion be made about the effectiveness of pulsed electrodeposition in the production of high strength and high conductivity Copper.

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