International Journal of Chemistry
http://www.ccsenet.org/ijc
Vol. 2, No. 1
February 2010

Studies on the Effect of Base Metal Composition in Pulse Plating of Silver over Silver Alloy

C.Shanthi (Corresponding author)
Department of Physics, Sona College of Technology
Salem 636005, Tamilnadu, India
Tel: 91-427-409-9791 E-mail: shanthi_rec@yahoo.co.in

S.Barathan
Department of Physics, Annamalai University
Annamalai nagar-608002, Tamilnadu, India
Tel: 91-414-422-2751 E-mail: sbarathan_au@rediffmail.com

R.M. Arunachalam
Department of Mechanical Engineering,
Sona College of Technology, Salem-636005, Tamilnadu, India
Tel: 91-427-409-9716 E-mail: arun_rm@yahoo.com

K.Karunakaran
Department of Chemistry, Sona College of Technology
Salem-636005, Tamilnadu, India
Tel: 91-427-409-9998 E-mail: drkk@sonatech.ac.in

The research is financed by All India Council for Technical Education (AICTE), New Delhi under the Research Promotion Scheme File No. 8023/BOR/RPS-145 /2006-07 and Sona College of Technology.

Abstract

This research attempt is made to study the effect of base metal composition in pulse plating of silver over silver alloy. The effect of pulse parameters due to the electro deposition of silver over 50% silver alloy is studied and the results are compared with the results obtained from the study of the effect of pulse parameters because of the electro deposition of 75% silver alloy. The surfaces are characterized by scanning electron microscopy and X-ray techniques. Higher the purity of silver, finer is the grain size. It is also evident that 75% silver alloy has more corrosion resistant than 50% silver alloy. It is suggested that the properties are improved in pulse plating if the concentration of silver in silver copper alloy is more.

Keywords: Pulse plating, Silver alloy, Deposition, Corrosion, X-ray techniques

1. Introduction

Pulse plating is becoming popular in the recent times because of its advantages in overcoming the problems of DC plating (Nasser Kanani, 2004). The pulse plating technique is found to be particularly an effective technique for the high quality silver coatings with minimal consumption of silver (Canning, W., 2005). Pulse plating can yield grain sizes less than 100 nm because of which the properties exhibited by nanostructured coatings (Erb, 1995) are quite different from conventional coatings (Frederick, 1966). Moreover, pulse plating is evolving as an advantageous process over many nano processing technique because of the potentially very large number of pure metals, alloys and composite materials (Low, *et al*., 2004) that can be electrodeposited with grain sizes less than 100nm (Kim, *et al*., 2004). Pulse plating improves hardness (Mohan, *et al*., 2005), wear resistance, microstructure and mechanical properties (Yong Choi, *et al*., 2003). Electrodeposition of single metals as well as alloys can be carried out with beneficial effects by this technique (Puippe, *et al*., 1986).The effect of DC plating parameters on the composition and morphology of silver copper alloy has been already dealt with and published in the article (Shanthi, *et al*.,2009). The effect of pulse parameters in electrodeposition of 75% silver with 25% copper alloy has been already discussed in the article published earlier (Shanthi, *et al*., 2008). As the number of variables combination is large in pulse plating, possible improvements in properties can be achieved by research work for specific application. Further, it is true for alloy plating as one more variable that is the concentration of the alloy metal, is involved. In the present study the base metal composition has been varied to 50% silver with 50% copper and the effects are studied by comparing the results obtained in 75% silver alloy to know the alloying behavior of the base metal.

2. Parameters Studied

Pulse plating of silver over silver alloy of composition 50% silver with 50% copper is studied for peak current densities of 4.013A/dm^2, 2.106 A/dm^2, 1.338 A/dm^2 and 1.070 A/dm^2 under a constant average current density 0.803 A/dm^2 with a real time of 120 seconds in a suitable bath composition (Shanthi, *et al*., 2008). The cathode is weighed before and after electroplating. Theoretical, experimental thickness and current efficiency are calculated. This result is compared with the results obtained (Shanthi, *et al*., 2008) in the pulse plating of 75% silver alloy under constant average current density of 0.803 A/dm^2 and 1.873 A/dm^2. The surface roughness is estimated using surface roughness tester (surftest211) and the reflectance is measured with a specimen area 1.315 dm^2 using Novo glass 60^0 universal medium glassometer (ASTM D523/02457) with Novosoft QA software and the values are recorded. The optimum current density is 1.444 A/dm^2 above which the quality of the deposit is not significant for 50% silver alloy. This current density is optimum to compare the results obtained for 75 and 50% silver alloy. To show the effect of frequency on surface roughness, three frequencies (25, 50 and 100 Hz) at higher duty cycle (80%) are chosen. The lower end of the duty cycle is chosen to study the surface roughness and the reflectance effect with duty cycle. From the studies conducted (Shanthi, *et al*., 2008), it is found that the deposit quality is good at 60% duty cycle and 10 Hz frequency and hence this parameter is also chosen for the study of surface roughness and reflectance. Table 1 shows the measurement of surface roughness and reflectance for 75% silver alloy with a peak current density 1.444 A/dm^2.

3. Results and discussion

3.1 Effect of current density

Samples from two different compositions namely 50% and 75% silver alloy (Shanthi, *et al*., 2008), have been analyzed. In the Silver-copper alloy, the surface morphology is influenced by current density, silver concentration in the bath and the type of current applied. The increase of current density has improved the amount of weight electrodeposited. Therefore, the thickness of the silver deposit also increases. Experimentally, it is determined that the peak current density for minimum time and maximum deposition as 4.013 A/dm^2 for 50% silver alloy and 4.815 A/dm^2 for 75% silver alloy for a specimen size of 0.7dm × 0.25dm. The current efficiency is found to be maximum for a peak current density 1.07 A/dm^2 for 50% silver alloy at a duty cycle of 60% and 10 Hz frequency. In the case of 75% silver alloy, the current efficiency is maximum for a peak current density 3.2 A/dm^2 at a duty cycle of 60% and 10 Hz frequency. It is found that the concentration of silver in silver alloy has an effect in the weight electrodeposited over cathode in pulse plating. The weight electrodeposited in 75% silver alloy is more than that in 50% silver alloy for the same constant average current density 0.803 A/dm^2. This may be attributed to the low resistance and high conductivity of 75% silver alloy when compared with 50% silver alloy. As the weight electrodeposited is more in 75% silver alloy, the experimental thickness and efficiency will also be more in 75% silver alloy when compared to 50% silver alloy. In 50% silver alloy, burnt deposits are formed when peak current density exceeds 4.0 A/dm^2 for a specimen size of 0.7 dm × 0.25 dm whereas in 75% silver alloy, burnt deposits are formed when peak current density exceeds 5 A/dm^2. Therefore, it is observed that when the purity of silver is high, the specimen withstands high peak current density without the formation of burnt deposit.

3.2 Porosity and Grain size

Figure 1 shows the SEM micrograph for 20% duty cycle, 10Hz frequency for 50% silver with 50% copper alloy for an average current density 0.803 A/dm^2. It is observed that the porosity is more in 50% silver alloy. The average grain size is calculated by Debye Scherrer equation using XRD pattern as shown in figures 2 and 3. The average grain size for 20% duty cycle, 10 Hz frequency and average current density 0.803 A/dm^2 is 101nm and 32 nm for 50% and 75% silver alloy respectively. Hence, it is found that the grain size is finer for 75% silver alloy when compared to 50% silver alloy. The average grain size is also calculated for 80% duty cycle, 25 Hz frequency and average current density 0.856 A/dm^2 as around 57 nm for 50% silver alloy and the grain size for 75% silver alloy for the same duty cycle and frequency with slightly higher peak current density as 48 nm.

3.3 Surface roughness and reflectance

From the measurement obtained for surface roughness and reflectance, it is observed that the deposits are almost smooth for higher duty cycle with lower frequency and for lower duty cycle with higher frequency. But the surface roughness value is lower for higher duty cycle and lower frequency when compared to lower duty cycle and higher frequency. Specular reflectance decreases with increase in surface roughness. The reflectance value is high for higher duty cycle and lower frequency when compared to higher duty cycle with higher frequency and lower duty cycle with higher frequency. The surface roughness value is higher for lower duty cycle with lower frequency and hence the reflectance value is minimum for lower duty cycle and lower frequency.

3.4 Corrosion Study

The corrosion study of the silver alloy is made using salt spray apparatus (ASTM B 117). The salt spray test is the exposure of the surface coating to a fine mist containing 5 % of sodium chloride for a given time at room temperature. The constant temperature maintained within the chamber is 50^0C and the test duration is one hour and two hours for the specimen area 0.3738dm^2. The onset value indicates the minimum time required for the tarnishing effect to start. The onset of blackish brown oxide formation on the sample takes 4 minutes for pulse plating (80% duty cycle and 25 Hz frequency) until tarnishing of the silver alloy is first evident. The coating has been consumed by the corrosion reaction and the corrosion of the base metal begins. It is also evident that 75% silver alloy has more corrosion resistant than 50% silver alloy as the weight loss and hence the loss in thickness is found. This is due to more corrosion in 50% silver alloy than 75% silver alloy. It is also observed that for 75% silver alloy, 60% duty cycle and 10 Hz frequency has less weight and the loss in thickness is also less when compared to 80% duty cycle, 25 Hz frequency whereas this effect is dominant in 80% duty cycle, 25 Hz frequency for 50% silver alloy.

4. Conclusion

Based on the studies conducted on pulse plating of silver over silver alloy for two different compositions namely 75% silver with 25% copper and 50% silver with 50% copper, it is found that the concentration of silver in the cathode plays a major role in deciding the amount of silver deposited on the cathode. It is observed that the amount of silver deposited, thickness of the deposit and the current efficiency are more for 75% silver alloy than for 50% silver alloy for the same current and voltage settings. The current density above 4.0 A/dm^2 for 50% silver alloy and 5.0 A/dm^2 for 75% silver alloy leads to burnt deposits. The 75% silver alloy can withstand more current density than 50% silver alloy. When 50% silver is subjected to higher peak current density of 5.0 A/dm^2, the current efficiency decreases to a large extent due to the formation of burnt deposit on the specimen and the hardness also increases. It is suggested that the properties are improved in pulse plating if the concentration of silver in silver copper alloy is more. Higher the purity of silver, finer will be the grain size. The surface roughness is minimum for higher duty cycle and lower frequency and it is maximum for lower duty cycle and lower frequency. The reflectance and the brightness of the specimen are greater for higher duty cycle and lower frequency. It is also evident that 75% silver alloy has more corrosion resistant than 50% silver alloy.

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Table 1. Measurement of Surface Roughness and Reflectance for 75 and 50% Silver alloy with a peak current density 1.444 A/dm^2

Parameter settings		Composition of the silver alloy			
		75% silver with 25% copper		50% silver with 50% copper	
Duty Cycle (%)	Frequency (Hz)	Average roughness value µm	Reflectance @ 60 ^{0} (G.U.)	Average roughness value µm	Reflectance @ 60^0 (G.U.)
80	25	0.27	443	0.26	296
80	50	0.32	217	0.37	194
80	100	0.35	172	0.41	132
60	10	0.19	494	0.31	245
20	10	0.52	123	0.61	112
20	100	0.39	247	0.48	224

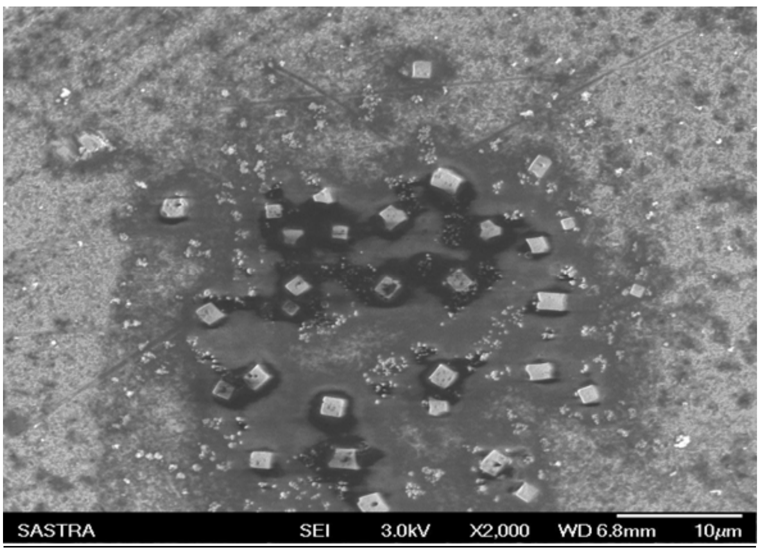

Figure 1. SEM picture for 20% duty cycle, 10Hz frequency for 50% silver with 50% copper alloy for an average current density 0.803 A/dm^2

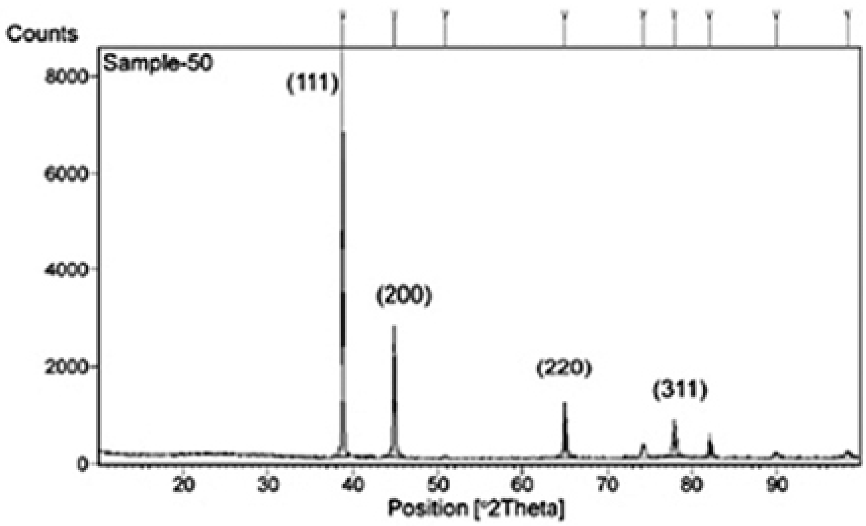

Figure 2. XRD pattern for 20% duty cycle, 10Hz frequency for an average current density 0.803 A/dm^2 for 50% silver with 50% copper alloy

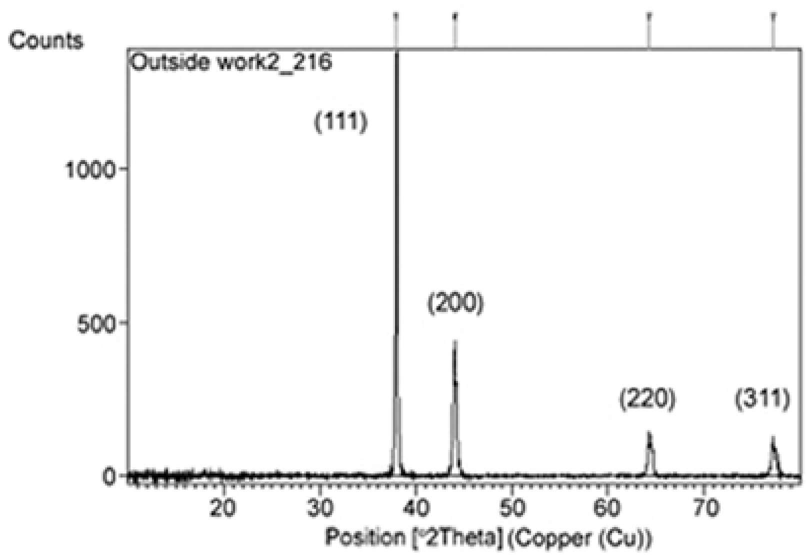

Figure 3. XRD pattern for 20% duty cycle and 10 Hz frequency for an average current density of $0.803A/dm^2$ for 75% silver with 25% copper alloy