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The effect of pulse parameters in electro deposition of silver alloy

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ABSTRACT

Pulsed electro deposition of silver alloy is aimed at the improvement of some properties like finer grain size, hardness, anti-tarnishing, lower porosity, improvement in surface property. The pulsed electro deposition of silver alloy has been analyzed from an alkaline cyanide bath with brightener. Pulse duty cycles of 20% to 80%, at frequencies 10 Hz, 25 Hz, 50 Hz and 100 Hz with peak current densities ranging from 1 A/dm^2 to 9.3 A/dm^2 are employed. The influences of pulse duty cycle, peak current density and pulse frequency on the thickness, hardness of silver deposit, and current efficiency of the plating process are studied. Good quality deposits (less porosity and fine grains) can be obtained at lower peak current density and higher duty cycle.

1. Introduction

Traditional method of electro deposition is DC plating. This has been modified by the use of current interruption or even current reversal termed as pulsed electro deposition. In DC plating, only the current or potential can be varied [1]. However, in pulse plating many variables such as pulse duration, pulse duty cycle and pulse current exist [2]. A major limitation of the electrodeposits produced by direct current is porosity and rough deposits [3]. Pulse plating improves the deposit properties viz., porosity, ductility, hardness, electrical conductivity plating thickness distribution, finer grain size and anti-tarnishing property. Pulsed electro deposition of silver is aimed at the improvement of some properties that is not achievable in DC plating like finer grain size improvement, hardness, anti-tarnishing [4], lower porosity, improvement in the life of the coating, immense saving in the consumption of the raw material and improvement in surface property. Pulse plating seems to be predestined for precious metal electro deposition where the higher equipment costs may be outweighed by substantial savings in metal consumption and higher quality deposits [5–7].

In the present study, a systematic investigation of silver deposition from an alkaline silver cyanide bath has been undertaken with the application of square wave pulse current. The influences of pulse conditions on thickness, hardness of silver deposit, current efficiency of the plating process have been studied.

2. Experimental

A silver alloy of composition 75% pure silver and 25% copper is used as the test coupon [7]. The test coupon size is 70 mm × 25 mm × 1.7 mm. Prior to plating, the surface of the test coupon is cleaned with acid pickling and polished in a vibrator polisher and hand brushed and finally cleaned with tap water [8]. An electrolyte consisting of 120 g of potassium cyanide per litre with metal content 35 g/l, potassium carbonate 100 g/l and the brightener potassium thio sulphate with the pH value 12.28 are used [9–11]. Silver deposits on the cathode silver alloy (test coupon) which undergoes a displacement of 87.5 mm/s. The anode employed is an annealed pure silver (99.99%). Pulse duty cycles of 20% to 80%, at frequencies 10 Hz, 25 Hz, 50 Hz and 100 Hz with peak current densities ranging from 1 A/dm^2 to 9.3 A/dm^2 are employed as shown in Table 1. The influences of pulse duty cycle, peak current density and pulse frequency on the thickness, hardness of silver deposit and current efficiency of the plating process are studied. The experiments are carried out with a constant time of 120 s.

3. Results and discussion

3.1. Effect of pulse duty cycle

3.1.1. Influence on thickness of the silver deposits obtained at various frequencies

As the pulse duty cycle increases, thickness of the silver deposit also increases for constant average current of 0.3 A and 0.7 A. As the duty cycle increases, current on-time increases and off-time decreases. At a lower duty cycle, the peak current is flowing for

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Table 1
Pulse parameters used for pulse plating of silver alloy

Duty cycle %	Pulse frequency/Hz and pulse on–off time/ms				Current density/A/dm^{-2}	
	10	25	50	100	Peak	Average
20	20–80	8–32	4–16	2–8	9.36, 4.01	0.803, 1.873
40	40–60	16–24	8–12	4–6	4.68, 2.00	0.803, 1.873
60	60–40	24–16	12–8	6–4	3.13, 1.34	0.803, 1.873
80	80–20	32–8	16–4	8–2	2.34, 1.00	0.803, 1.873

less time and hence the overall amount of deposition is lesser than that obtained at higher duty cycle. At very high duty cycles and at high frequencies the pulse current is very low. Therefore, a reduced thickness is obtained. As frequency increases, thickness of silver deposit reduces. A maximum thickness of the deposit is obtained at a duty cycle of 60% and frequency of 10 Hz and peak current density of 3.13 A/dm^2.

3.1.2. Influence on current efficiency

It has been found that current efficiency of silver plating increases slightly as pulse duty cycle increases from 40% to 60% as can be seen from Fig. 1. However, an increase from 60% to 80% duty cycle results in slight decrease in the current efficiency. This may be attributed to the evolution of hydrogen at cathode during plating. Maximum current efficiency has been observed at 60% duty cycle and frequency of 10 Hz at a peak current density of 3.13 A/dm^2. The current efficiency is lower at higher frequencies.

3.1.3. Influence on hardness

The hardness of the silver deposit has been found to increase with increase in duty cycle. A maximum hardness value is obtained at 80% duty cycle and 100 Hz at a constant current density of 1.873 A/dm^2. At lower pulse duty cycle, a higher peak current is passed and this produces a powdery or burnt deposit with poor adhesion and considerable porosity. This porosity leads to a decrease in hardness of the deposit. However, at higher duty cycles, the peak current is lower almost nearing the optimum average current resulting in the formation of a smooth fine grained deposit. Improved surface coverage with denser build-up of grains is to be expected.

3.2. Effect of pulse frequency

3.2.1. Influence on thickness

As frequency increases, the thickness of silver deposit decreases in general. Maximum thickness is obtained at a frequency of 10 Hz and a duty cycle of 60%. As frequency increases, the on-time decreases and so thickness of the deposit also decreases.

3.2.2. Influence on current efficiency

As frequency increases, the current efficiency almost decreases. In most cases, the maximum current efficiency is obtained at 60% duty cycle. This may be due to the effect that as frequency increases, the on-time decreases and also during short pulses a very thin pulsating diffusion layer is formed which makes the transport and diffusion of metal ions from bulk electrolyte to the cathode surface difficult.

3.2.3. Influence on hardness

It is observed that as pulse frequency increases the hardness is also found to increase. During short pulses at higher frequency, a very thin pulsating diffusion layer has been formed leading to an enhanced nucleation rate and surface coverage with denser building up of fine grained deposits [12]. This leads to lower porosity and correspondingly higher hardness values. Maximum hardness is obtained at a frequency of 100 Hz for the current density of 1.873 A/dm^2.

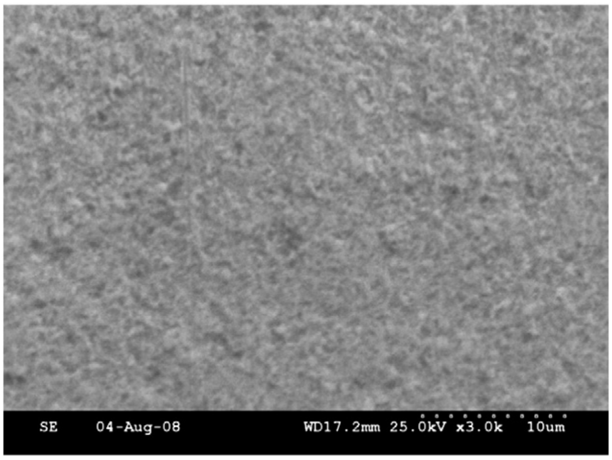

Fig. 2. SEM micrograph of silver deposit obtained at 60% duty cycle and 10 Hz frequency for a peak current density of 3.13 A/dm^2.

3.3. Effect of average current density

For an average current density of 0.8026 A/dm^2 and 1.873 A/dm^2, the current efficiency and thickness of silver deposit is maximum at 60% duty cycle and 10 Hz frequency. As average current density increases, thickness of the silver deposit also increases. For an average current density of 1.873 A/dm^2 and 20% duty cycle, the sample has a burnt appearance. Good quality deposits are mostly obtained at an average current density of 1.873 A/dm^2 and higher duty cycles.

3.4. Effect of peak current density

As duty cycle increases, the peak current density decreases. Current efficiency and thickness of the silver deposit is maximum for a peak current density of 3.13 A/dm^2 for 60% duty cycle at 10 Hz frequency. Higher peak current density especially at lower duty cycle produces burnt deposits with poor adhesion and considerable porosity resulting in lower hardness [13]. The highest peak current density beyond which burnt deposits formed is 4.815 A/dm^2.

3.5. Scanning electron microscope (SEM) analysis

The surface morphology and porosity of the silver deposit formed by pulse plating are studied by SEM analysis. On analyzing the two microstructures shown in Figs. 2 and 3, it is found that the silver deposit formed by pulse plating at 60% duty cycle and 10 Hz has less number of pores compared to that formed at 40% duty cycle and 100 Hz frequency. Also the grain size formed at higher duty cycle and lower frequency is finer than that formed at lower duty cycle and higher frequency.

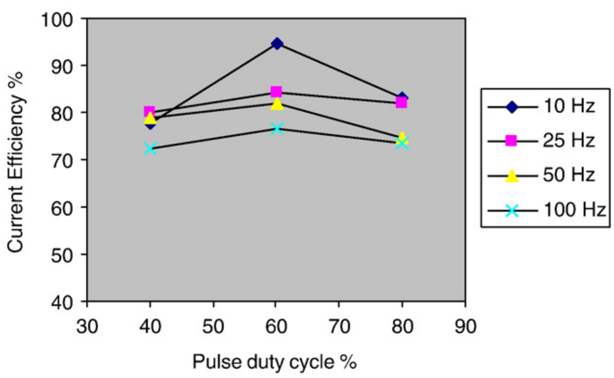

Fig. 1. Effect of pulse duty cycle on current efficiency (I_{av}=0.7 A).

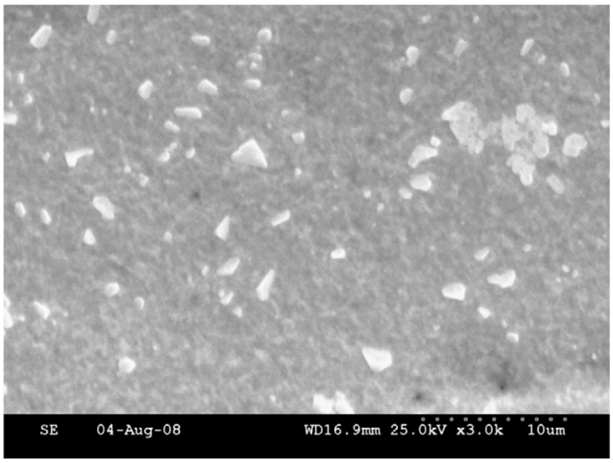

Fig. 3. SEM micrograph of silver deposit obtained at 40% duty cycle and 100 Hz frequency for a peak current density of 4.6816 A/dm^2.

4. Conclusion

The influence of pulse duty cycle, pulse frequency, peak current density and average current density on the thickness of the deposits, current efficiency and hardness have been studied. From the data obtained, the following conclusions are made:

1. Good quality deposits (less porosity and fine grains) can be obtained at lower peak current density and higher duty cycle. For example, good quality deposit has been obtained at 60% duty cycle and 10 Hz frequency for a peak current density of 3.13 A/dm^2.
2. Poor quality deposits are generally obtained at higher peak current density. Burn deposits are obtained at 20% duty cycle and 10 Hz frequency for a peak current density of 9.3633 A/dm^2.

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