# Effect of pulse parameter on pulsed electrodeposition of copper on stainless steel

**A. Balasubramanian, D. S. Srikumar, G. Raja, G. Saravanan and S. Mohan***

The pulsed electrodeposition of copper on stainless steel has been studied in copper sulphate bath and the effect of duty cycle and frequency on the thickness and current efficiencies were compared at 50°C and at room temperature with average current density of 4 A $dm^{-2}$. A new strike bath based on cupric chloride and hydrochloric acid was developed for the first time. The Cu coatings were characterised by SEM, AFM and XRD. Crystallite sizes of Cu coatings were calculated for various duty cycles from the Scherer's equation. The deposits were smaller nodules and fine grained.

**Keywords:** Pulsed electrodeposition, On time, Off time, Duty cycle, Grain size

## Introduction

Pulsed current electrodeposition[1–3] has received much attention in recent years in order to improve the mechanical, chemical and electronic properties of deposits. The advantages of pulse platting are numerous, such as the reduction of porosity,[4–8] fine grained deposits[9–11] and low electrical resistance.[12–15] In pulse plating, an interrupted current or potential is used. The current may or may not drop to zero between pulses. Three parameters are independently variable in practical pulse plating: pulse peak current, on time and off time, which determine the physical characteristics of the deposits obtained from the given electrolyte. The surface of stainless steel is resistant to a wide variety of corrosive elements. Stainless steel differs from carbon steel in the amount of chromium present. Carbon steel rusts when exposed to air and moisture. This iron oxide film is active and accelerates corrosion by forming more iron oxide. Stainless steel has sufficient amount of chromium present so that a passive film of chromium oxide forms which prevents further corrosion. This is due to the presence of a thin transparent film of oxides which reappears after it has been stripped off or penetrated. This film not only protects the metal against attack by corrosive agents but also prevents adhesion of electrodeposits. Once this film has been removed and prevented from reforming, any of the common metals can be electroplated on stainless steel. Various techniques for electroplating stainless steel have been recommended. Perhaps the method most commonly used in industry to prepare the metal for electroplating is wood's nickel strike. But the nickel strike has got the following drawbacks: nickel is costly; there is a passivation problem, that is, after nickel strike, immediately the substrate has to be transferred to subsequent electroplating. If there is a time delay, nickel will get passivated and further plating is not possible, resulting in nonreliability of copper adhesion on the nickel strike. With high rate of rejection, any defects in the strike are visible. In view of these drawbacks, the authors have developed a new strike bath based on cupric chloride and hydrochloric acid. Copper is preferred from the point of good thermal conductivity, cost and ease of plating. Copper is one of the metals most extensively used in industry, either because of its intrinsic properties or as a base for further formation of metallic deposition. Copper is gradually replacing metals like aluminium in microelectronics industry as an interconnect and via system. There are advantages in using acid based sulphate bath. The benefits are: uniformity in strength, relatively fast deposition, and lower cost and toxicity. Electroplated copper is used as coating on utensils for their heat resistance. Electrodeposition is one of the methods most generally employed to obtain metallic deposition of adequate thickness, porosity free structure and good adhesion. Electrodeposited copper have been widely investigated with respect to their morphological characteristics,[16,17] electrical properties, corrosion resistance[18–21] and thermal resistance. By controlling variables such as current density, applied current signal, temperature, bath composition, etc., a variety of films with different characteristics can be achieved. Copper is thus a versatile material for various applications in industries.[22–24]

In the present work, a systematic investigation of copper deposition on stainless steel from a copper sulphate bath had been undertaken with the application of square wave pulse current and direct current.

## Experimental

An electrolyte made up of 200 g $L^{-1}$ $CuSO_4.5H_2O$ and 100 g $L^{-1}$ $H_2SO_4$ was prepared. Before that, the copper strike with thickness of 3 μm was given using solution consisting of 10 g $L^{-1}$ cupric chloride and 100 mL HCl (3·23M). Generally, it is difficult to deposit metal on stainless steel owing to surface oxide layer on the base

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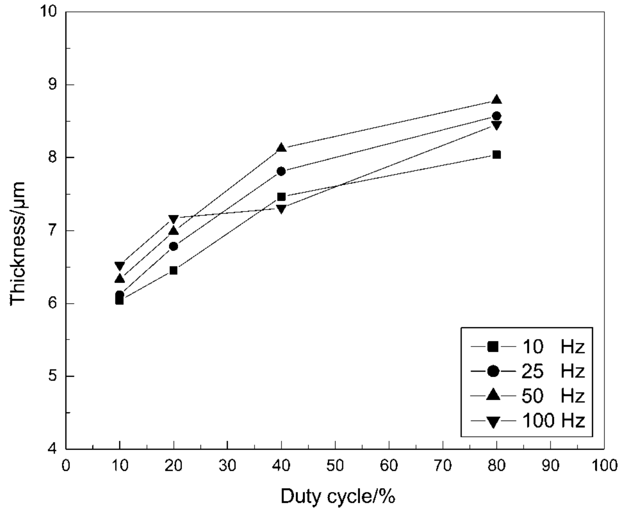
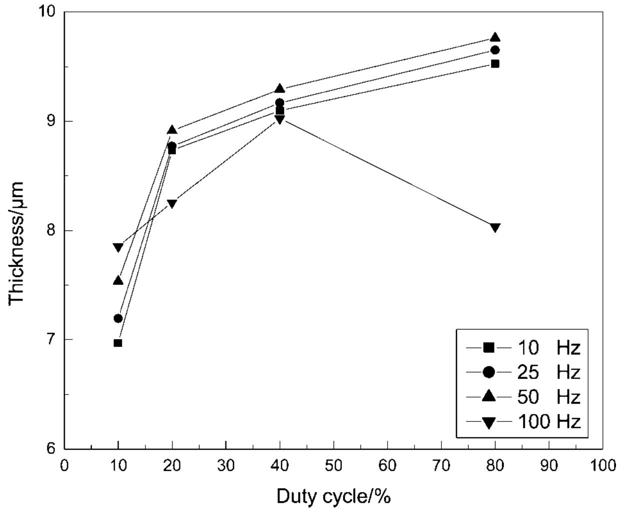
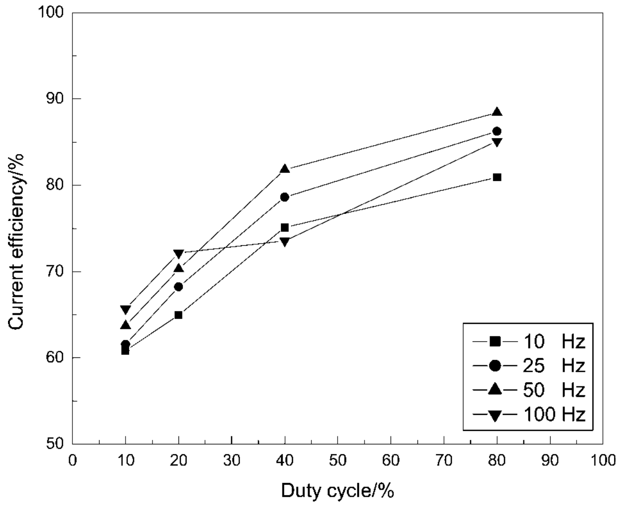


**1 Effect of duty cycle at various frequencies on thickness of copper deposit at room temperature**



**2 Effect of duty cycle at various frequencies on thickness of copper deposit at 50°C**



**3 Effect of duty cycle at various frequencies on current efficiency of copper deposit at room temperature**

metal. Hence, copper strike was carried out by pulse plating in order to remove the surface oxide layer as well as to improve the adhesion of copper on stainless steel. Deposition of copper was on stainless steel cathode along with copper as an anode. The deposition was carried out using pulse conditions. The pulse current operations were carried out at room temperature and 50°C. Pulse plating was carried out using Dynatronix (USA) DPR20-10-5 Model. The averages current density was set at 4 A dm$^{-2}$. Pulse plating parameters were given in Table 1.[6]

## Results and discussion

### Effect of duty cycle on thickness of Cu deposits

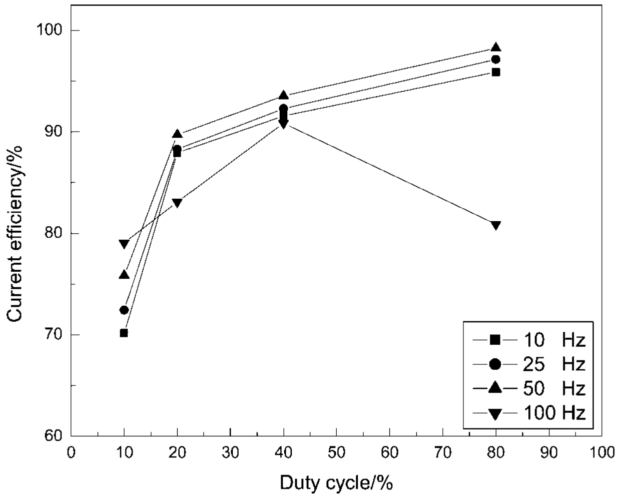
Figures 1 and 2 show the effect of pulse duty cycle on the thickness of Cu deposits obtained for both room temperature and 50°C at average current density 4 A dm$^{-2}$. From these figures, it is observed that the thickness of the copper deposit increased with increasing pulse duty cycle. As the duty cycle increases, current on time increases and off time decreases. At a lower duty cycle, the peak current is flowing for a short time and so the overall amount of deposition is less than for a higher duty cycle. The maximum thicknesses of 8 and 9 μm were obtained at 80% duty cycle for moderate pulse frequencies (25 and 50 Hz) at room temperature and 50°C respectively. The increasing thickness at 50°C is due to increasing rate of deposition.

### Effect of pulse duty cycle on current efficiency of Cu deposits

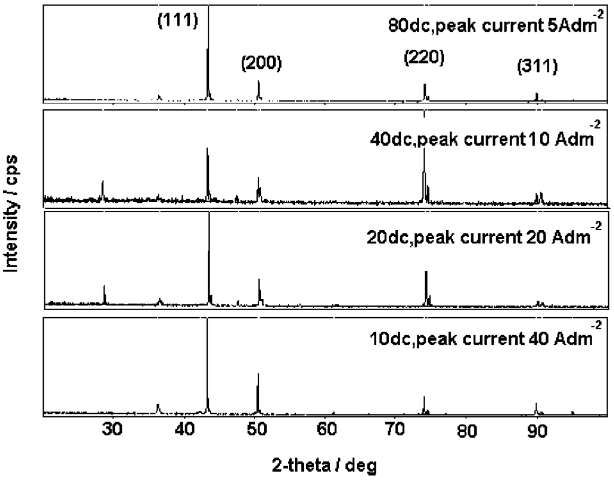
Figures 3 and 4 show the effect of pulse duty cycle on current efficiency of Cu deposits obtained for both room temperature and 50°C at average current density 4 A dm$^{-2}$. The maximum current efficiencies of 85 and 95% are obtained at 80% duty cycle for moderate pulse frequencies (25 and 50 Hz) at room temperature and 50°C respectively. As pulse frequency increases, the pulses are very short and they produce very thin pulse diffusion layers. Thus transport and diffusion of metal ions from bulk electrolyte to the cathode surface through these layers are possible and much easier than through the thick diffusion layers, which are obtained at larger pulses. At higher frequencies (100 Hz) hydrogen evolution was favoured, leading to a reduction in current efficiency. So at 80% duty cycle at moderate

**Table 1 Pulse parameters used for pulse plating of copper**

| | Pulse on–off time, ms | | | | Current density, A dm$^{-2}$ | |
|---|---|---|---|---|---|---|
| Duty cycle, % | 10 Hz | 25 Hz | 50 Hz | 100 Hz | Peak | Average |
| 10 | 10–90 | 4–36 | 2–18 | 1–9 | 40 | 4 |
| 20 | 20–80 | 8–32 | 4–16 | 2–8 | 20 | 4 |
| 40 | 40–60 | 16–24 | 8–12 | 4–6 | 10 | 4 |
| 80 | 80–20 | 32–8 | 16–4 | 8–2 | 05 | 4 |



**4 Effect of pulse duty cycle at various frequencies on current efficiency of copper deposit at 50°C**



**6 XRD pattern of pulse electrodeposited copper for different duty cycles on stainless steel**

pulse frequencies, enhancement of migration of ions increases the nucleation rate, uniformity of deposit,[25,26] deposition rate, and hence, current efficiency is increased. Increasing current efficiency at higher temperature is due to enhancement of the rate and migration of ions.

## Morphology of copper deposit

### *Scanning electron microscopic studies*

The surface morphology of copper electrodeposit was significantly changed by pulse current. The SEM images of copper electrodeposits obtained from pulsed current plating were shown in Fig. 5. In the PC deposition, the peak current density is higher than average current density, leading to decreased grain size with particle size of copper 3 and 8 μm at room temperature and 50°C respectively. The decreased porosity and denser packed surface are due to the desorption of hydrogen during the off time of pulse cycle.

### *X-ray diffraction studies*

The deposit crystallographic structures were determined by means of XRD. Figure 6 shows XRD patterns of deposited copper by electroplating. In order to analyse the structure of deposits with crystalline structure, their XRD patterns were compared with the JCPDS cards. It can be seen that there are four peaks at 2θ, 43·24, 50·37, 74·05 and 89·88, corresponding to Cu(111), (200), (220) and (311) respectively in XRD patterns of Fig. 6. And it indicates that there exists a crystal structure substance.

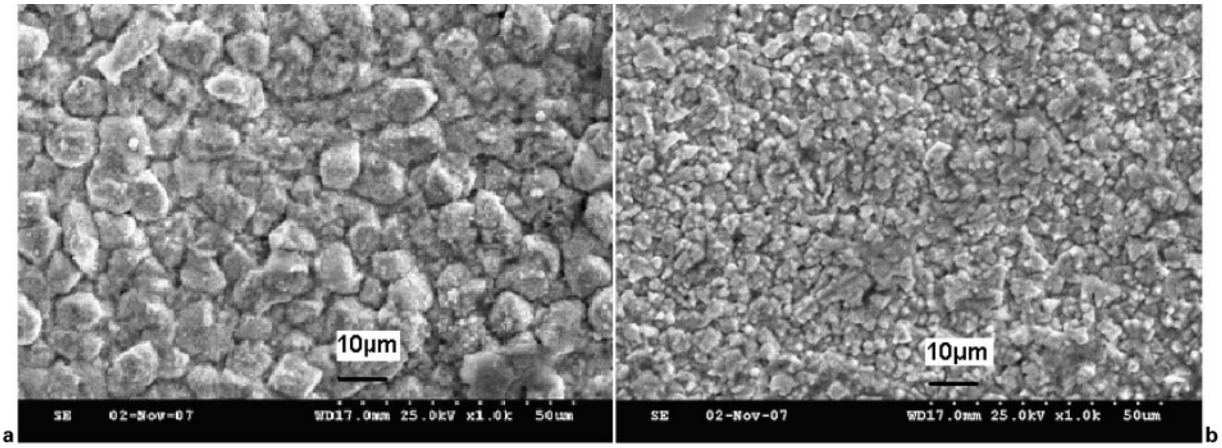
The crystallite sizes of Cu coatings were calculated from the Scherer's equation

$$D=\frac{0{\cdot}94\lambda}{\beta\cos\theta} \tag{1}$$

where $D$ is the grain size, $\beta$ is the full width at half maximum (FWHM) of the diffraction peak, $\lambda$ is the wavelength of the incidental X-ray (1·54 Å) and θ is the diffraction angle. Based on equation (1), the crystallite sizes were calculated and given in Table 2.

## Conclusion

Cu coatings with good adhesion were electrodeposited on stainless steel from sulphate bath. Pulse plating was carried out at different duty cycles and the effects of pulse parameters were compared both at room temperature and at 50°C. For pulse plating, the influences of pulse duty cycle and pulse frequency on the thickness and current efficiency of copper deposited were studied. From the authors' experimentations for copper deposition at 4 A dm$^{-2}$ for pulse plating, it was found that at 80% duty cycle and 50 Hz, a maximum thickness and current efficiency were given at 50°C.



**5 SEM images of pulsed electrodeposited copper on Stainless steel at *a* room temperature and *b* 50°C**

**Table 2 Crystallite sizes of copper deposits at different duty cycles from XRD patterns**

| | Crystallite size, nm | | | |
|---|---|---|---|---|
| *hkl* | 10% duty cycle | 20% duty cycle | 40% duty cycle | 80% duty cycle |
| 111 | 93·10 | 93·13 | 58·19 | 93·14 |
| 200 | 95·64 | 95·68 | 79·71 | 79·74 |
| 220 | 108·4 | 90·40 | 90·37 | 90·41 |
| 311 | 101·9 | 50·9 | 76·44 | 76·47 |

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