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Optimising Electroless Copper Plating Parameters on Insulative Substrate for Enhanced Efficiency and Quality

Yuyin Gan,[1] Jun Du Ong,[1] Swee Kah Lee,[2] Tatt Wai Wan[3] and Siew Chun Low[1*]

[1]School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
14300 Nibong Tebal, Pulau Pinang, Malaysia
[2]Infineon Technologies (Malaysia) Sdn. Bhd., Free Trade Zone, Batu Berendam,
75350 Melaka, Malaysia
[3]Infineon Technologies (Kulim) Sdn. Bhd., Infineon Plant, Jalan A7, Kulim Hi-Tech,
09000 Kulim, Kedah, Malaysia

[*]Corresponding author: chsclow@usm.my

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ABSTRACT: *The operating parameters of electroless copper plating significantly dictate the deposition rate and the quality of the metal layer deposited on the substrate surface. This study investigates the impact of pH and temperature on electroless copper plating on an insulative substrate, pioneering a departure from the conventional metal-based substrate. Varied pH levels (12, 12.5, 13) at a constant 70°C and adjusted temperatures (60°C, 70°C, 80°C) using the optimal pH were explored. Optimal conditions were found to be a pH of 12.5 and 70°C, yielding a deposition rate of 0.758 mg/hr and a surface roughness of 0.422 μm. Despite a 17.34% reduction in deposition rate compared to 60°C, 70°C offered superior surface coverage and minimised roughness. X-ray diffraction (XRD) confirmed high copper purity and minimal oxide presence at 70°C. Nanoindentation revealed peak hardness (1.173 GPa) and low elastic modulus (13.35 GPa) at this temperature, reflecting a compact copper grain structure. These findings establish an optimum parameter set for efficient electroless copper plating on a non-metal substrate, enhancing both process efficacy and reliability.*

Keywords: electroless plating, insulative substrate, deposition rate, roughness, copper

1. INTRODUCTION

Electroless plating is a fundamental technique used in various industries to uniformly deposit metal layers on insulative substrates without the need for electrical currents. Among the array of metals used, copper (Cu) is notable for its affordable conductivity, making it a staple in the microelectronic domain for tasks such as interconnects and packaging.[1,2] Particularly in shielding against electromagnetic interference (EMI), electroless Cu plating on insulative substrates plays a vital role. The insulative substrate is crucial in providing essential electrical insulation and effective thermal management. This allows for efficient heat dissipation, addressing local heat accumulation and ensuring reliable device operation. Additionally, the substrate acts as a protective layer against moisture and heat, offering corrosion resistance, design flexibility, lightweight characteristics and cost-effectiveness. However, managing bath solutions and maintaining precise control over operating parameters are significant challenges that are critical for achieving a consistent deposition rate and quality.[3]

The electroless Cu plating bath consists of metal ions, a complexing agent and a reducing agent. Cu ions serve as the metal source, while the complexing agent, functioning as a chelating ligand, fosters stability by forming intricate complexes with cupric ions Cu^{2+} at elevated pH levels, thus preventing the precipitation of Cu (II) hydroxide [$Cu(OH)_2$]. The reducing agent facilitates electron donation for the reduction process. The plating mechanism unfolds via the reduction of Cu^{2+} coupled with the oxidation of the reducing agent.[4] Utilising glyoxylic acid (GA) as the reducing agent yields the following overall reaction:

$$Cu^{2+} + 2CHOCOOH + 4OH^{-} \rightarrow Cu^{0} + 2HC_2O_4^{-} + 2H_2O + H_2\uparrow \qquad (1)$$

Temperature exerts a profound influence on ion activity and growth kinetics, thereby intricately impacting both the rate and quality of deposition.[5,6] Likewise, pH is a crucial factor affecting bath stability, reducing agent efficacy, Cu nuclei formation and Cu^{2+} disproportionation dynamics.[7] Understanding the interaction between temperature and pH is crucial for achieving high-speed electroless Cu plating. However, there remains a significant gap in research addressing their combined effects. Inadequate control over these parameters bears the potential for substantial issues, including non-uniform thickness, elevated surface roughness and compromised interface adhesion. Bragaglia et al. used statistical analysis to optimise the processing parameters for electroless Cu plating on a carbon-epoxy substrate, focusing on pH, temperature and the concentrations of the complexing and reducing agents.[4] They identified temperature and reducing agent concentration as key factors affecting morphology, adhesion and electrical resistance of the plating. This study builds on previous findings by providing a detailed analysis of how optimising operating parameters (pH and temperature) affects the quality and performance of electroless Cu plating on an insulative substrate. It identifies specific optimal values for pH and temperature and examines material properties, including deposition rate, surface roughness, material purity and mechanical strength.

In contrast to conventional approaches that isolate the effects of individual operating parameters, this study systematically explores the synergistic impact of temperature and pH on electroless Cu plating on an insulative substrate. By adjusting pH levels at a constant temperature and fine-tuning temperatures at an optimised pH, this research aims to identify the precise conditions for maximal deposition rates and superior quality. The focus is on enhancing surface smoothness, material integrity and mechanical robustness of the Cu layer. The findings provide valuable insights to improve the efficacy and reliability of the plating process by effectively calibrating these key operating parameters.

2. EXPERIMENTAL

2.1 Electroless Plating

In the formulation of the electroless Cu plating bath, Cu sulphate $CuSO_4$, ethylenediaminetetraacetic acid (EDTA), and glyoxylic acid (GA) are key constituents obtained from Sigma-Aldrich. To adjust the pH, 30% w/v potassium hydroxide is added gradually. The insulative substrate (with an active area of 24 mm^2) underwent surface activation using a circuit patterning technique.[8] This laser activation method facilitates selective surface metallisation to bolster adhesion properties by forming microscopic roughness. After substrate preparation, the plating process unfolds with the bath solution heated for 10 min per layer, amounting to a cumulative total of six layers, at predefined study temperatures. pH modulation spans the range of 12, 12.5 and 13, while temperature exploration encompasses 60°C, 70°C and 80°C, with the optimal pH derived from preceding experiments serving as the reference point for temperature investigations. A pH range of 12–13 is selected to achieve optimal deposition rates while ensuring bath stability. Temperatures from 60°C to 80°C were investigated to systematically assess their influence on plating quality and material properties, starting with an optimal baseline at 60°C.[4]

2.2 Characterisations

The deposition rate was quantified by measuring the mass of Cu deposited per hour. Surface roughness and morphology were evaluated using a laser confocal scanning microscope (Zeiss LSM 700 MAT with Axio Imager.Z2 Vario). Surface morphology characterisation and visual assessments were performed with a Hitachi Tabletop Microscope TM3000. The crystalline structure of the deposited Cu was analysed via X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with a CuKα radiation source, scanning at 0.1°/s over a 2θ range of 10°–100°. Mechanical properties, including hardness and Young's modulus, were assessed using nanoindentation. This involved a Micro Materials Nano Test Platform 3 equipped with a diamond indenter, applying a load of 10 mN, with loading and unloading rates of 1 mN/s, and a holding time of 2 s.

3. RESULTS AND DISCUSSION

This study examines the combined impact of pH and temperature on electroless Cu deposition on an insulative substrate. Experiments were first conducted at a constant temperature of 70°C, exploring pH values of 12, 12.5 and 13. The results, shown in Figure 1(A), indicate that the Cu deposition rate increased significantly with pH, from 0.109 mg/hr at pH 12 to 0.758 mg/hr at pH 12.5 and peaking at 7.928 mg/hr at pH 13. This trend is attributed to the higher concentration of hydroxide ions (OH^-) at elevated pH levels, which enhances the deprotonation and catalytic oxidation of the reducing agent, as supported by the studies of Jayalakshmi et al. and Huang et al.[1,9] The significant increase in deposition rate from pH 12.5 to pH 13 is attributed to the exponential behaviour of reaction kinetics. As the pH increases from 12.5 to 13, the concentration of OH^- rises exponentially. This elevated OH^- concentration at pH 13 enhances the Cu reduction process, resulting in a substantially higher deposition rate. However, despite the high reaction rate at pH 13, the resulting poor plating quality is characterised by increased surface roughness, oxidation and potential interface delamination. The dark colouration observed at pH 13 indicates high surface roughness, which increases Cu oxidation by providing more active sites. The resultant formation of cuprous oxide (Cu_2O) and cupric oxide (CuO) due to prolonged exposure to the plating bath weakens the interfacial adhesion strength, leading to potential delamination, especially under thermal cycling and mechanical stress.[10,11] This situation can cause short circuits and connection failures during packaging fabrication.[12]

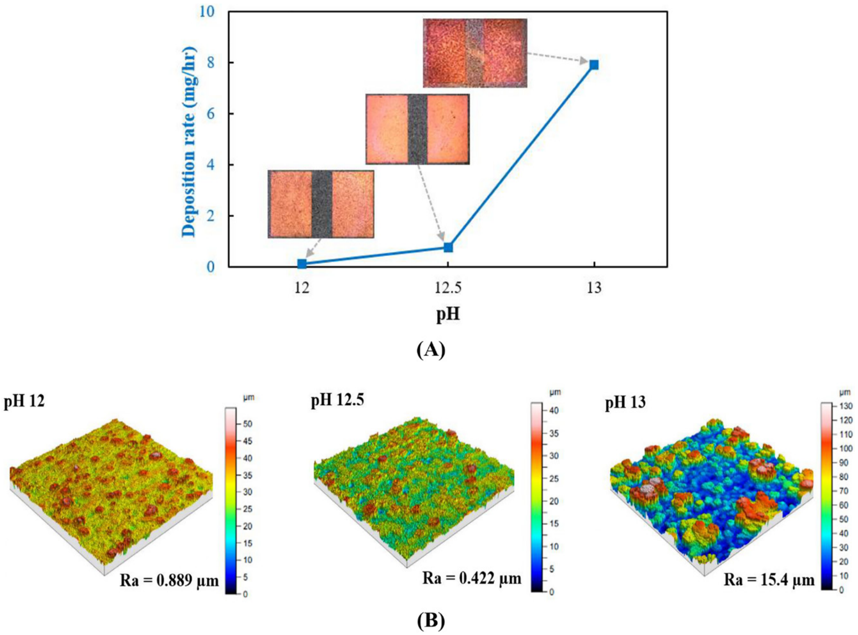


Figure 1: (A) Deposition rates and (B) 3D surface morphology of deposited Cu with activate area of 24 mm² at different pH levels.

Conversely, pH 12.5 not only achieves a higher deposition rate than pH 12 but also significantly improves plating quality. As illustrated in Figure 1(B), the surface roughness at pH 12.5 is minimised to 0.422 µm, compared to 0.889 µm at pH 12 and 15.4 µm at pH 13. Surface profile analyses reveal unevenness at pH 12, pronounced peaks and valleys at pH 13, and minimal height variation at pH 12.5. The increased surface roughness observed at pH 12, compared to pH 12.5, is attributed to the lower deposition rate and insufficient Cu coverage, resulting in an irregular surface morphology. At pH 12.5, the enhanced deposition rate facilitates a more uniform and smoother surface, as the plating process effectively fills gaps and voids. Conversely, at pH 13, the accelerated reaction kinetics induce substantial hydrogen evolution, which disrupts the plating process and results in pronounced surface roughness characterised by distinct peaks and valleys. Given that high surface roughness can lead to poor adhesion, pH 12.5 is identified as the optimal condition, striking a balance between deposition rate and plating quality.[10,11]

The operating temperature plays a critical role in influencing the deposition rate and quality of Cu on an insulative substrate. This study, using an optimal pH of 12.5 identified previously, examined the effects of various temperatures (60°C, 70°C and 80°C) on Cu deposition. Ideally, higher temperatures are expected to enhance deposition rates due to increased kinetic energy and collision frequency, which facilitate the reduction process and promote larger Cu grain formation.[1,13] Contrary to expectations, an inverse relationship between temperature and deposition rate was observed, aligning with findings by Liang et al., who noted a peak deposition rate at 60°C, decreasing as temperatures increased to 85°C.[14] As illustrated in Figure 2, the highest deposition rate was recorded at 60°C, measuring 0.917 mg/hr. At 80°C, the deposition rate decreased by 58.78%. Scanning electron microscopy (SEM) images in Figure 2 show full Cu coverage at 60°C, diminishing at 70°C and significantly reduced at 80°C.

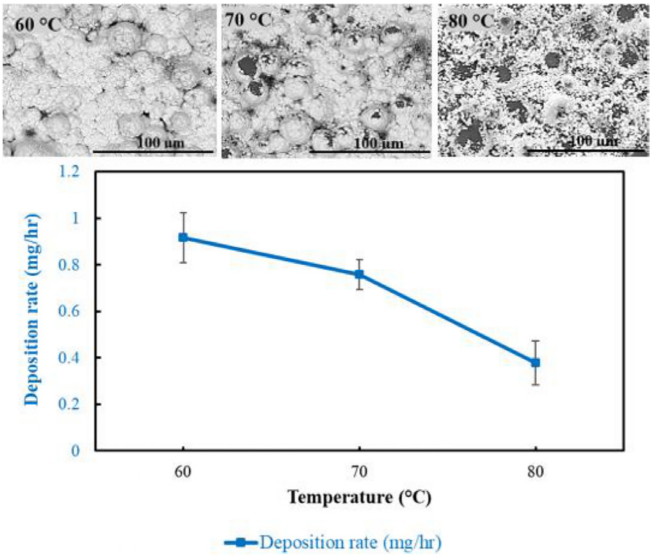


Figure 2: Deposition rate of Cu deposited on insulative substrate at different temperatures.

The decrease in deposition rate at higher temperature is attributed to the accelerated Cannizzaro reaction, which leads to the degradation of the reducing agent (glyoxylic acid) into by-products such as oxalate and glycolate ions. Consequently, a significant proportion of the reducing agent was consumed in this side reaction, decreasing its availability for the primary reduction reaction and resulting in less Cu being deposited on the substrate surface. Additionally, incomplete oxidation of Cu^{2+} ions result in the formation of cuprous ions (Cu^+), which can further convert into Cu_2O under alkaline conditions. This by-product undermines bath stability and may revert to Cu^{2+} and OH^-, as shown in reactions (2) and (3).[15] The increased ionic nature of the bath solution at higher temperatures potentially leads to these reversible reactions, generating more. Interestingly, at 60°C, large grains with a well-compacted structure were observed, whereas at 80°C, smaller grain sizes indicated a decrease in structural compactness and plating efficiency. It is hypothesised that rapid nucleation at higher temperatures limits the growth period for Cu seeds, resulting in finer grains and less effective plating.

$$2Cu^{+} + 2OH^{-} \leftrightarrow 2\,(CuOH) \leftrightarrow Cu_2O + H_2O \tag{2}$$

$$Cu_2O + O + 2H_2O \leftrightarrow 2Cu^{2+} + 4OH^{-} \tag{3}$$

The XRD patterns in Figure 3(A) display characteristic peaks for pure Cu at orientations (111), (200), (220) and (311) across the tested temperatures of 60°C, 70°C and 80°C. Peaks corresponding to CuO at orientations (002) and (200), as well as Cu_2O at (110) and (200), are also observed.[16] Notably, at 80°C, the intensity of the Cu peaks is reduced compared to those at 60°C and 70°C, suggesting an increased presence of oxides at higher temperatures. This is corroborated by the slightly higher intensity of CuO and Cu_2O peaks at 80°C, indicating more impurities, which can detrimentally affect conductivity.[17] Conversely, the 70°C condition shows the highest intensity for pure Cu, indicating optimal conditions for maintaining Cu purity.

The 2D surface profile in Figure 3(B) reveals large grains at 60°C and smaller grains at 80°C, consistent with SEM observations in Figure 2. Typically, smaller grains result in a more compact and homogeneous surface, theoretically leading to smoother textures and lower roughness, which enhance mechanical strength and mitigate delamination. However, at 80°C, despite the smaller grains, the highest surface roughness (0.757 µm) is observed, likely due to an unstable roughness profile with continuous height fluctuations, as depicted in Figure 3(B). Upon closer examination, the 2D profile and roughness morphology reveal that the large grains at 60°C result in higher surface roughness (0.713 µm), nearly equivalent to that at 80°C, due to variations in height structure. The medium grains at 70°C, however, provide the smoothest surface texture with the lowest roughness of 0.422 µm, making 70°C the optimal temperature for electroless Cu plating. This temperature balance ensures high Cu purity, minimal impurities and superior surface morphology, enhancing the overall quality and reliability of the Cu layer.

Nanoindentation analysis was employed to assess the mechanical robustness of the deposited Cu. Figure 4(A) delineates the load-displacement curves, where the loading curve indicates Cu's hardness, with a steeper slope reflecting higher hardness, and the unloading curve represents the elastic modulus, with a steeper slope indicating a higher modulus.[18] As shown in Figure 4(A), the steepest loading curve at 70°C suggests maximum hardness, while the steepest unloading curve at 60°C indicates the highest elastic modulus. The maximum hardness value of 1.173 GPa was observed at 70°C, showing increases of 29.67% and 58.03% compared to values at 80°C and 60°C, respectively [Figure 4(B)]. This enhancement can be attributed to the smaller grain size and higher compactness at 70°C, which reduce voids and porosity. The presence of pure Cu with minimal oxides at 70°C further enhances hardness, as metallic bonds in pure Cu provide superior mechanical properties compared to the brittle ionic and covalent bonds in Cu oxides.

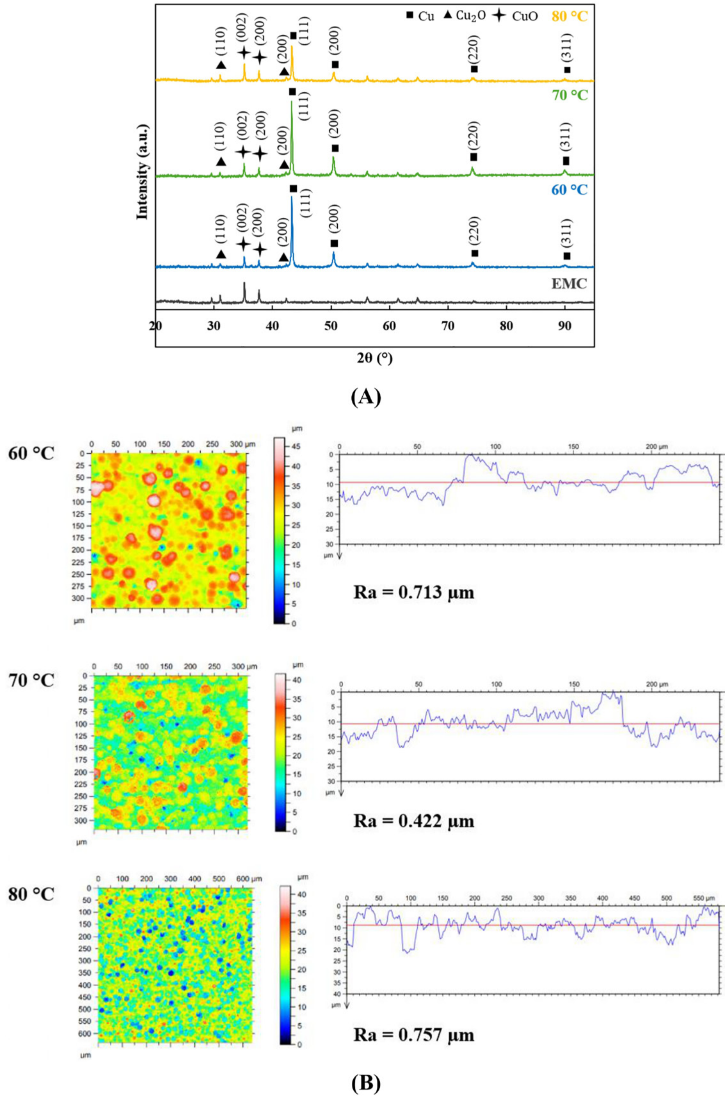
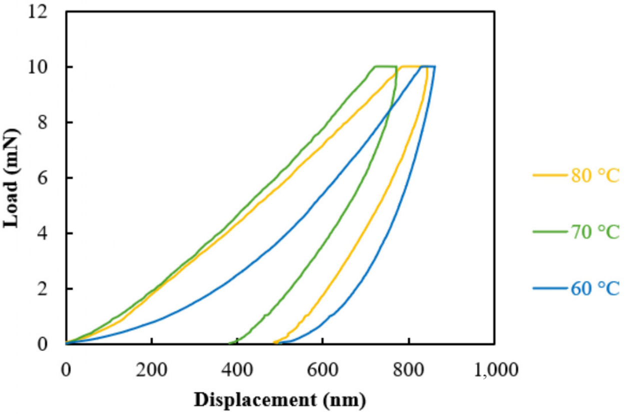
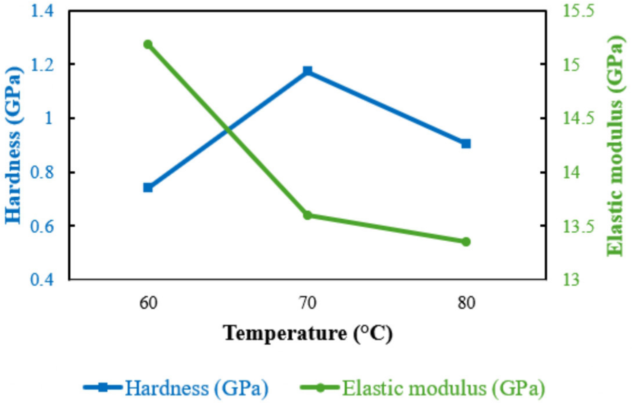


Figure 3: (A) XRD patterns and (B) 2D surface and roughness profiles of Cu deposited at 60°C, 70°C and 80°C.



(A)



(B)

Figure 4: (A) Load-displacement plots and (B) hardness and elastic modulus measurements of Cu deposited at 60°C, 70°C and 80°C.

Despite the smaller grains at 80°C, low coverage and a loose grain arrangement weaken the mechanical strength. Hardness is critical in determining the Cu layer's resistance to deformation under operational loads. High hardness reduces the risk of fractures under thermal and mechanical stress, addressing key failure causes and reliability concerns in microelectronic applications.[18] Additionally, high ductility is crucial for the Cu layer to withstand thermal cycles during fabrication, which is inversely related to the elastic modulus. The minimum elastic modulus was 13.354 GPa at 80°C, with increases of 1.84% and 13.67% at 70°C and 60°C, respectively [Figure 4(B)]. The relatively low modulus at 70°C indicates high ductility, enhancing reliability and mechanical performance. Thus, the optimal temperature for electroless Cu plating is 70°C, as it provides a combination of high Cu purity, low surface roughness, high hardness and favourable ductility. These properties collectively ensure deformation resistance and mechanical stability, making 70°C the preferred temperature for achieving high-quality Cu deposits in microelectronic applications.

4. CONCLUSION

A comprehensive analysis of the operating parameters, specifically temperature and pH, affecting electroless Cu plating on an insulative substrate was conducted. This study examined the influence of these parameters on deposition rate, surface roughness, material purity and mechanical robustness of the deposited Cu layer. Through systematic experimental characterisation, the optimal pH was identified as 12.5, and the optimal temperature as 70°C. A pH of 12.5 achieved a high deposition rate and low surface roughness, while higher pH levels, although increasing the deposition rate, led to over-deposition and compromised surface quality. The optimal temperature of 70°C provided superior material purity, minimal roughness and robust mechanical strength. Optimising these operating parameters is crucial for enhancing the efficiency and reliability of the electroless Cu plating process on an insulative substrate in microelectronic applications.

5. ACKNOWLEDGEMENTS

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