

Corrective Estimation of Copper Deposition Density onto Stainless Steel Substrate by Electroplating

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Abstract

Deposition patterns and density calculation of the copper (Cu) electroplating from CuSO₄ solution onto stainless steel substrate were studied in order to gain better understanding of the relationship between correlated structures and their properties. Square non-porous stainless steel disks (316L SS), having a dimension of 1×1 cm, with a thickness of 1 mm, were used as the substrate. The electroplating system consisted of a Cu bar as the anode and 25 wt% CuSO₄ plating solution. A potential of 2.0 volts was applied for the Cu plating at room temperature. The amount of the deposited Cu was determined by measurement of its weight increment. Layer thickness was obtained from the Scanning Electron Microscope (SEM) micrograph analysis. Density estimation of the deposited Cu was calculated from the mass difference and volume of plated layer, as described. Total Cu atoms using Faraday's equation was used to obtain the theoretical density estimation. The density gradually decreased with the increasing thickness, suggesting that the Cu atoms deposited onto the growing nucleation were less packed at a longer period of plating time. Additionally, the rate of thickness increasing was higher over a longer time. It is believed that void formation was presented in the later state of the coagulation, in which complexity in nucleation growth occurred.

Keywords: Copper electroplating, deposition density, density estimation, amorphous, stainless steel substrate

Introduction

Incorporation of Cu in the formation of palladium-based alloy membranes has resulted in improved resistance towards rich sulfur environments that would deteriorate the separation performance of the membranes utilized in hydrogen enriching applications [1-3]. Among various techniques, the electroplating of Cu onto foreign substrates to form multi-layer deposition has found to be efficient and has become more economically viable, since the process is relatively uncomplicated [4]. However, understanding of the plating mechanism and its controlling factors is of interest, in order to achieve uniform thickness and obtain the preferred properties. Grujicic *et al.* [5] reported the nucleation mechanism of the Cu electroplating deposition on the substrate, in which the individual nuclei are formed and eventually coalesce with each other to form a continuous Cu film. The coalescence process is initiated at the wafer edge and propagates toward the wafer center with a constant current density that is proportional with the plated area on the wafer [4-6]. Several studies have extensively investigated Cu

nucleation on various substrates [7-11]. Typically, the uniformity of the electroplating depends on various parameters, including the substrate resistance and the electrolyte compositions. A study on nucleation and coalescence simulation by Willey and West suggested that the coalescence thickness greatly affects the macroscopic uniformity of the deposited film, and is directly correlated with the nucleus density [12]. Coalescence thickness variation along the distance from the contact can occur due to the non-uniform potential distribution on the resistive substrate. Qiao and West proposed that the Cu film formation on a substrate involves the following mechanism: (a) nucleation, (b) nucleus growth, (c) start of coalescence, and (d) film formation [4]. The amount of the deposited Cu is proportionally related to the electrical current applied between the electrodes and the plating time that allows diffusion to take place resulting in increasing thickness as the coalescence process proceeds. Theoretical density calculation is based on the thickness and the amount of deposited Cu atoms as described above. However, the actual densities are always observed to be lower than the calculated values. It is worth noting that coalescence plays an important role in controlling the deposition process. To achieve the desired thickness and uniformity of the Cu layer, the structure of the deposited layer and its properties should be well understood. The correlation between the thickness and the density would allow more precise composition control of the deposited elements in a sequential multilayer membrane preparation process. In this work, the mechanism of electroplating of the Cu was investigated by observing the deposition propagation of the Cu onto the substrate. The amount of the deposited Cu was determined by weighing the electrode before and after the plating.

Materials and methods

Materials and chemicals

- 1) Non-porous 316L stainless steel sheet
- 2) Sodium carbonate (Na_2CO_3), Carlo Erba, Lab grade
- 3) Sodium hydroxide (NaOH), Carlo Erba, Lab grade
- 4) Sodium Phosphate Dodecahydrate $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, Carlo Erba, Lab grade
- 5) Copper (II) sulphate (CuSO_4), Ajex finechem, AR grade
- 6) Isopropanol ($(\text{CH}_3)_2\text{CHOH}$, 99.5%, Merck

Non-porous stainless steel disks (316L SS), cut into 1×1 cm square shapes with 1 mm thickness, were used as a substrate. Prior to the plating process, SS disks were ultrasonically cleaned in an alkaline solution consisting of 0.12 M $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 0.61 M Na_2CO_3 , 1.13 M NaOH , and 5 g/L detergent at 60 °C for 1 h. Then, the pre-washed disks were washed thoroughly 3 times with deionized water until the rinsing water had a pH of 7. Finally, the disks were immersed in isopropanol and dried at 120 °C for 3 h. Copper plating used a Cu bar as an anode and 25 wt% CuSO_4 plating solution to selectively plate the Cu onto the substrates. Polishing and cleansing of the Cu bar electrodes were carefully done several times using distilled water, with the electrodes allowed to air dry. The Cu plating was operated at room temperature and at 2.0 volts for 30 - 180 sec. A distance of 2.0 cm was maintained between the working anode in 50 ml plating solution. Copper was plated onto both sides of the SS substrate. A representative schematic of the Cu electroplating is presented in **Figure 1**.

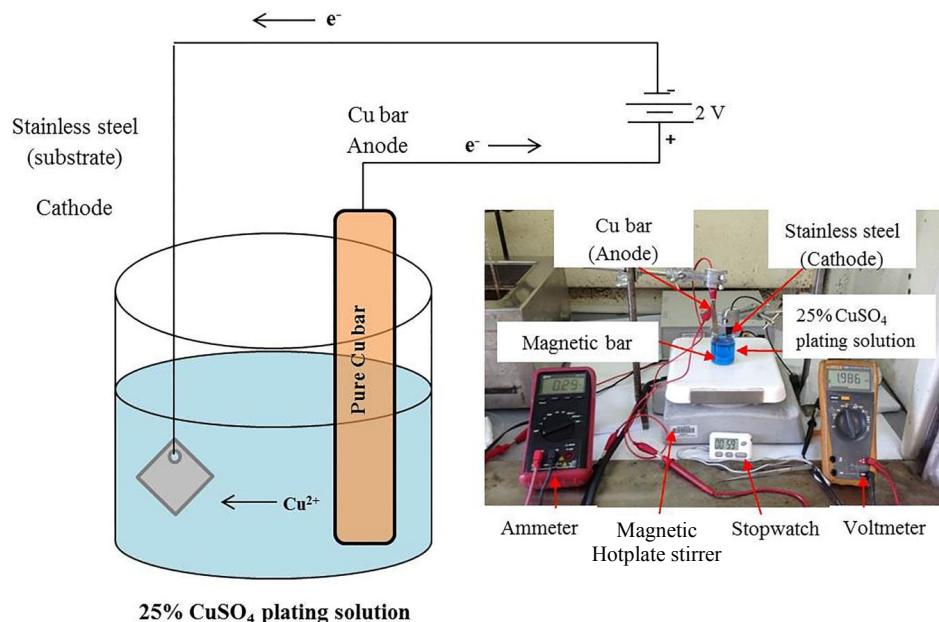


Figure 1 Schematic of Cu electroplating.

After the deposition of Cu, the substrate was immediately immersed in 0.01 M HCl, in order to neutralize any residual plating solution, followed by rinsing with deionized water and ethanol to facilitate drying and prevent oxidation of the Cu layer.

The amount of the deposited Cu was determined by weighing the electrode before and after the plating. The total electrical charge, or number of coulombs passed during the plating, can be calculated by using the formula, $Q = \int I dt$, where Q is the charge in coulombs, I is the average current in amperes, and t is the plating time in seconds. From the coulombs of charge that pass through the cell, the numbers of Cu can be theoretically calculated with Faraday's equation, as per the following Eq. (1).

$$\text{Total Cu atom (atoms)} = \frac{\left(I \left(\frac{C}{sec} \right) \times t (sec) \right)}{2 \left(\frac{\text{electrons}}{\text{Cu ion}} \right) \times (1.6 \times 10^{-19}) \left(\frac{C}{electron} \right)}, \quad (1)$$

where I is average current and t is plating time.

On the other hand, it can be also calculated from the increment in SS plate, as per the following Eq. (2);

$$\text{Total Cu atom (atoms)} = \frac{(W_1 - W_0)(g) \times 6.022 \times 10^{23} \left(\frac{ion}{molCu} \right)}{63.546 \left(\frac{g}{molCu} \right)}, \quad (2)$$

where W_1 is plated stainless steel weight and W_0 is original stainless steel weight.

The thickness of the Cu layer was obtained from the SEM micrograph analysis, in which the distance from the substrate surface to the out rim was averaged out using 5 points measurement along the layer length. The density of the deposited Cu was calculated from the mass difference and the volume of plated layer (width × length × thickness).

The Cu thickness measurement was performed using a scanning electron microscope (SEM), JEOL model JSM-5800LV. For the cross-sectional analysis, the samples were prepared by mounting with phenolic resin powder, curing at 180 °C and applying 30 kN of compression force in a Smithells II mounting press, then grinding with silicon carbide paper of 300, 600, 800, 1200, and 200 grit and polishing on a Metaserv 2000 grinder-polisher with a suspension of 3 µm grade diamonds.

Results and discussion

Figure 2 shows the images of the plated specimens at various plating times. At the beginning, Cu plating was found to be located around the shape edge where there was most electron concentration (as shown in **Figure 2(b)**). The deposition was propagated along the specimen length towards the anode with increasing plating time. After the Cu plating covered the whole specimen area, further deposition obviously resulted in incremental thickness.

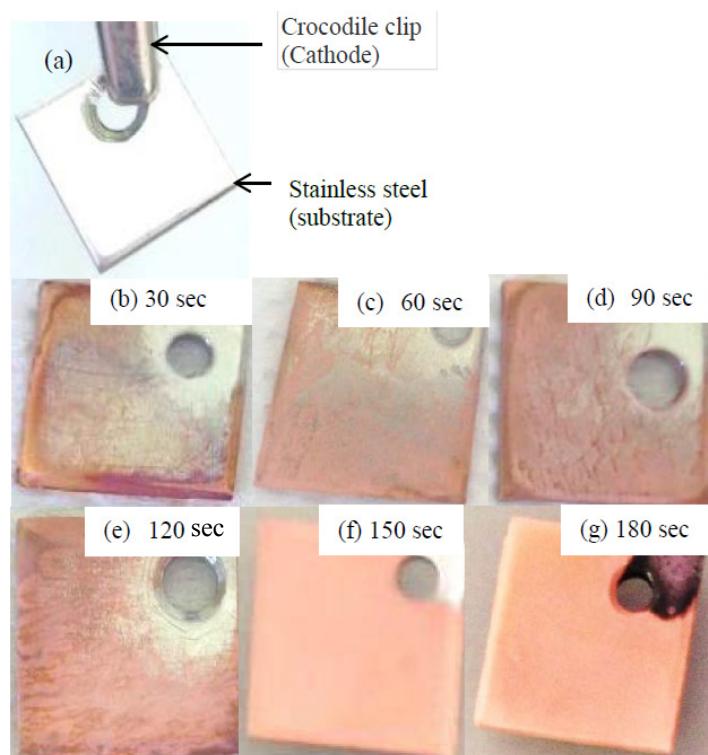
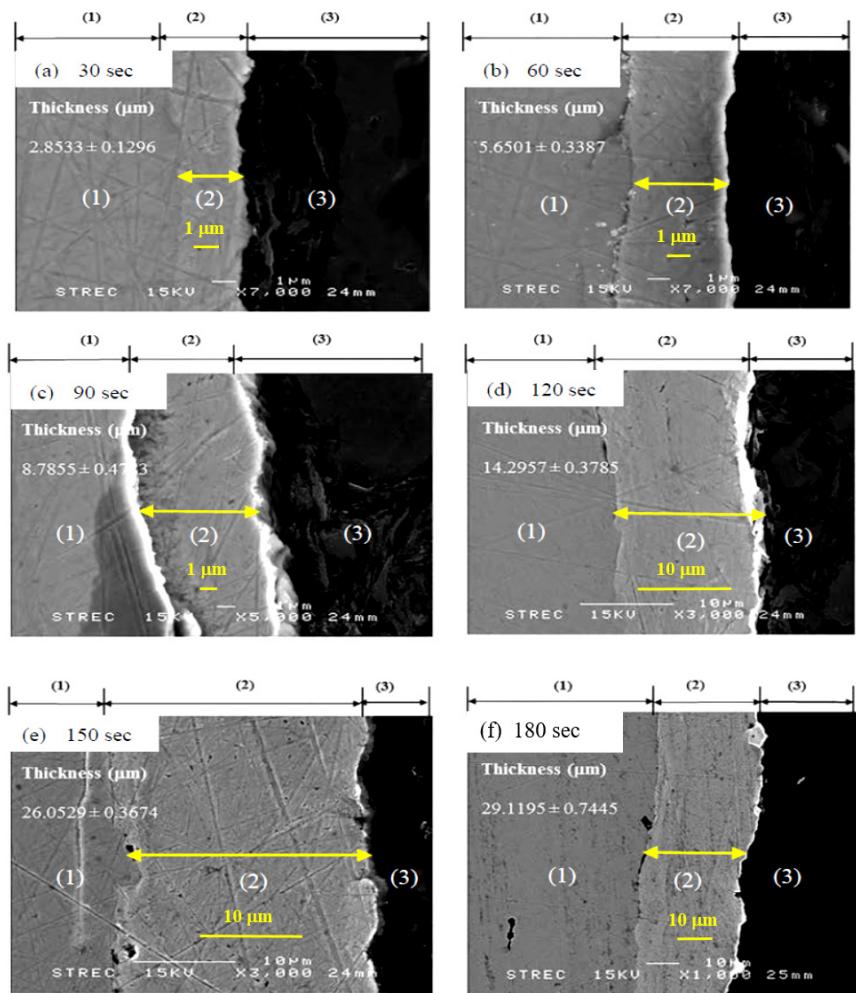


Figure 2 Images of before (a) and after plated specimens with various plating time for 30 sec (b), 60 sec (c), 90 sec (d), 120 sec (e), 150 sec (f), and 180 sec (g).



Remark: (1) = Substrate, (2) = Cu layer, (3) = Fixation resin

Figure 3 Cross-sectional SEM micrographs with thicknesses of the various Cu depositing times, 30 sec (a), 60 sec (b), 90 sec (c), 120 sec (d), 150 sec (e), and 180 sec (f).

The cross-sectional SEM micrographs of the deposited layers with the evolution times are displayed in **Figure 3**, and the results are summarized in **Table 1**. Thin films were observed, particularly at the beginning of the plating process, whereas a void presence was obviously noticed at much longer deposition times (as shown in **Figures 3(e)** and **3(f)**). Nakahara [13] reported that these voids could be generated during the growth of multiple-atomic steps, and it was implied that the layers contained unfilled regions inside the lattice. This can be called “coalescence-induced void formation” [14].

From the results discussed above, it could be implied that the packing of the Cu atoms onto the deposited layer involving the nucleation process with some degree of imperfection resulted in the formation of micro-scale crystalline structures, along with amorphous regions within the growing layer.

Table 1 Summary of theoretical and experimental deposition average densities as a function of time.

Plating time (sec)	Cu atom ($\times 10^{19}$ atom)		Δ atoms	Deposition (%)	^a Thickness (μm)	Average density (g/cm ³)
	Theoretical	Experimental				
30	2.09 ± 0.14	1.45 ± 0.24	0.64	69	2.85 ± 0.13	5.26 ± 0.67
60	4.31 ± 0.38	2.81 ± 0.22	1.50	65	5.65 ± 0.34	5.49 ± 0.64
90	6.19 ± 0.28	4.07 ± 0.16	2.11	66	8.79 ± 0.48	5.01 ± 0.62
120	9.25 ± 0.43	7.01 ± 0.49	2.24	76	14.30 ± 0.38	5.18 ± 0.61
150	11.72 ± 0.47	8.53 ± 0.19	3.19	73	26.05 ± 0.37	3.46 ± 0.52
180	13.69 ± 0.65	9.73 ± 0.36	3.96	71	29.12 ± 0.75	3.54 ± 0.54

^ameasuring by cross-sectional SEM micrographs

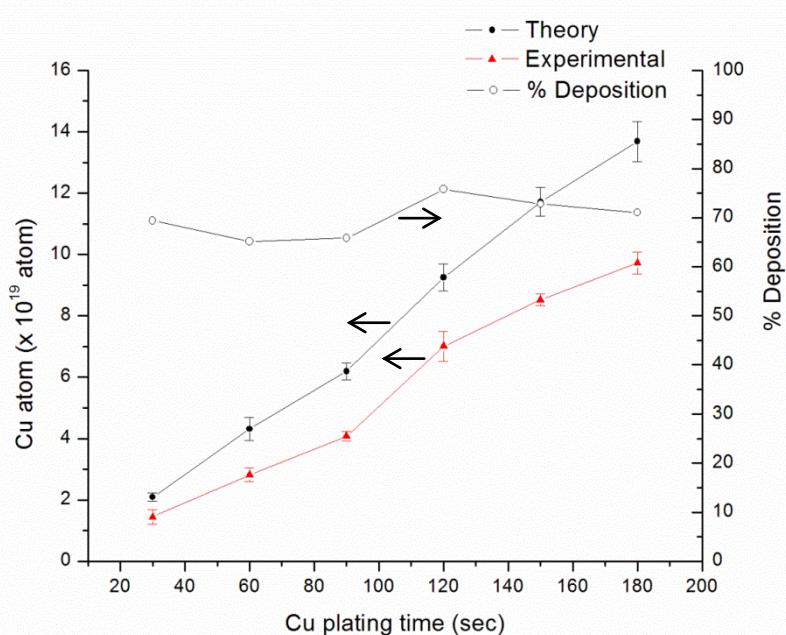


Figure 4 Theoretical and experimental values of deposited Cu atoms as a function of plating time.

Figure 4 illustrates the number of Cu atoms deposited by electroplating as a function of plating time, with both estimated and experimental values. Generally, the deposited Cu atoms increased with increasing plating time, as expected. The estimated and actual Cu deposition atoms were relatively proportional to the plating time; however, the actual Cu deposited atoms, which were calculated from the weight increment, showed lower values when compared to the estimated atom at the same length of deposition time. At any considered plating time, the difference between the estimated and the actual deposited atoms reflected the efficiency of the undergoing electroplating process. The actual depositions were in a range of 69 - 71 % of the estimated value. As the plating times increased, the plating efficiency of the Cu atoms tended to decrease. At the initial stage of plating, the Cu formed nuclei. Sequentially, as the plating time proceeded, the addition of Cu atoms to the existing formed nuclei contributed to the nucleation growth, which resulted in the increase in thickness. It could be explained that the Cu atoms were more easily moved to the coalescent nuclei sites at the beginning of the process, whereas complexity

in shape and surface arose as the plating time increased, in which the Cu atoms from the solution had more obstacles to successful transportation to the propagating nuclei [4,5,15].

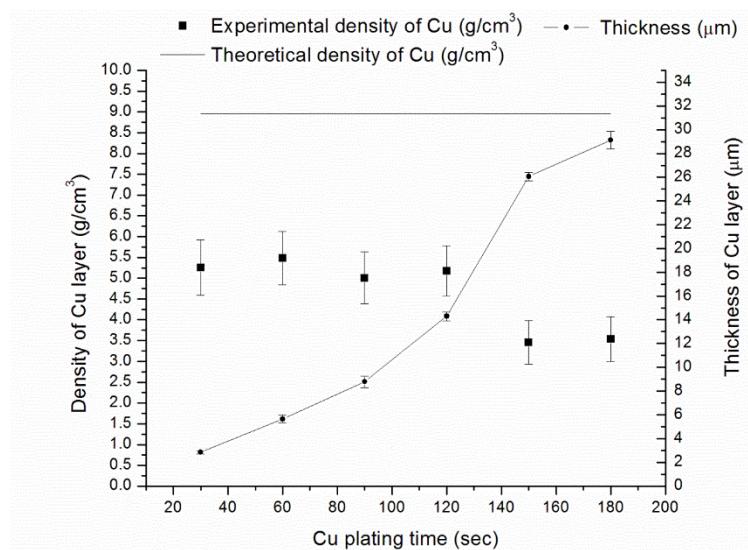


Figure 5 Density and thickness evaluation of deposited Cu layer at various plating times.

Figure 5 shows density of the Cu layer and wafer thickness as a function of plating time. The density was relatively constant at the beginning of the electroplating process, and tended to reduce slightly with longer undergoing plating time, obviously noticed when the deposition time was longer than 120 sec. The deposited layer thickness was observed to be gradually increased at the early stage of the process; however, the rate of thickness increasing was higher at a longer time. These results were believed to be due to the void formation that was presented in the later state of the coagulation, in which complexity in nucleation growth occurred [14,15].

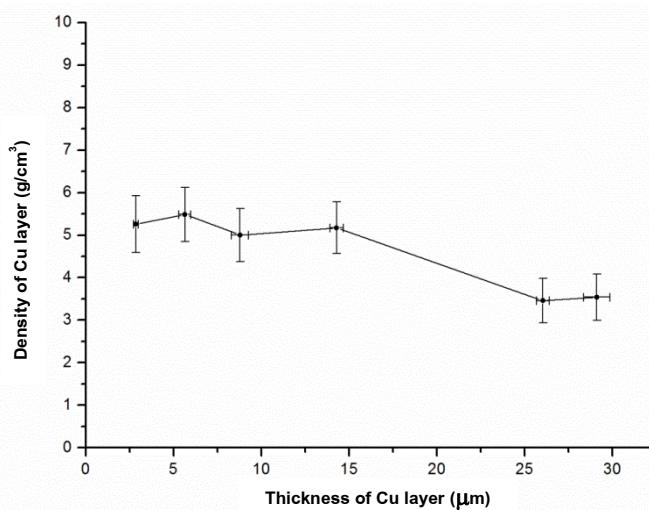


Figure 6 Copper deposition density as a function of layer thickness.

Figure 6 demonstrates the relation between the density of the deposited Cu and the layer thickness. It is clearly seen that the density gradually decreased with increasing thickness. This result suggests that the Cu atoms deposited onto the growing nucleation were less packed at longer periods of plating time.

Conclusions

Deposition and density calculations of Cu electroplating from CuSO₄ solution onto stainless steel substrate were studied. The average density of Cu gradually decreased with increasing deposition thickness. It was found that the thickness increased at an increasing rate. The difference between the estimated and the actual depositions were in a range of 65 to 76 %. It is believed that void formation presented in the later stage of coagulation in which complexity in nucleation growth occurred.

Acknowledgements

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