

# A Study on the Deposit Uniformity and Profile of Cu Electroplated in Miniaturized, Laboratory-Scale Through Mask Plating Cell for Printed Circuit Board (PCBs) Fabrication

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**Abstract** – A miniaturized lab-scale Cu plating cell for the metallization of electronic devices was fabricated and its deposit uniformity and profile were investigated. The plating cell was composed of a polypropylene bath, an electrolyte ejection nozzle which is connected to a circulation pump. In deposit uniformity evaluation, thicker deposit was found on the bottom and sides of substrate, indicating the spatial variation of deposit thickness was governed by the tertiary current distribution which is related to  $\text{Cu}^{2+}$  transport. The surface morphology of Cu deposit inside photo-resist pattern was controlled by organic additives in the electrolyte as it led to the flatter top surface compared to convex surface which was observed in the deposit grown without organic additives.

Key words: Printed Circuit Boards, Metallization, Electroplating, Plating Cell, Uniformity

## 1. Introduction

Metal electroplating, a simple, common, and cost-effective method for the formation of metal film, is based on the reduction of metal ion in the liquid electrolyte by the supply of the external electron source. It is one of the oldest techniques used for the production of raw materials, the precious metal coating in the jewelry industry, and the electronics industry. Cu electroplating has been used for the fabrication of conductive and fine Cu line (interconnection) on printed circuit boards (PCBs). It also has been employed in the semiconductor device manufacturing process for the formation of nanometer-scale interconnection of integrated circuits (ICs) and memory devices [1-4].

Several process steps proceed for the fabrication of Cu interconnection on PCB. Briefly, Cu layer ( $< 10 \mu\text{m}$ ) is formed on an epoxy substrate through the growth of Cu film via physical vapor deposition or electroless plating, or through the lamination of Cu foil. And then, the following photo-lithography develops the micro-pattern, which is filled selectively with Cu via electroplating. This is called 'through mask plating'. Subsequent removal of photo-resist leaves the patterned Cu interconnect line on the substrate and this process cycle repeats for the fabrication of multilayer structure.

In Cu electroplating, there are many processing parameters such as electrolyte, applied current, and plating cell configuration that have a crucial influence on the mechanical and electrical properties of Cu film, deposit uniformity, and deposit profile. In the manufacturing

process, these are being monitored carefully and continuously as it is correlated to the product quality and yield, though not many studies on the uniformity and the shape of Cu deposit in through mask plating have been carried out [5-14]. Most manufacturers usually optimize their processing parameters with industry-scale plating cell prior to mass production; unfortunately, it costs considerable time, electrolyte, and labor due to the tremendous scale of plating cell.

This cost can be reduced by miniaturizing the plating cell, which can reflect on industry-scale plating condition, for the process optimization. We fabricated a miniaturized lab-scale plating cell which can be adapted to single PCB board of conventional small electronic device ( $6 \times 8 \text{ cm}^2$ ) and systematically evaluated the effects of the plating conditions on the deposit uniformity and shape. A lab-scale cell can be used for analyzing the plating phenomena more easily and more precisely with less cost.

## 2. Experimental

### 2-1. Fabrication of the plating cell

The plating cell used in this study was designed as the approximate 1:10 miniaturization scale of the mass production plating cell used in PCB manufacturing process. Fig. 1a shows a schematic diagram of the cell and its dimension. The cell mainly consists of bath, electrodes, nozzle, and pump. The bath was made of acid-resistant polypropylene with 27 cm in width, 10 cm in length, and 15 cm in height, where it can take about 6 liters of the plating solution. A Cu-deposited PCB substrate was immersed vertically in the electrolyte and placed in front of electrolyte-injecting nozzles. Cu metal plate ( $7 \times 8 \text{ cm}^2$ , 3 mm thick) counter electrode was placed behind the nozzle arrays, and a saturated calomel electrode (SCE) reference elec-

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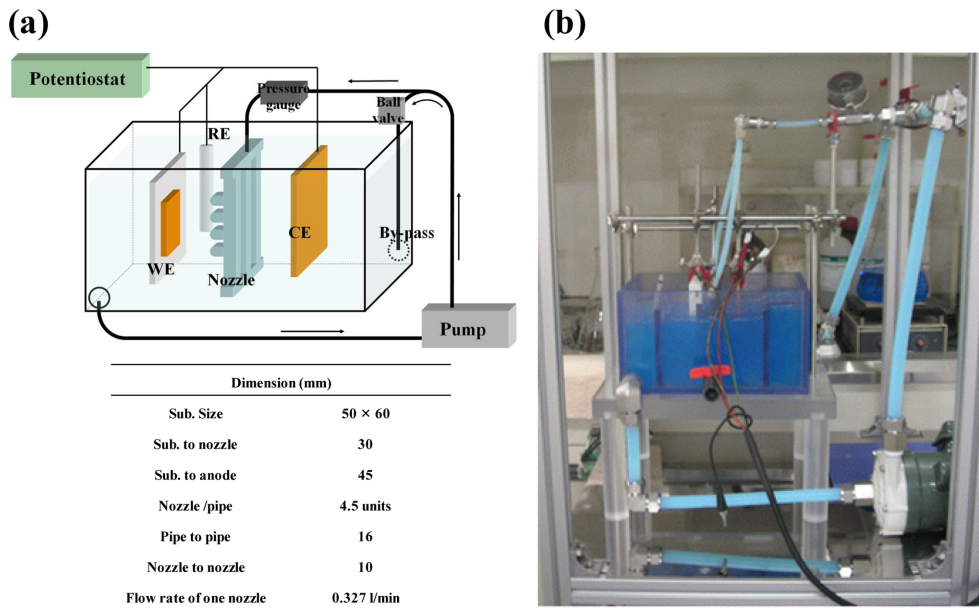


Fig. 1. (a) Schematic diagram of the plating cell designed as a lab-scale with its detailed dimensions and (b) its real image.

trode was near the PCB substrate. The continuous and thick (a few  $\mu\text{m}$ ) Cu deposition requires a vigorous copper ion supply to the deposit surface, and it was completed by introduction of nozzles connected to the magnetic pump (MD70RZ, IWAKI PUMPS, Japan) through exterior Teflon pipe. Thirteen nozzles made of polypropylene were arranged with 1 cm gap as shown in Fig. 2. The hole size in each nozzle was 0.06 cm; the correlation between pressure and flow rate in a single nozzle is shown in Fig. 2b. By the numerical evaluation of

manifold flow with orifices [14], the estimated flow rate deviation of nozzles was 1.5% and the actual deviation was measured about 3.1% (Inset table in Fig. 2b exhibits the flow rates on individual at 0.8 kgf/cm<sup>2</sup>). The amount of the electrolyte supplied into nozzle system was controlled by ball valve (316 stainless steel) inserted between pump and inlets; the rest of circulating electrolyte went into the by-pass inlet. Applied pressure applied on the nozzle was monitored with diaphragm pressure gauge (316 stainless steel). As the plating solution circulated continuously, the gradual rise of the electrolyte temperature was observed, which is due to the heat transfer from the magnetic pump. To maintain the electrolyte temperature at 25 °C, a heat exchanger made by stainless steel pipe with passing cool water was placed in the bath.

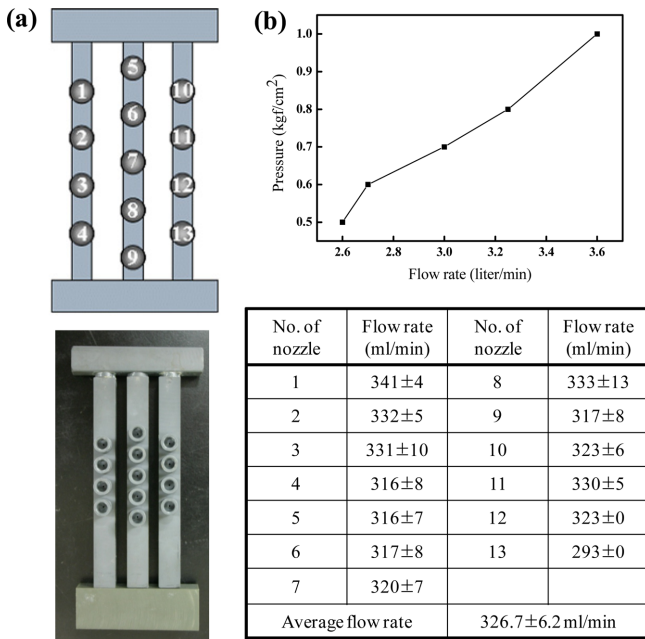


Fig. 2. (a) Schematic diagram and the real image of nozzle system which has 13 orifices arranged with the 1 cm space. (b) The relation between the pressure and the flow rate on single orifice, and the measured flow rate on an individual orifice mounted on the nozzle system at 0.8 kgf/cm<sup>2</sup>.

## 2-2. Plating condition

PCB substrate was 5 cm-wide and 6 cm-long epoxy plate covered with a 10  $\mu\text{m}$  thick Cu film as a seed layer grown by electroless plating. The thickness of seed layer also affects the deposit uniformity as it can induce additional voltage drop from the current flow through thin and resistive seed layer. To remove the effect of seed layer, we used thick Cu seed layer. Dry film photo-resist patterns (Hitachi RY-3025, Japan), where its width and height were 35  $\mu\text{m}$  and 26  $\mu\text{m}$ , had already been developed on the Cu seed layer, as illustrated in Fig. 3. A plating solution was composed of 0.25 M CuSO<sub>4</sub>·5H<sub>2</sub>O, 1 M H<sub>2</sub>SO<sub>4</sub>, and DI water. The conventional combination of organic additives, which are 88  $\mu\text{M}$  poly (ethylene glycol) (PEG, Mw 3400, Aldrich, USA), 1 mM NaCl, and 50  $\mu\text{M}$  bis (sulfopropyl) disulfide (SPS, Raschig GmbH, Germany), was added to the electrolyte [16-18]. Plating was carried out in the electrolyte using the 3-electrodes system, which consisted of PCB substrate, 99.9% Cu plate, and a saturated calomel electrode (SCE). The plating potential or current was applied by scanning

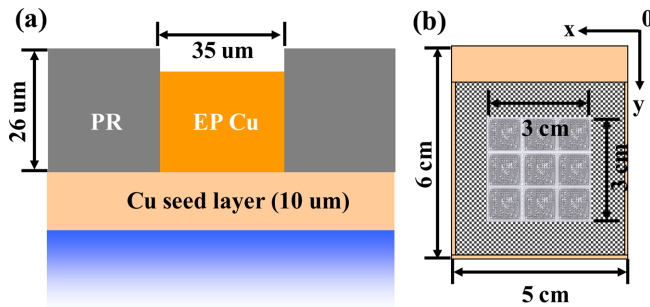


Fig. 3. Schematic diagrams of (a) the cross-section and (b) the plane of substrate where photo-resist mask was developed.

potentiostat Model 362 (EG&G Princeton Applied Research Corporation). After plating was finished, the substrate was cleaned with DI water and dried under  $N_2$  flow. For the observation of thickness and topology, the substrate was sectioned and molded with epoxy, and then the sectioned surface was polished with SiC paper. Afterwards, it was observed with an optical microscope (Sometech ICS-305B) and the measurement error was about  $1.2 \mu\text{m}$ , which was about 4% of total thickness ( $30.1 \mu\text{m}$ ).

### 3. Results and Discussion

#### 3-1. Deposit uniformity

In general, Cu electroplating in manufacturing process is performed on a large substrate ( $\sim\text{m}^2$  scale) where many individual circuits (devices) are embedded. The non-uniform deposit causes a deviation of the interconnection height and consequent distortion of the multilayer feature, and finally results in a loss in device reliability and a decrease in the manufacture production yield [16]. The deposit uniformity is determined by the current distributions during the electroplating, and it is known that there are three types of current distribution in electrochemical system [19]. If the electrolyte resistance governs the rate of plating reaction (e.g., when the supporting electrolyte is not presented in the electrolyte), current density can be expressed as follows:

$$j = -\kappa \nabla \Phi \quad (1)$$

where  $j$  is the current density,  $\kappa$  is the conductivity of solution, and  $\Phi$  is the electrostatic potential. It is called primary current distribution. The solution adjacent to a cathode is taken to be an equipotential surface and the current density is proportional to the surface-normal potential gradient, which is maximized at the interface between conductive substrate and insulating wall. It leads to thicker deposit at the edge of substrate (edge effect). On the other hand, electrode kinetics should be taken into account when the electrochemical reaction is slow and current flow requires additional overpotential, that is, surface overpotential ( $\eta_s$ , or activation overpotential). In this circumstance, the current density is limited by charge-transfer resistance ( $d\eta_s/dj$ ) as well as electrolyte resistance. This is called secondary current distribution and its governing equation is as follows [19]:

$$j = \eta_s \left( \frac{dj}{d\eta_s} \right) = -\kappa \nabla \Phi \quad (2)$$

where  $d\eta_s/dj$  can be derived from Butler-Volmer relation. Due to the additional overpotential, more uniform distribution is usually achieved. Tertiary current distribution takes into consideration reactant mass transfer, that is, concentration overpotential, as well as surface reaction rate. Accordingly, the agitation, convection and reactant concentration become key factors in determining deposit uniformity.

The crucial factor which influences the deposit current distribution varies with the scale of analysis area and size, which is categorized into three groups: whole substrate (work-piece scale), individual pattern (pattern scale), and deposit micro-structure (feature scale, roughness). If target deposit thickness is comparable to the diffusion boundary layer thickness ( $1 \mu\text{m} \sim 100 \mu\text{m}$ ), which is in the range of work-piece scale analysis size, the mass transfer of Cu ions determines the deposition rate whereby the deposit uniformity on the work-piece scale depends on its spatial variation (tertiary current distribution). Accordingly, work-piece scale uniformity is usually influenced by the electrolyte convection and agitation. The variation in the pattern density on the substrate also results in the thickness non-uniformity of the deposit because of the variation of actual deposit area ('active area') and the above-mentioned edge effect. As the analysis range decreases into single pattern or feature scale, the surface reaction as well as mass transfer becomes important, whereby organic additives which affect the rate of surface reaction change the deposit profile in pattern structure. It also affects the roughness of the deposit. Note that the uniformity in this study means the thickness variation on the work-piece scale.

Figure 4 exhibits the distribution of Cu deposit thickness over the whole substrate, indicating that the mean deposit thickness and the standard deviation were  $30.1 \mu\text{m}$ , and  $7.2 \mu\text{m}$ , respectively (at  $0.25 \text{ M CuSO}_4$ ,  $1.0 \text{ M H}_2\text{SO}_4$ , PEG-Cl-SPS,  $20 \text{ mA/cm}^2$ ,  $2000 \text{ s}$ ). As the work-piece scale uniformity with thick ( $>10 \mu\text{m}$ ) layer deposition would be determined by the mass transfer of Cu ion. In fact, relatively large deposit was found on the bottom and side edges where the ejected electrolyte flows fast as illustrated in Fig. 4b. It indicates

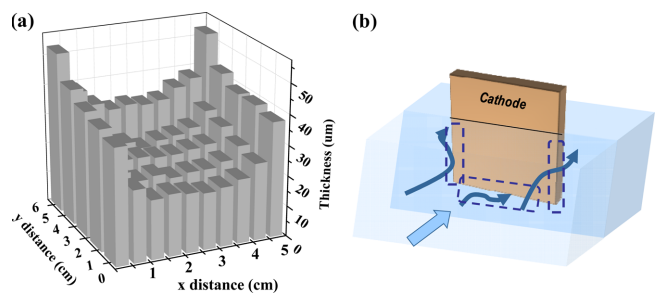


Fig. 4. (a) Three-dimensional diagram of the thickness distribution of Cu electrodeposited on the substrate under the standard condition ( $0.25 \text{ M CuSO}_4$ ,  $1.0 \text{ M H}_2\text{SO}_4$ , PEG-Cl-SPS,  $20 \text{ mA/cm}^2$ ,  $2000 \text{ s}$ ) and (b) the general flow pattern of the electrolyte near the substrate.

that the deposit distribution of this plating cell is governed by the tertiary current distribution. As the plating proceeds, Cu ions near the substrate are consumed whereby the diffusion boundary layer is gradually developed and the boundary layer thickness varies with the local convective flow rate. The higher flow rate generates a thinner diffusion boundary layer and consequently maintains the higher current (deposition rate) compared to other region. The change in the work-piece scale uniformity with the change of parameters (plating current density, electrolyte composition) is shown in Fig. 5. Among them, the current density was found to have the most significant effect on the uniformity (Fig. 5a). The decrease in current density improved the plating uniformity (the decrease in the standard deviation of deposit thickness). This result was attributed to the alleviation of the mass transfer limit by less-consuming of Cu ions. Unfortunately, the reduction in the plating current density means an increase of the plating time in aspect of manufacturing process, which is not desirable for

mass production, and therefore optimization between the uniformity and the process time is required. High Cu ion concentration in the electrolyte was expected to relax the mass transfer limit, but it was found that it is not very influential to the uniformity (Fig. 5b). Rather, the higher concentration made the uniformity worse, and it is speculated that higher Cu ion results in the stronger diffusional flux of Cu ion, and, consequently, the more deposit at the thick plating region. Sulfuric acid as a supporting electrolyte, which is added in order to reduce a solution resistance without the interference in the overall reaction, is generally added with the excess amount ( $> 0.1$  M) in the electrolyte where the solution resistance becomes negligible in most cases. However, for an electrochemical system with large surface area where the total current is in the range of a few hundred or thousand milli-amperes, even small resistance makes a considerable potential drop ( $\Delta V = I \times R$ ) across the electrolyte. Accordingly, small  $H_2SO_4$  amount manifests the effect of the solution resistance, that is, "edge effect" as the characteristic of primary current distribution. As shown in Fig. 5c, small concentration of  $H_2SO_4$  made the uniformity worse, whereas the addition over 0.6 M did not make a further change, indicating that the effect of the solution resistance became negligible.

There is a dimensionless parameter associated with determining of the type of current distribution called Wagner number (Wa) which is numerically defined and expressed as follows:

$$Wa = \frac{\kappa}{L} \frac{dj}{d\eta_s} = \frac{\kappa}{L} \left( \frac{RT}{\alpha n F j} \right) = \frac{\kappa}{L} \left( \frac{RT}{\alpha n F} \right) \left( \frac{1}{j_0 \exp\left(\frac{\alpha n F \eta_s}{RT}\right)} \right) \quad (3)$$

where  $L$  is the characteristics length.  $Wa$ , therefore, indicates the ratio of charge-transfer resistance (which corresponds to electrode kinetics) to ohmic resistance. Small  $Wa$  indicates that the current is distributed in more primary characteristics, whereas large  $Wa$  implies a secondary current distribution and, that is, more uniform distribution. Obviously, the change in the experimental parameters would change the Wagner number, and more uniform distribution was expected at smaller current density, smaller  $Cu^{2+}$  concentration (smaller exchange current density), and higher sulfuric acid concentration (higher electrolyte conductivity). These might be considered as a consistency of the experimental results; however, the effect of the change in the electrolyte conductivity (which is roughly proportional to sulfuric acid concentration) was insignificant for changing uniformity and the degree of the impact of each factor are different, which cannot be understood by evaluating of  $Wa$  number. This indicated that the uniformity is determined by more complicated factor, that is, mass transfer, and accordingly, it showed tertiary current distribution. In summary, the uniformity in the miniaturized lab-scale plating cell was governed by tertiary current distribution, and the plating current density had the most profound effect on the uniformity and the smaller one made it better.

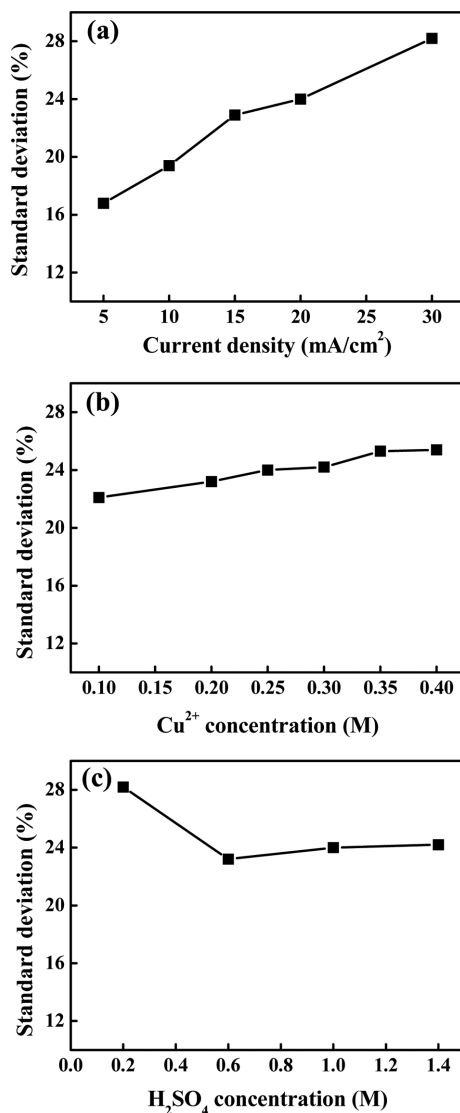


Fig. 5. Change in the standard deviation of deposit thicknesses over the whole substrate according to the deposition conditions: (a) current density, (b)  $Cu^{2+}$  concentration, (c)  $H_2SO_4$  concentration.

### 3-2. Deposit profile

The shape (profile) of Cu deposit in the pattern is within the scope

of pattern scale uniformity. Most PCBs or microprocessors have a multilayer structure of patterned circuit, so that the flatness of the deposit top surface is desirable for the multilayer formation since the topology of surface would be transferred to upper layer. In general, the pattern scale uniformity is closely related to the surface reaction of  $\text{Cu}^{2+}$  reduction. In conventional Cu electroplating, the surface is under control of organic additives which adsorb on the surface and enhance or suppress the reduction reaction. The local variation of their distribution induces a difference in the local deposition rate and determines the final shape of Cu deposit [1,16,17]. Fig. 6 shows the cross-sectional optical microscope images of Cu electroplated with and without organic additives (PEG-Cl-SPS). The plating in the presence of additives exhibited uniform and well-defined rectangular deposit features (Fig. 6a), whereas the additive-free plating deposit showed in some of patterns un-filled, especially at low current density (Fig. 6b). As well, a domed top surface was found on all deposits from additive-free bath compared to more flat surface of Cu deposit with additives. A dimensionless number,  $L$ ,

$$L = \frac{T_{\text{middle}} - T_{\text{edge}}}{T_{\text{middle}}}$$

was introduced for the quantitative comparison of the deposit shape

where large  $L$  value indicates domed top surface and small  $L$  means a flat top surface. Figure 7 shows “ $L$ ” values from various plating conditions. Obviously, organic additives generated a more flat top surface over all plating current density range. The formation of the domed surface can be explained as follows: the continuous supply of Cu ion into the pattern via the diffusion and electrolyte convection is required for the pattern filling. In the vicinity of the photo-resist, the supply decreased due to the friction on the photo-resist wall, which reduced electrolyte flow velocity with building-up of hydrodynamic boundary layer [13] (Fig. 7a). The hydrophobicity of the photo-resist surface also limited the approach of Cu ion to the edge of pattern inside. These resulted in less deposit on the edge. When additives (PEG-Cl-SPS) are present in the electrolyte, the deposit process is controlled in a more uniform way. Introduction of additives usually increases the surface overpotential whereby the current distribution becomes more uniform. In addition, this additive combination can enhance the deposition rate at the recessed region, which is based on the geometry-induced change in the coverage of PEG and SPS on Cu surface [17,18]. The formation of convex surface at the early stage makes the edge recessed, but this function of additives induces faster deposition rate at the recessed region, and eventually balances the deposition rate over all region and makes

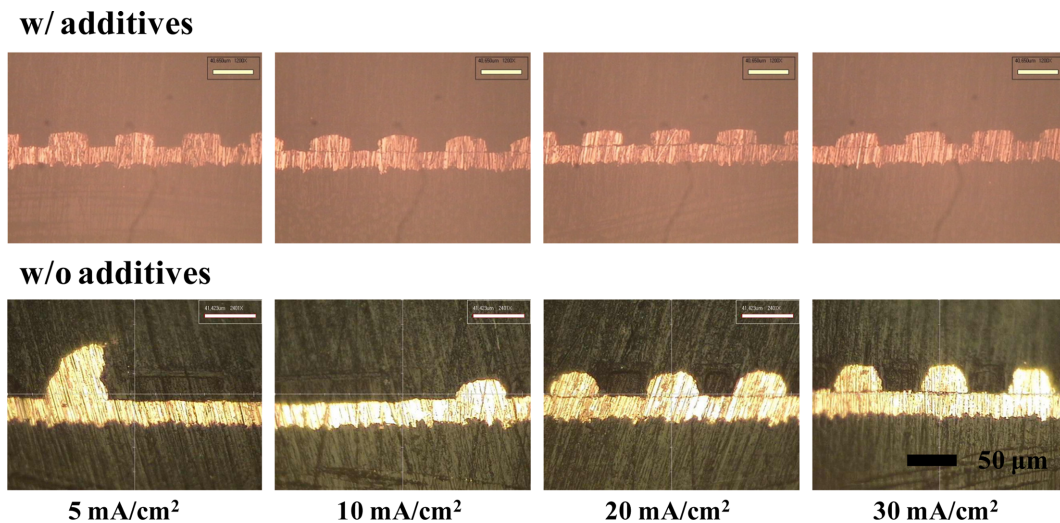


Fig. 6. Deposit profiles of Cu filled in photo-resist pattern with various plating condition.

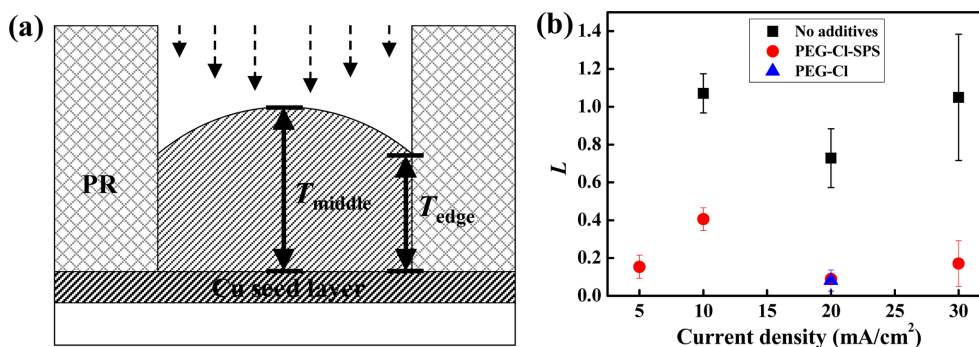


Fig. 7. (a) Schematic diagram of the deposit profile and mass-transfer rate inside the photo-resist pattern, and (b) the change in the flatness parameter “ $L$ ” according to the plating condition.

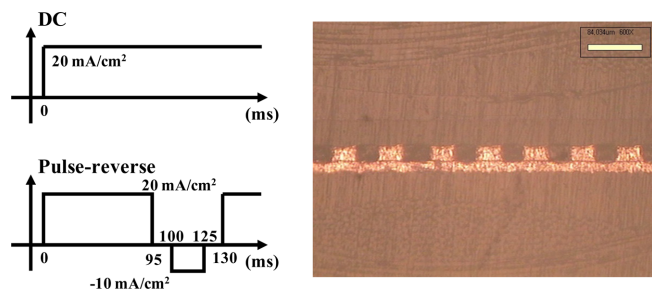


Fig. 8. Deposit profile of Cu filled in photo-resist pattern, which was deposited with pulse-reverse current.

a flat surface. Moreover, the surfactant function of PEG helps the mass transfer of Cu ion near the photo-resist. Interestingly, negative L (thicker deposit at the edge) was observed when the reverse current (dissolution of Cu deposit) was introduced to the plating current, which is called pulse-reverse plating (Fig. 8). The thicker deposit at the edge indicates that the dissolution of Cu occurred mostly at the center and it might be closely related to the change in the additive function.

#### 4. Conclusion

A lab-scale plating cell was fabricated by the miniaturization of the manufacturing plating cell on a 1/10 scale. The Cu deposit generated from the cell exhibited 24% thickness deviation over the whole substrate, and thicker deposits on the sides and bottom of the substrate, indicative of the relevance to tertiary current distribution. Current density had a critical effect on the uniformity, and low current density showed more uniform deposit. Meanwhile, the top shape was affected by the function of additives, which generated a more flat top surface.

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