

## FUNDAMENTALS STUDIES OF ELECTRO-SILVER PLATING PROCESS

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### ABSTRACT

The growth of electronic industry as a whole, and the demand to support the expansion of its underlying infrastructure will continue to drive the improvements in electroplating process. In order to improve existing electroplating process, the study of fundamentals aspects for electroplating process has become important. The influences of several electroplating parameters such as geometry of the bath, the movement of electrolyte, electrodeposition current, and bath temperature on the uniformity of the electrodeposition have been widely investigated. In this paper, the study of fundamentals aspect for electroplating will focus on silver plating due to this process currently play very important role in semiconductor industry especially in lead frame manufacture process. In order to study the fundamentals aspect, a simple lab scale silver plating experiment will be carried out to deposit a silver coating on a copper electrode by using a cyanide based plating bath. Based on the experimental result, the influence of bath concentration and current density to the process current efficiency will be presented. By combining the suitable concentration and type of plating bath, amount of current density and appropriate anode, it will contribute to the enhancement of uniformity for the electrodeposition. The optimum conditions of the silver plating process are proposed at the end of the paper.

**Keywords:** Electroplating, Silver Plating, Fundamentals Aspect, Optimum Conditions

### 1 INTRODUCTION

Electroplating is one of the important processes in electronic industries. The original purpose of electroplating process is to enhance the value of metal articles by improving their appearance. However, the importance of metal finishing for purely decorative purposes has decreased. Currently, the trend is toward surface treatments which will impart corrosion resistance or particular physical or mechanical properties to the surface (e.g. conductivity, heat or wear resistance, lubrication or solderability), and hence to make possible the use of cheaper substrate metals or plastics covered to give essential metallic surface properties or decorative for coating purposes (Pletcher, 1982).

Electrochemical technology entered the electronics industry about 50 years ago as a manufacturing process for low-end printed-circuit boards. Today, electrochemical technology is employed widely for the processing of advanced microelectronic components, including copper (Cu) chip, high end packages and interconnects, thin film magnetic heads and micro-electro-mechanical systems (MEMS). The continuing improvements in photo lithography and the theoretical understanding of the electrochemical engineering principles including current distribution, mass transport, electrode kinetics and nucleation and growth phenomena help to develop electrochemical technology in advanced microelectronic industry. At the same time, materials science and

engineering provided the experimental and theoretical tools permitting to relate the properties of electrochemically produced materials to their structure. All these developments led to new sophisticated cell designs and to improved reliability of electrochemical microfabrication processes permitting their industrial implementation for automated large scale manufacturing. Electrochemical microfabrication technology is expected to play an important role in the electronics and microsystems industry because of its cost effectiveness and high precision. In addition, electrochemical processes are attractive from an environmental point of view because material deposition or removal is highly selective thus minimizing waste (Datta & Landolt, 1999). With the miniaturization of electronic devices, the connection reliability between integrated circuit (IC) and the external circuits has become important. Electroplating and electroless plating have been applied for the metallization of electronic components. Recently, advanced plating technology is strongly in demanded for the manufacturing of electronic components, because many devices are becoming finer and more complicated (Honma, 2001).

The use of electrochemical technologies is increasing in the semiconductor industry. In packaging, electrochemical materials are used to address power delivery and dissipation, including electroless deposition and electroplating for substrates, electroplating bumps to connect die to substrate, plating for die sacking and 3D interconnects. In chip metallization, electrochemical materials are used to reduce RC delay and increase electromigration resistance, including electroplated damascene interconnects with low resistivity and higher electromigration resistance than Al interconnects, and electroless plating for cladding, barrier and seed layer applications. In transistor, electrochemical materials are used to form silicon on isolator (SOI) by employing porous silicon to reduce transistor leakage. Electrochemical processing offers low cost, excellent scalability to smaller feature sizes and the capability of preferential, selective growth to form patterns (Dubin, 2003).

A thorough understanding of the underlying principles of mass transport and current distribution is crucial for successful industrial implementation of electrochemical microfabrication processes. Mass transport limits the ultimate rate in an electrochemical microfabrication process and therefore has a direct implication on throughput and investment cost. The current distribution on a macroscopic level determines the uniformity of the thickness of an electrodeposits and the depth of dissolution in an anodic process (Datta & Landolt, 1999). To study the effects of offset voltage on electroplating uniformity, the degree of uniformity has improved with decreasing offset voltage. Higher temperature and changing anode position have also influenced the uniformity positively. With the introduction of agitation during electroplating, the current distribution uniformity would be improved through the more equalized feeding of depleted metal ions. Lower offset voltages, suitable amount of bath agitation, elevated temperatures, appropriate cathode-anode separation and bath concentration were found to contribute to the enhancement of current distribution uniformity when they were assessed individually. However, it is also been found that the combination of these parameters did not produce the expected synergistic effect in uniformity improvement (Datta & Landolt, 1999).

Electrochemical or electroplating process is rapidly evolving as a technology of choice in the electronics and microsystems industries. The successful implementation of electroplating process in manufacturing industry has become possible thanks to progress achieved through fundamental research in electrochemistry, electrochemical materials science and electrochemical engineering. However, further miniaturization trends of the microelectronics industries provide new opportunities and challenges which include issues related to nanoscale structuring, fabrication of high aspect ratio structures, new functional alloys, multidimensional interconnects, and automated large scale processes including additive control and recycling of electrolytes. To successfully overcome such challenges, fundamentals as well technology oriented research will be needed and interactions between the two should be stimulated (Datta & Landolt, 1999).

Silver is a soft, white metal with pleasing appearance. It is malleable and ductile and an excellent conductor of heat and electricity. The good conductivity of silver contributes to the use of the metal in decorative as well as technical applications. Silver plating, developed well over one hundred years ago, was one of the earliest electroplating successes (Mohler, 1969). Currently, silver plating is one of the important processes in lead frame manufacture industry. Silver was selectively coated on the copper lead frame to

improve the conductivity and also act as protection layer to avoid oxidation during wire bonding process.

In this study, the electro-silver plating experiment is carried out in a cyanide based plating solution with a copper cathode and a platinum anode. Silver deposits are chosen to be evaluated with different parameters of electroplating because of its importance usage such as in electronic, jewelry and decorative industries. The electroplating process will be evaluated for certain parameters that will greatly affect the process. The parameters are the type and plating bath concentration and the amount of current supply during plating process. Finally, the optimum conditions that result in a uniform deposit are proposed.

## 2 EXPERIMENTAL SETUP

The experiment consisted of an electrolysis cell with 100 ml electrolyte in a 100 ml beaker. The anode was a 5 cm platinum wire and the cathode was a 5 cm x 1cm copper plate with a 0.004 dm<sup>2</sup> as plating surface area. The electrolyte was considered to be well mixed by a constant stirring rate of a magnetic stirrer. For the stirring and heating source, a hotplate stirrer LMS-1003E Carolina plate was used. The experiments were conducted with different concentration of electrolyte, current supplied, stirring rate and temperature.

To study the effect of bath concentration, the concentration for potassium argentum cyanide was varied from 66.87g/l to 100g/l with 5 different concentrations were used (66.87g/l, 70g/l, 80g/l, 90g/l, 100g/l). The increasing of concentration of potassium argentum cyanide was followed by increasing of potassium cyanide to maintain the free cyanide level in solution bath (35g/l, 36.63g/l, 41.86g/l, 47.09g/l, 52.32g/l).

In the experiment to study the effect of current density, the current supplied to the bath was varied from 0.04 Ampere to 0.2 Ampere with 5 different current supplies were used (0.04A, 0.08A, 0.12A, 0.16A, 0.20A). In this study, 2 set of experiment were carried out with different potassium argentum cyanide concentration (66.87g/l, 80g/l). The purpose using two different concentration baths is to study the effect of current density and concentration when it applied together in the solution.

## 3 RESULTS AND DISCUSSION

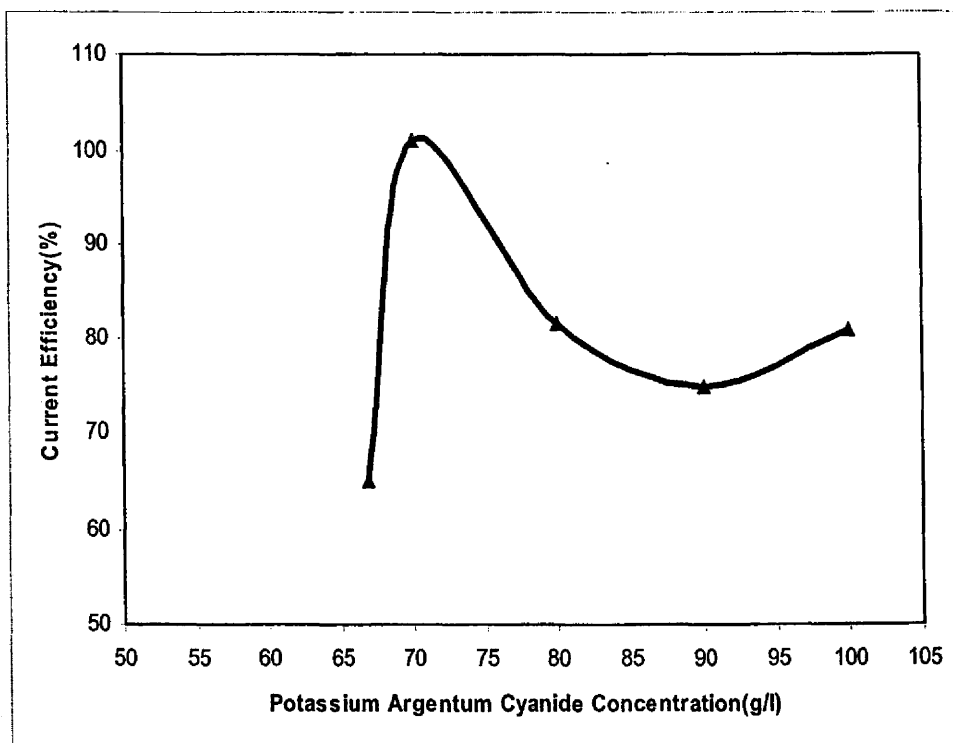


FIGURE 1. The effect of Potassium Argentum Cyanide concentration to current efficiency of the process; Plating Temperature 27°C, Plating time 30 minutes, Bath pH 12, Agitation 360rpm, Current density 1A/dm<sup>2</sup>, K<sub>2</sub>CO<sub>3</sub> 40g/l, KNO<sub>3</sub> 40g/l, KOH 1g/l.

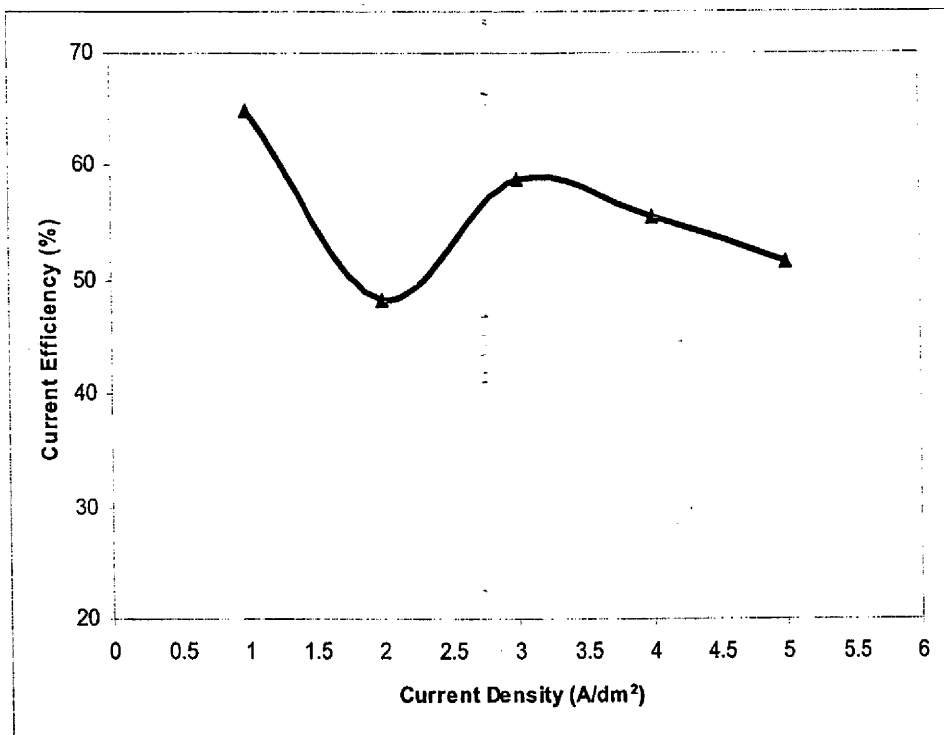


FIGURE 2. The effect of current density to current efficiency of the process; Concentration of  $K(Ag(CN)_2)$  66.87g/l,  $K_2CO_3$  40g/l,  $KNO_3$  40g/l, KOH 1g/l, Agitation 360rpm, Plating Temperature 27°C, Plating time 30 minutes, Bath pH 12.

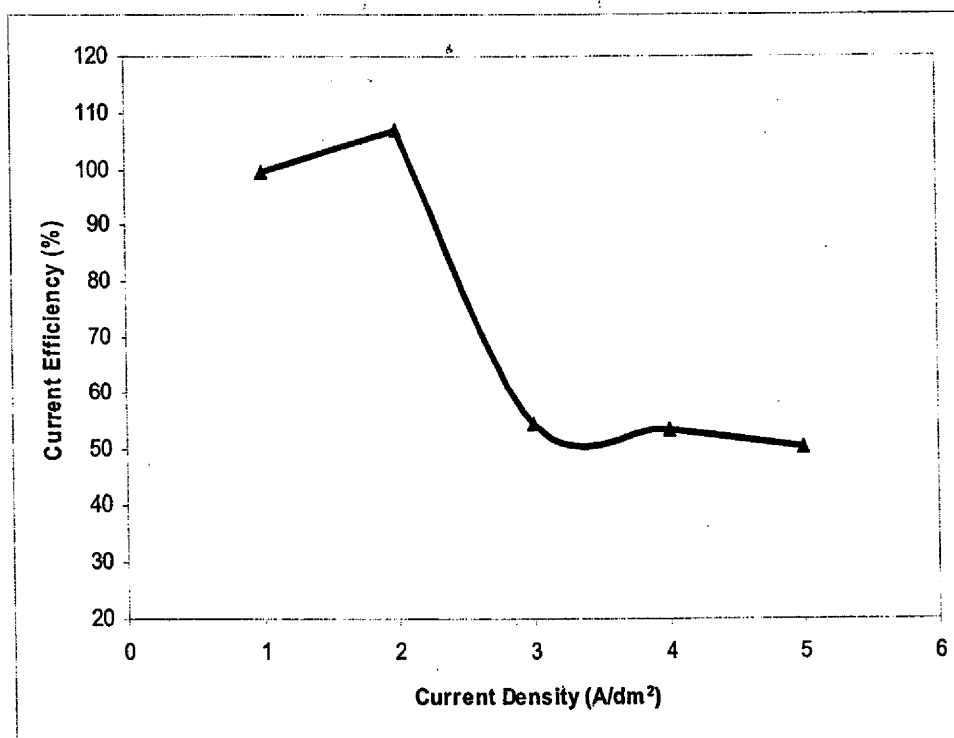


FIGURE 3. The effect of current density to current efficiency of the process; Concentration of  $K(Ag(CN)_2)$  80.00g/l,  $K_2CO_3$  40g/l,  $KNO_3$  40g/l, KOH 1g/l, Agitation 360rpm, Plating Temperature 27°C, Plating time 30 minutes, Bath pH 12.

Figures 1 to 3 show the effect for certain parameters to the current efficiency of silver plating process. The effect of the potassium argentum cyanide concentration to the process efficiency is shown in figure 1. From figure 1, it can be seen that the process current efficiency increase when the concentration of  $K(Ag(CN)_2)$  is increased from 66.87g/l to 70g/l. However, the efficiency decrease with the further increment of  $K(Ag(CN)_2)$  concentration. The increment of  $K(Ag(CN)_2)$  concentration will increase the concentration of  $Ag^+$  in solution, thus lead to increment of the  $Ag^+$  flow to cathode which increase the current efficiency of process. However, further increment of  $K(Ag(CN)_2)$  concentration drops the process efficiency. It is happened because the increment of  $Ag^+$  will increase cathodic polarization and decrease anodic polarization which tends to resist the flow of current to the cathode. To ensure high current efficiency, the increment of  $Ag^+$  must followed by the increment of current supply.

Figure 2 shows the result for the effect of the current density to the process efficiency. The concentration of  $K(Ag(CN)_2)$  used is 66.87g/l. As shown in figure 2, the current efficiency drops with the increase of current density and then maintain in the range around 55%. The increase of current density increased the transfer rate of  $Ag^+$  to cathode, however in this case, the concentration of  $Ag^+$  in the solution is low, thus cause insufficient supply of  $Ag^+$  to cathode. Beside that, the increment of current density might cause the current supplied exceeding process limiting current which cause the hydrogen evolution. Thus, the process current efficiency will drop. The assumption is proved with the result in figure 3. In figure 3, at the same current density (as in figure 2) but with higher concentration of  $K(Ag(CN)_2)$  led to higher process efficiency. The result from this two experiments shows that the increment of current density must be followed by the increment of  $Ag^+$  concentration to ensure high process current efficiency.

Figures 1 and 3 show that at some of the points, the current efficiency is more than 100%. In reality, this is impossible, but in this experiment, the current efficiency was calculated by dividing the actual weight of silver deposit to the theoretical weight of silver deposit. The weight of silver deposit is measured immediately after the copper plate is taken out from the deposition solution, thus improper dry of the copper plate might happen and cause the weight measured higher than the actual silver deposited weight. This will cause the calculated efficiency is higher than actual.

From the experiments, the optimum condition obtain for the concentration of potassium argentums cyanide is around 70 ~ 75g/l. While, the optimum condition obtain for the current density is around 1 ~ 2 A/dm<sup>2</sup>.

#### 4 CONCLUSION

A simple lab scale silver plating experiment to deposit a silver coating on a copper electrode by using cyanide based plating bath was carried out. The results of the experiment showed that:

- a. Increase of  $K(Ag(CN)_2)$  will increase the  $Ag^+$  in the solution and consequently increase the current efficiency. However, to ensure high current efficiency, the increase of  $K(Ag(CN)_2)$  concentration must be followed by increasing of amount of current applied. The optimum condition for  $K(Ag(CN)_2)$  obtain from this experiment is 70 ~ 75g/l.
- b. Increase of current density will increase process current efficiency with the condition that the current supply not exceeding the limiting current supply. In more of the plating case, increase of current density is followed by increasing of  $Ag^+$  in solution to ensure high process current efficiency. However, the metal adhesion is poor when plating with high current density. The optimum condition for current density obtain from this experiment is 1 ~ 2A/dm<sup>2</sup> (with  $K(Ag(CN)_2)$  80g/l).

From the result obtain in the experiments, it can be conclude that the parameters such as potassium argentums cyanide concentration and current density have a great influence to the process efficiency. The optimum condition obtain from these experiments is only the optimum condition for individual parameter. By combining all this optimum condition together, it might not give the maximum current efficiency to the process due to the chemical and physical condition of the process might change when applied these parameters together.

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#### REFERENCES

Pletcher, D.(1982). Industrial Electrochemistry 1<sup>st</sup> Edition, Chapman and Hill, New York.

Datta, M. and Landolt, D.(1999). Fundamental aspects and applications of electrochemical microfabrication. *Electrochimica Acta*, 45 (2000), 2535-2558.

Hideo Honma (2001). Plating technology for electronics packaging. *Electrochimica Acta*, 47 (2001), 75-84.

J.B. Mohler (1969). Electroplating and related processes, Chemical Publishing Co., Inc., New York.

Valery M. Dubin, (2003). Electrochemical aspects of new materials and technologies in microelectronics. *Microelectronic Engineering*, (2003).