Non-sintering Preparation of Copper (II) Oxide Powder for Electroplating via 2-step Chemical Reaction

Seung Bum Lee¹, Rae Yoon Jung¹, Sunhoe Kim²*
¹Department of Chemical Engineering, Dankook University, Yongin 16890, Republic of Korea
²Department of New Energy & Resource Engineering, Sangji University, Wonju 26338, Republic of Korea

ABSTRACT

In this study, copper (II) oxide was prepared for use in a copper electroplating solution. Copper chloride powder and copper (II) oxide are widely used as raw materials for electroplating. Copper (II) oxide was synthesized in this study using a two-step chemical reaction. Herein, we developed a method for the preparation of copper (II) oxide without the use of sintering. In the first step, copper carbonate was prepared without sintering, and then copper (II) oxide was synthesized without sintering using sodium hydroxide. The optimum amount of sodium hydroxide used for this process was 120 g and the optimum reaction temperature was 120°C regardless of the starting material.

Keywords : Copper (II) oxide, 2-step reaction, Electroplating, Via-filling plating

1. Introduction

The copper electroplating processes generally requires virgin plating solutions composed of copper sulfate, chloride compounds, and brighteners, as well as a soluble copper ball anode containing 0.04-0.06% phosphate to supply the Cu²⁺ makeup cations to the solution. Recently, however, sludge emanating from phosphorous impurities and difficulties in the control of the copper ion concentration in the plating bath have forced the replacement of the copper ball with an insoluble anode together with a copper (II) oxide solution as the copper source in the plating process [1-3]. Copper (II) oxide facilitates the generation of fine patterns and fine-hole plating by reducing the surface tension of the plating bath. Moreover, copper (II) oxide enables easy control of the thickness of the copper plating and better management of the conventional plating process. Various types of via-hole filling methods are applied for the execution of the micro process unit (MPU), graphic process unit (GPU), IC substrate, motherboard, and high-density interconnects.

In general, copper (II) oxide is produced commercially by reacting hydroxide salts, such as NaOH or KOH, with alkali salt carbonates including, Na₂CO₃, K₂CO₃, or NaHCO₃, in an acidic copper solution, for example, CuCl₂, CuSO₄, or Cu(NO₃)₂, to convert the copper precursor into Cu(OH)₂ or CuCO₃·Cu(OH)₂ followed by sintering in the temperature range 250-800°C [4-6]. Sintering of copper hydroxide at temperatures below 300°C will cause the material to thermally decompose. However, a particle size of <1 µm will reduce the angle of repose and liquidity of the powder. Nonetheless, in this state, it is difficult to remove byproducts such as chlorine or sulfuric acid from the mixture. Sintering of alkaline copper carbonate with a particle size >15 µm produces improved liquidity, so that copper (I) oxide can be produced in a high sintering temperature range from 400 to 800°C [7-11]. Therefore, in this study, we proposed a novel, two-step chemical method for the production of copper (II) oxide for electrolytic copper plating using copper chloride without a sintering process. The characteristics of the reaction were evalu-
ated by varying the experimental parameters including, the quantity of sodium carbonate used, the temperature of the first reaction step, the amount of sodium hydroxide, and the reaction temperature of the copper (II) oxide used for electrolytic copper plating, less than 100°C. Moreover, the liquidity (angle of repose), solubility in sulfuric acid to produce a consistent copper concentration, and optimum conditions for the chloride ions in the electrochemical redox bridge were established. In addition, in the plating bath formulated using the prepared Cu(II) oxide, the thickness of the dimples in the plating hole needed to be established to determine the physical properties of the copper (II) oxide for electrolytic copper plating.

2. Experimental Section

2.1. Production of copper (II) oxide

In this reported study, copper (II) oxide was produced from a copper (II) chloride solution via a two-step chemical reaction. Basic copper carbonate was synthesized by reacting copper chloride with sodium carbonate (Na₂CO₃, 99 wt.%, OCI product) as shown in Equations (1) and (2), which formed the first reaction step in the process. Copper oxide (CuO) was then synthesized by reacting copper carbonate and sodium hydroxide as shown in equation (3).

\[ \text{CuCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CuCO}_3 + 2\text{NaCl} \quad (1) \]

\[ (m + n)\text{CuCO}_3 \cdot n\text{H}_2\text{O} \rightarrow m\text{CuO} \cdot n\text{Cu(OH)}_2 + n\text{CO}_2 \quad (2) \]

\[ m\text{CuCO}_3 \cdot n\text{Cu(OH)}_2 + 2m\text{NaOH} \rightarrow (m + n)\text{CuO} + m\text{Na}_2\text{CO}_3 + (m + n)\text{H}_2\text{O} \quad (3) \]

Experiments were conducted where the temperature of the reaction was varied as well as the mole ratio of copper chloride solution to sodium carbonate in the reaction to prepare the alkaline copper carbonate. The first reaction product was obtained using a reaction temperature of 80°C. The mole ratio of copper (II) chloride to sodium carbonate in the reaction was between 1.08 and 1.68. In this manner, 10 wt.% copper chloride was reacted with aqueous sodium carbonate, under mole ratio mentioned above, for 60 min at a set temperature. The alkaline copper carbonate was collected from the reaction mixture by filtration, washed with water to remove excess chloride ions and then dried for further use. Next, copper (II) oxide was produced by reacting 80 to 160 g of sodium hydroxide in a 20 wt.% aqueous solution for 60 min at 80°C with 300 g of the alkaline copper carbonate dissolved in 2L of distilled water.

2.2 Copper (II) oxide reaction parameters

A number of the properties of the alkaline copper carbonate and copper (II) oxide products were measured to assess their relative quality, including, solubility in sulfuric acid, angle of repose and particle size. The angle of repose is the steepest angle of descent to the horizontal plane to which a material can be piled without slumping. A small angle of repose is indicative of good flowing ability of the powder. The angle of repose of the synthesized products was measured after thoroughly drying the particulate powders using an angle of repose measurement device, (model BT-200D, product of K-ONE Co. LTD., Seoul, Korea). The basic copper carbonate particles were analyzed with particle size analyzer (model BT-2000, product of K-ONE Co. LTD., Seoul, Korea). The particle size designations, D10, D50, and D90 in particle size analysis, represent 10%, 50%, and 90% of size distribution of the sample’s particle. The parameter SPAN represents the uniformity of the particle size distribution and can be expressed as:

\[ \text{SPAN} = \frac{D_{90} - D_{10}}{D_{50}} \quad (4) \]

The morphology of the particles was measured using a scanning electron microscope (SEM, COXEM, Daejeon, Korea model, CX-20).

2.3 Via-filling plating analysis

The via-filling plating capabilities of the CuO plating solutions were analyzed using a Harring cell electrolytic bath. A titanium plate with a height, width and thickness of 68, 100, and 0.3 mm, respectively, was used as cathode. The titanium plate was clad with a 1-μm iridium oxide layer to prevent corrosion. The electric layer thickness, laser via-hole size, and the expanded hole size ranged from 59.7 to 85.7 μm, 91.0 to 117.8 μm, and 103.4 to 129.3 μm, respectively. Nafion®, a perfluorocarbon cation exchange membrane, was used as the proton exchange separator between the anode and cathode in
the plating bath. The plating solution for use in the Harring cell electrolytic bath was prepared with the addition of additives such as 0.8 mL/L EVF brightener, 8 mL/L EVF leveler, and 20 mL/L of EVF carrier, product of Dow Chemical Co., into the plating solution, which contained 210 g/L of sulfuric acid, 70 g/L of copper oxide (II), and 50 mg/L of chloride ions. A BVH board served as the cathode, and it was activated by first degreasing with sulfuric acid for 2 min. at 45°C followed by acidification with 5 wt.% sulfuric acid for 30 s. Each plating process was conducted for one hour at a current density of 2 A/dm². The etching solution was agitated using air bubbling for 5 s and then the BVF board was washed with distilled water. The spectrum of the dimples in the cross section of the board were examined using a metallurgical microscope, model MX51, Olympus Co. Ltd.

3. Results and Discussion

3.1 Effect sodium carbonate stoichiometry at first reaction step

The mole ratio of sodium carbonate to copper (II) chloride in the first reaction was maintained at 1.08 to 1.68. Fig. 1 shows the XRD patterns of synthesized copper carbonate powder. As shown by these diffractions patterns, with a reactant molar ratio of 1.08, paratacamite (Cu₂Cl(OH)₃) and alkaline copper carbonate were formed, because of an incomplete reaction between the CuCl₂ and the Na₂CO₃ at a copper content of 53.9 wt.%. A lack of sodium carbonate in this reaction may have caused the incomplete reaction with the copper (II) chloride, because of the low pH (6.0) of the solution [12]. The copper content of the copper carbonate products increased to 57.7,
58.8, and 59.8 wt.% at reactant molar ratios of 1.20, 1.44, and 1.68. The color of the copper carbonate changed based on this mole ratio [13]. The malachite copper carbonate product [CuCO$_3$·Cu(OH)$_2$] exhibited a bright green color, whereas azurite product [2CuCO$_3$·Cu(OH)$_2$] exhibited a strong blue color. In this study, most of the copper carbonate products were bright green malachite copper carbonate when the molar ratio of copper was more than 1.20. Referring to equations 2 and 3, at a low molar ratio of sodium carbonate, the stoichiometric coefficient of CuCO$_3$, m, was greater than the stoichiometric coefficient of Cu(OH)$_2$, n; therefore, more CuCO$_3$ was produced than Cu(OH)$_2$. Since the mole ratio of sodium carbonate, m was lower than n, the rate of production of CuCO$_3$ was lower than that Cu(OH)$_2$. Therefore, the copper content in the product increased as the mole ratio of sodium carbonate in the reaction was increased. Assuming that the values of m and n were the same, the theoretical copper content of the product would be 57.5 wt.% since the calculated theoretical copper content is 57.5 wt.% when molar ratio of the two was greater than 1.20.

Fig. 2 shows that the particle size analysis of the basic copper carbonate reaction product as a function of the mole ratio of sodium carbonate to copper (II) chloride in the reaction. At a reactant molar ratio of 1.08, the values of D50 and SPAN were 26.43 and 1.772, which represented a uniform particle size for the product. The maximum SPAN value of 1.772 resulted when the ratio of sodium carbonate was 1.08. The decomposition of basic copper carbonate resulted in a heterogeneous particle size distribution. Moreover, with the reactant molar ratios of 1.20, 1.56, and 1.68, the SPAN values were in the range 0.826-0.848, which also represented a heterogeneous particle distribution. By contrast, the SPAN values for the reactant molar ratios of 1.32 and 1.44 were 0.751 and 0.7, which was indicative of a uniform particle size distribution.

Fig. 3 shows that the change in the solubility of the alkaline copper carbonate in sulfuric acid and angle of repose of the synthesized copper carbonate. The sulfuric acid solubility of the alkaline copper carbonate produced in the first reaction step initially increased and then decreased with the increase in the reactant molar ratio. Moreover, the angle of repose of the copper carbonate decreased initially and then increased with the increase of the reactant molar ratio. A reactant molar ratio of 1.08, resulted in a copper carbonate product with the shortest dissolution time in sulfuric acid (27s).

With increment of reactant molar ratio from 1.20 up to 1.44, the dissolution time in sulfuric acid of the copper carbonate increased from 33s up to 40s. However, the dissolution time began to decrease to 39 s and 33 s with the reactant molar ratios of 1.56 and 1.68, respectively. The angle of repose represents the fluidity of powder, with an ideal number of 36°. In general, a smaller angle of repose represents a powder with good fluidity, resulting in a uniform supply of raw material. Otherwise, a supplemental power may be required for use of the copper carbonate as a
raw material in the second reaction to produce CuO. The characterization tests showed that the dissolution time of the copper carbonate in sulfuric acid was a function of the reactant molar ratio. The dissolution rate increased and then decreased in synchrony with the increment in the reactant molar ratio. If the stoichiometric ratios of CuCO$_3$ (m) and Cu(OH)$_2$ (n) in the alkali copper carbonate reaction are smaller, than the molar ratio of sodium carbonate, m, more CuCO$_3$ will be produced than Cu(OH)$_2$. In the case of a molar ratio of 1.20, where the value of m was equal to n, the angle of repose of the product was 39.6°, indicating decreased fluidity. The dissolution time of the product in sulfuric acid also increased. With a reactant molar ratio of 1.32, m is larger than n, which resulted in increased production of Cu(OH)$_2$ with a high copper content. Moreover, the dissolution time of the product in sulfuric acid increased. The best angle of repose for any of the synthesized products was 32.5°. With a reactant molar ratio of 1.44, the increase in the copper content of the product, and its dissolution time in sulfuric acid increased with an increase in the angle of repose. For the reactant molar ratio of 1.56, the dissolution time of the product in sulfuric acid decreased comparing to other cases, and the angle of repose increased to 43.3°. In the case of a high n, the product exhibited a high angle of repose, and a decrease in the dissolution time in sulfuric acid, because of smaller particle size of the product. As a result of these experiments, it was found that the best product physical properties were obtained at an optimum reactant molar ratio of 1.32.

3.2 Effect of the amount of sodium hydroxide in the second reaction step

In this study, 300 g of alkali copper carbonate, produced at 80°C and a reactant molar ratio of sodium carbonate to copper (II) chloride of 1.32, was reacted with sodium hydroxide to produce copper (II) oxide. The amount of sodium hydroxide in the second reaction ranged from 80 to 180 g. The XRD analysis of copper oxide produced using various amounts of sodium hydroxide indicated that 100 g of sodium hydroxide was sufficient to convert the copper carbonate completely to copper (II) oxide.

Fig. 4 shows the CuO content in the manufactured copper (II) oxide and chloride ion concentration according to the usage of sodium hydroxide. The CuO content increased with increasing sodium hydroxide usage. In contrast, the chloride ion concentration increased and then decreased with increasing sodium hydroxide usage. The chloride ion used in alkali copper carbonate surface is difficult to remove, while that attached on the surface of alkali copper carbonate may be easily removed by rinsing with water. Sodium hydroxide may disassemble the alkali copper carbonate and then convert into copper (II) oxide, removing chloride ions. The chloride ion concentration was relatively high at the sodium hydroxide usage of 100 g. The chloride ion concentration decreased to 6.6 mg at a sodium hydroxide usage of 120 g. The chloride ion concentration increased again from the sodium hydroxide usage of above 140 g. From those results, the removal of chloride ion was difficult at the hydroxide usage of 140g. Moreover, more rinsing with water was required because of increasing pH, as a result of the high usage of sodium hydroxide. Moreover, residual chloride ions formed a black film on the anode copper surface. The chloride ion control is very important, as it may form black film during electroplating, degrading the plating quality because of the chloride ions.

Fig. 5 shows that solubility and angle of repose of the copper (II) oxide product as a function of the quantity of sodium hydroxide in the reaction. As shown, the dissolution time of the copper oxide in sulfuric acid initially decreased and then increased with the increase of sodium hydroxide in the reaction mixture. The time for solvation of the copper oxide in sulfuric acid (37 s) was faster than the solvation of
the copper carbonate. The angle of repose of the copper oxide decreased and then increased with the increase in the quantity of sodium hydroxide in the reaction. The values for the angle of repose for the copper oxide were 34.6°, 33.8°, 33.5°, 33.6°, 33.8° and 34.0° for 120, 140, 160, and 180 g sodium hydroxide. Although there was some variation, these values were smaller than the criterion used for good fluidity; 36°. This did not seem to affect the fluidity of the copper oxide powder. Compared to the smaller angle of repose of the copper carbonate, the original angle of the copper oxide was maintained regardless of the particle size.

Fig. 6 shows the distribution of the particle size of the copper (II) oxide as a function of the amount of sodium hydroxide used. As shown, the particle size of the product decreased with the increase in the amount of sodium hydroxide. The sodium hydroxide, that converted the copper carbonate to copper (II) oxide, deformed the copper (II) oxide, which reduced the particle size of the powder during the decomposition reaction of the alkaline copper carbonate to copper (II) oxide and CO$_3^{2-}$. Moreover, the SPAN value and the particle size distribution for alkali copper carbonate were both 0.751, which indicated a very narrow size distribution. However, the SPAN value of copper (II) oxide was in the range 1.736-2.083, which represented a very wide particle size distribution. Based on the analysis of the particle size and size distribution, the particle size of the copper (II) oxide decreased and size distribution was wide as the amount of sodium hydroxide in the reaction mixture increased due to decomposition of the copper carbonate. Here again, the sodium hydroxide deformed the copper (II) oxide so that the particle size was reduced during the decomposition of the alkaline copper carbonate to copper (II) oxide.

Fig. 7 shows the SEM images of the shape of the copper (II) oxide particles, as a function of the quantity of sodium hydroxide in the reaction. The particle shape appeared to be the same regardless of the quantity of sodium hydroxide used in the range of 80 and 120 g. A portion of the particles’ surface appeared to be deformed from a spherical shape to a planar shape. The spherical particles were deformed at the higher concentrations of increased sodium hydroxide from 140 g to 180 g. This change in the shape of the particles shape reflected the effect of sodium hydroxide on the physical properties of the copper oxide. At concentrations of sodium hydroxide in excess of 140 g, the average shape of the copper oxide particles was changed from spherical to planar.

3.3. Characteristics of via-filling plating

A copper plating bath was prepared using the synthesized copper oxide and a number of additives. This bath was used to plate to fill holes in the blind via hole (BVH) board and the thickness of the plating of the inner wall of these holes was measured to be between 0.2 and 0.5 µm. The plating characteristics were evaluated from the plating thickness, and the diameter and depth of the hole using the standard dimple test. The small via-filling value represents uniform electrodeposition and favorable plating quality. Fig. 8 shows the results of via-filling using cop-
per oxide (II) produced using varying amounts of sodium hydroxide. At a sodium hydroxide content of 80 g, the via-filling was the deepest (74.0 µm). There was a lack of copper, because of the low CuO content in the internal recesses of the via-filling. The via-filling depth values were 19.8, 4.9, 7.8, 8.5, and 10 µm with the sodium hydroxide contents of 100, 120, 140, 160, and 180 g, respectively. The targeted via-filling value was 15 µm at a sodium hydroxide amount of 120 g. Excess sodium hydroxide may require more rinsing with water, which would increase the amount for wastewater for later treatment. Based on these results, the optimum sodium hydroxide content was set as 120 g.

4. Conclusions

Copper (II) oxide for electroplating was synthesized using a two-step non-sintering reaction beginning with using copper (II) chloride powder. The
experimental variables for the first reaction step were the quantity of sodium carbonate and reaction temperature, whereas the dependent variable in the second reaction step was sodium hydroxide concentration. The reaction parameters of each reaction step were investigated. The angle of repose, solubility in sulfuric acid, chlorine ion concentration, and via-filling hole thickness were tested to evaluate the quality of the copper oxide (II) for electroplating. The experimental results produced the following conclusions:

1. In the case of the alkaline copper carbonate, \( \text{CuCO}_3 \cdot \text{Cu(OH)}_2 \), the product of the first reaction, when \( m \) was larger than \( n \), the production of \( \text{CuCO}_3 \) was favored over \( \text{Cu(OH)}_2 \) when the mole reaction ratio of sodium carbonate was low. With an increase in the mole reaction ratio of sodium carbonate, \( m \) became smaller than \( n \), which decreased the production of \( \text{CuCO}_3 \) and increased the amount of \( \text{Cu(OH)}_2 \) produced. The optimum reactant molar ratio at a reaction temperature of \( 80^\circ C \) was 1.32, based on an optimum theoretical copper content of 57.5 wt.\%.

Fig. 8. Cross sectional areas after via-filling plating of copper (II) oxide with the amount of NaOH.
time in sulfuric acid, and angle of repose of the optimum copper carbonate product were 58.5 wt.%, 35.29 µm, 37 s, 1.15, and 32.5°.

2. The optimum amount of sodium hydroxide amount in the reaction mixture used to produce CuO was 120 g. In this reaction the sodium hydroxide was reacted with the alkaline copper carbonate produced in the first reaction step. The copper(II) content and chloride ion concentration of the product were 96.5 wt.% and 6.6 mg/L. The range of mean particle size, dissolution time in sulfuric acid, and angle of repose of the product ranged between 18.55 and 20.09 µm, 60 and 63 s, and 33.5 and 34.8°.

3. The via-hole filling depth of the copper oxide (II) at a sodium hydroxide usage of 120 g was 4.9 µm of the filling depth. This value satisfied the via-hole control range of <15 µm.

Acknowledgement

The present research was conducted by the research fund of Dankook University in 2015.

References