Manufacturing of Copper(II) Oxide Powder for Electroplating from NaClO_3 Type Etching Wastes

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ABSTRACT

In this study, copper (II) oxide powder for electroplating was prepared by recovering CuCl_2 from NaClO_3 type etching wastes via recovered non-sintering two step chemical reaction. In case of alkali copper carbonate $[\text{mCuCO}_3 \cdot \text{nCu(OH)}_2]$, first reaction product, CuCO_3 is produced more than Cu(OH)_2 when the reaction molar ratio of sodium carbonate is low, since m is larger than n . As the reaction molar ratio of sodium carbonate increased, m is larger than n and Cu(OH)_2 was produced more than CuCO_3 . In the case of m has same values as n , the optimum reaction mole ratio was 1.44 at the reaction temperature of 80°C based on the theoretical copper content of 57.5 wt. %. The optimum amount of sodium hydroxide was 120 g at 80°C for production of copper (II) oxide prepared by using basic copper carbonate product of first reaction. At this time, the yield of copper (II) oxide was 96.6 wt.%. Also, the chloride ion concentration was 9.7 mg/L. The properties of produced copper (II) oxide such as mean particle size, dissolution time for sulfuric acid, and repose angle were 19.5 mm, 64 second, and 34.8° , respectively. As a result of the hole filling test, it was found that the copper oxide (II) prepared with 120 g of sodium hydroxide, the optimum amount of basic hydroxide for copper carbonate, has a hole filling of 11.0 mm, which satisfies the general hole filling management range of 15 mm or less.

Keywords : Copper(II) Oxide, NaClO_3 Type Etching Wastes, Electroplating, Via-Filling Plating

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1. Introduction

An etching technique for removing unnecessary portions by etching is widely used when arranging necessary elements by any pattern such as semiconductor or PCB. When oxidizing and dissolving copper exposed to acid, a dry film acts as an etching resist and forms a circuit. Such an etching technique is to dissolve unnecessary copper components other than the circuit conductor by dissolving the copper of the inner or outer layer using an acid or alkali solution or forming the surface roughness. Hydrogen peroxide and sodium chlorate are the most commonly used etching agents for copper (II) chloride [1-3]. Among them, the sodium chlorate type (NaClO_3 type) is used in combination with sodium chloride

and other salts, and has a merit of less self-decomposition and less chlorine gas generation and high etching rate. Since the composition ratio of the PCB etching waste solution differs depending on each exhausting company, it is necessary to grasp the property and the contents in advance. Generally, in the case of sodium chlorate type, general copper is 13.0 ~ 15.0 wt.% and specific gravity is 38 ~ 43 kg/m^3 . These etchant wastes occur more than 50,000 tons a year and are designated as environmentally harmful substances because they are highly corrosive. Recently, as the interest in the increase of the raw material price of copper and the recycling of resources have increased, a variety of technologies for copper recovery have been developed. Therefore, in this study, copper (II) chloride for electrolytic plating is prepared by using copper chloride etching solution using sodium chlorate only and only the second step chemical reaction without sintering process.

Generally, copper (II) oxide is produced by reacting an acidic copper solution (CuCl_2 , CuSO_4 , or

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$\text{Cu}(\text{NO}_3)_2$ with a hydroxide (NaOH , KOH) or alkali carbonate to convert it to copper hydroxide ($\text{Cu}(\text{OH})_2$) or alkali copper carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), followed by calcination at 250 to 800°C [4-5]. However, when copper hydroxide is calcined, copper (I) oxide may be generated as a by-product at a high temperature of 400 to 800°C. Also this process requires high energy cost [6-8].

In this study, CuCl_2 was recovered from NaClO_3 type etching wastes and copper (II) oxide powder for electroplating was prepared via non-sintering two step chemical reaction. Experimental parameters production of copper (II) oxide were the amount of sodium carbonate added in the first step and the amount of sodium hydroxide added in the second step. Finally, via-filling plating was performed to evaluate the electroplating performance of the produced copper (II) oxide.

2. Experimental

2.1. Preparation of copper (II) oxide powder

Copper (II) oxide was prepared by two step reaction of copper chloride from Na_2CO_3 type etching wastes. In the first step reaction, basic copper carbonate [$m\text{CuCO}_3 \cdot n\text{Cu}(\text{OH})_2$] was prepared by reacting copper chloride with sodium carbonate (Na_2CO_3 99 wt.%, product of OCI) as shown in equations (1) and (2). The first reaction product of copper (II) oxide was prepared by reacting alkali copper carbonate with sodium hydroxide (NaOH , 99 wt.%, product of OCI) shown at the second reaction step as shown in equation (3) [9-10].

In order to prepare alkali copper carbonate, product of first reaction step, the reaction molar ratio of Na_2CO_3 type etching wastes to sodium carbonate was varied from 1.92 to 3.12. At this time, the reaction temperature was kept constant at 80°C. Also, the copper (II) oxide was prepared by reacting alkali copper carbonate of 300 g, prepared at the first reaction step,

in 2 liters of distilled water and reacting 60~200 g of 20 wt.% sodium hydroxide at 80°C for an hour.

2.2. Analysis of physical properties

In order to confirm the physical properties of the alkali copper carbonate and copper (II) oxide prepared through the second reaction step, the dissolution time, repose angle, particle analysis, and apparent specific gravity of sulfuric acid were evaluated. The repose angle was measured using an angle-of-inclination measuring device, BT-200D model, product of K-ONE, and particle size analyzer, Better-size model BT-2000, product of K-ONE, was used to confirm the flow characteristics of the powder. In the particle size analysis, D_{50} is the particle size of 50% in the distribution of the sample to be measured, which means the particle size median. The SPAN is the distribution width of the sample, which is calculated as $(D_{90} - D_{10})/D_{50}$ value. A smaller value of SPAN means that the particles are uniformly distributed. SEM, CX-20 model, product of COXEM, was used to observe the particle morphology.

2.3. Via-Filling plating analysis

Via-filling plating analysis was performed using a Harring cell electrolyzer [9]. To prevent corrosion of titanium, positive electrode plate coated with 1mm of iridium (IrO_2), which has highly corrosion resistant, was used for the insoluble anode. Base copper was used for the blind via hole, BVH, on the cathode. The plating solution for Harring cell plating was prepared by adding 0.8 mL/L of EVF brightener (Dow Chemical Co. Ltd.) based on 210 g/L of sulfuric acid, 70 g/L of copper oxide (II) and 50 mg/L, and 8 mL/L of EVF leveler (Dow Chemical Co. Ltd.). For the plating process of Harring cell plating, air agitator was attached and then plated at the current density of 2 A/dm² for an hour. After the plating, the cut surfaces of the specimens were observed with a metal microscope (MX51, Olympus Co. Ltd.).

3. Results and Discussion

3.1. Characteristics of basic copper carbonate manufacture

In order to prepare basic copper carbonate, the first step reaction product in the copper (II) oxide production process using the two step chemical reaction, NaClO_3 type etching wastes were used as the reaction

Fig. 1. Particle size distribution of basic copper carbonate as a function of $\text{Na}_2\text{CO}_3/\text{CuCl}_2$ mole ratio.

mole ratio of sodium carbonate.

Fig. 1 shows the particle size analysis of basic copper carbonate produced according to the molar ratio of NaClO_3 type etching wastes to sodium carbonate. The D50 values were 35.69 mm, 38.66 mm, 48.41 mm, 49.36 mm, 44.10 mm, and 36.88 mm for reaction mole ratio of 1.08, 1.20, 1.32, 1.44, 1.68, and 2.04, respectively. Also the SPAN values, indicating distribution of particles, were 1.653, 0.871, 0.763, 0.712, 0.781, and 1.068 for reaction mole ratio of 1.08, 1.20, 1.32, 1.44, 1.68, and 2.04, respectively. From this figure, it was confirmed that particle size increases and decreases with increasing reaction mole ratio. Also, the SPAN value decreased with increasing reaction mole ratio. When the reaction mole ratio was 1.08, the particle size was the smallest. It was confirmed that the SPAN value is broadest in the largest particle distribution. The lower the reaction molar ratio, the more the sodium chloride-based etching waste solution is used and the lower the pH (≈ 6.3) due to the high content of copper chloride in the etching solution and the hydrochloric acid. By decomposing the particles of basic copper carbonate produced, it is considered that the average particle size is small and the particle distribution is broadly formed together. In the case of the reaction molar ratio of 1.20, as the reaction molar ratio is 1.08, the amount of the sodium chlorate-based etching waste solution is larger than that of the sodium carbonate, so that the pH value of 7.1 is relatively low so that some of the particles are destroyed and the average particle size becomes smaller, and the particle distribution is also broadly formed. The reaction mole

Fig. 2. Variation in dissolution time of copper carbonate in H_2SO_4 and repose angle as a function of $\text{Na}_2\text{CO}_3/\text{CuCl}_2$ mole ratio.

ratio of 1.32 was also found to be small as the reaction mole ratio increased and the particle size increased. This means that the particle distribution is formed relatively narrowly. When the reaction mole ratio was 1.44, the particle size was the largest and the SPAN was the smallest. When the reaction mole ratio was 1.68, the particle size decreased again and the SPAN value also increased. When the molar ratio of sodium carbonate is low, the value of m in basic copper carbonate $[m\text{CuCO}_3 \cdot n\text{Cu}(\text{OH})_2]$ becomes larger than n , and when the molar ratio of reaction is high, the value of n becomes large, so that the alkaline ratio is high and thus changed the particle size of the basic copper carbonate[11].

Fig. 2 shows the solubility to sulfuric acid and the repose angle of basic copper carbonate prepared according to the molar ratio of NaClO_3 type etching wastes and sodium carbonate. With increase of the reaction molar ratio, the solubility of basic copper carbonate in the first reaction increased with sulfuric acid. Also, the repose angle of the basic copper carbonate produced decreased with increasing reaction molar ratio. The apparent specific gravity tended to increase with increasing reaction molar ratio and then decreased. The apparent specific gravity tended to increase with increasing reaction molar ratio and then decreased. The dissolution time to sulfuric acid was the shortest in the range of 55~57 second for the reaction molar ratio of between 1.08 and 1.20. the disso-

lution time to sulfuric acid was increased as the reaction molar ratio increased. The longest reaction time was 79 second at the reaction molar ratio of 2.04. It is considered that the dissolution time is fast due to the low content of copper and the short reaction time with sulfuric acid due to the inclusion of some basic copper chloride compound in the range between 1.08 and 1.20 where the reaction molar ratio is low. As the reaction molar ratio increases, the reaction time with sulfuric acid increases as the content of copper increases. In the case of repose angle, when the reaction mole ratio was at the range between 1.08 and 1.20, it was measured at $41.8^\circ \sim 47.8^\circ$, which indicates poor flowability of the powder. This is because the pH is lowered by the copper chloride (II) and hydrochloric acid present in the NaClO_3 type etching wastes, so that the generated particles of basic copper carbonate are decomposed to form particles having a small size, high repose angle due to wide range of distribution, and the low specific gravity of $0.72 \sim 0.90$. From the reaction molar ratio above 1.32, the repose angle tended to decrease. This is because the amount of sodium chlorate-based etching waste solution usage in sodium carbonate is decreased, and the decomposition ratio of particles is low due to strong acid so that constant particle shape has progressed. When the reaction molar ratio was 2.04, the tendency of the particles to become fine particles due to alkalinity was confirmed even when the amount of the hydrogen peroxide-based etching waste solution used for sodium carbonate was excessive. For this reason, when the particles are formed too small, the repose angle is high and the flowability of the powder is lowered, and thus the apparent specific gravity also tends to decrease. The particle size is related to the repose angle and the apparent specific gravity. It is well known that the average particle size of the basic copper carbonate, the primary product, is low, because the repose angle is increased. At the reaction mole ratio of 1.44, and the repose angle and the apparent specific gravity were 33.2° and 1.28, respectively. This suggests that the optimum conditions for the reaction of the sodium peroxide with the hydrogen peroxide etching waste solution are shown. The repose angle is less than 36° indicates very good flowability. Therefore, the raw material can be supplied constantly by flowing down the powder at the time of measurement. If it is more than that, a driving force is required. At the molar ratios of 1.32 and 1.62,

the repose angle was 35.3° and 36.2° , respectively. When the repose angle was measured, it was confirmed that the powder was falling down by itself. For the reaction molar ratios of 1.08, 1.20, and 2.04, the repose angle was 47.8° , 41.8° , and 38.9° , respectively. In this case, since the repose angle is 36° or more, it can be confirmed that it is physically supplied and measured. Therefore, the optimum molar ratio of sodium carbonate to the reaction molar ratio of sodium carbonate based on the particle size of basic copper carbonate, dissolution time to sulfuric acid, and repose angle, 36° or less, was 1.44.

3.2. Fabrication characteristics of copper (II) oxide

In this paper, sodium hydroxide was added to 300 g of basic copper carbonate, Cu content of 58.3 wt.%, sodium hydroxide prepared at a reaction molar ratio of 1.44 NaClO_3 type etching wastes and sodium carbonate at reaction temperature of 80°C . The usage of sodium hydroxide was varied in the range of 60 g to 200 g. Fig. 3 shows changes in CuO content and chloride ion concentration of copper (II) oxide prepared according to the sodium hydroxide usage. The CuO contents were 93.6 wt.%, 95.5 wt.%, 96.0 wt.%, 96.6 wt.%, 97.0 wt.%, and 97.4 wt.%, for sodium hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 200 g, respectively. Also the pH values were 9.5, 10.2, 10.7, 12.4, 12.7, and 12.8, for sodium hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 200 g, respectively. It was confirmed that the

Fig. 3. Variation of CuO content and Cl^- concentration with the amount of NaOH.

CuO content and the pH were increased as the use amount of sodium hydroxide was increased. In addition, the basic copper carbonate produced had a chloride ion content of 198 mg/L, which can be reduced by using an alkali solution, such as sodium hydroxide. The chlorine ion contents were 28.5, 20.7, 12.5, 9.7, 13.7, and 16.2 mg/L for sodium hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 200 g, respectively. From those results, it can be deduced that the chloride ion concentration decreased and increased as the amount of sodium hydroxide was increased. This is because, in the case of basic copper carbonate, the chlorine ion attached to the surface can be removed during washing the basic copper carbonate, but the chlorine ion contained therein is hardly removed. This means that sodium hydroxide is used to decompose basic copper carbonate and convert it to copper oxide (II), which is effective in removing chlorine ions. The sodium hydroxide usage should be optimized during the process. When sodium hydroxide usage was 60 to 80 g, it was converted into copper oxide (II), but the content of copper oxide (II) was measured to be low. It is considered that chlorine ions are present at a high level of 20.7 to 28.5 mg/L because some of them remain unconverted. When sodium hydroxide was used more than 100 g, chlorine ion was decreased slightly, it was 12.6 mg/L. When sodium hydroxide usage was 120 g, the best result was obtained as 9.7 mg/L. The chlorine ion content was increased again higher than 160 g of sodium hydroxide usage. From those results, when sodium hydroxide usage was 160 g or more, there was difficult to the decomposition of chlorine ion, the pH was increased so that unnecessary washing water is increased, and the residual chlorine ion is increased again. Therefore, it may be deduced that the optimum sodium hydroxide usage for converting basic copper carbonate into copper (II) oxide is 120 g, which has the lowest level of CuO content of 96.6 wt.% and chlorine ion of 9.7 mg/L.

Fig. 4 shows the particle distribution of copper (II) oxide produced according to the amount of sodium hydroxide. As the amount of sodium hydroxide increased, the particle size decreased and the SPAN value increased slightly. The D50 values were 21.09 μm , 19.46 μm , 19.02 μm , 19.49 μm , 18.38 μm , and 18.01 μm for hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 200 g, respectively. Also the SPAN values, indicating distribution

Fig. 4. Particle size distribution of copper (II) oxide with the amount of NaOH.

of particles, were 1.462, 1.508, 1.511, 1.551, 1.584, and 1.590 for hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 200 g, respectively. When sodium hydroxide with strong alkalinity is used for converting from basic copper carbonate into copper (II) oxide, during the decomposition of basic copper carbonate into copper (II) oxide and carbonate (CO_3^{2-}), the average particle size of basic copper carbonate decreased from 49.36 μm to 18.01 ~ 21.09 μm . It is considered that when the molecular weight of basic copper carbonate $m\text{CuCO}_3 \cdot n\text{Cu}(\text{OH})_2$ is decomposed by sodium hydroxide $(m+n)\text{CuO}$ is formed, resulting in a smaller molecular weight and smaller particle size. In the case of basic copper carbonate, the SPAN value was as small as 0.712, and the particle distribution was densely formed. However, after the second step reaction, the copper carbonate was decomposed and the SPAN value was widely distributed in the range of 1.462 ~ 1.590. Therefore, from the particle size and particle distribution analysis results, as the sodium hydroxide usage was increased, the particle size of copper (II) oxide was small and the particle distribution was wide due to the decomposition of copper carbonate.

Fig. 5 is a scanning electron microscope (SEM) image showing the shape change of copper (II) oxide particles produced according to the amount of sodium hydroxide used. When sodium hydroxide was used at 60 g and 80 g, the particle size was not significantly changed from the particle structure formed in the copper carbonate. However, when the amount of sodium hydroxide dosage was more than 100 g, it was confirmed that the particle structure of

Fig. 5. SEM micrographs of copper (II) oxide with the amount of NaOH.

the surface layer was slightly broken from the spherical shape, but the shape of the particle was not largely changed. As shown in this figure, it may be confirmed once again that there is no significant difference in particle size according to the sodium hydroxide dosage. In case of sodium hydroxide, which is a strong alkaline substance, when basic copper carbonate is converted to copper oxide (II), basic copper carbonate is decomposed copper (II) oxide and carbonate (CO_3^{2-}), when the amount of sodium hydroxide used in the powder is more than 100 g, it is considered that the shape of the particles is converted into copper oxide (II) without any significant deformation. Therefore, the sodium hydroxide in an amount of 100 g or more did not change the shape of the particles.

Fig. 6 shows the solubility and repose angle of copper (II) oxide prepared according to the sodium hydroxide dosage. The dissolution time for sulfuric acid decreased with increasing use of sodium hydroxide, and increased to 62 seconds at 120 g of sodium hydroxide usage, and then increased again with increase of sodium hydroxide usage. The dissolution time to sulfuric acid were 77, 70, 64, 62, 68, and 81 seconds for the sodium hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, 180 g, respectively.

The dissolution time to sulfuric acid of basic cop-

Fig. 6. Variation in dissolution time of copper carbonate in H_2SO_4 and repose angle as a function of the amount of NaOH.

per carbonate, the first reaction product, was 64s.

The dissolution time to sulfuric acid of copper (II) oxide, the second reaction product, was higher than that of the first reaction product when sodium hydroxide was used in an amount of 80g or less and 160 g or more. However, at sodium hydroxide usage of 100 to 120 g, it was found that the similar time was

increased in the range of 62 to 64 seconds. The values of repose angle were 34.2° , 34.5° , 34.7° , 34.8° , 35.5° , and 36.5° for sodium hydroxide usage of 60 g, 80 g, 100 g, 120 g, 160 g, and 180 g, respectively. As sodium hydroxide usage was increased, the repose angle of copper (II) was slightly higher than that of basic copper carbonate, 33.2° . However, the result satisfies criteria of flowability, 36° or less, which represents that the hydroxide usage rarely affects the flowability of the powder. It is confirmed that, when the basic repose angle of basic copper carbonate is used, most of the original repose angle is maintained in the flowability of the powder even if the particle size is small due to sodium hydroxide.

3.3. Characteristics of via-filling plating

The substrates used in this study were those coated

with electrolysis copper on the inner walls of the holes to provide conductivity. The plating test results are judged based on the hole filling test that satisfies the filling of the plating on the inner wall of the hole based on the plating judgment criteria. The lower the value of the hole-filling is, the more the plating film is uniformly deposited in the hole and the quality of the plating state is evaluated to be good [9]. Fig. 7 shows hole-filling in alkali copper carbonate according to the amount of sodium hydroxide used. When the amount of sodium hydroxide used was 60 g and 80 g, the hole filling was found to be 20.9 mm and 17.7 mm, respectively. It was confirmed that the hole filling was formed at a low level. This is because CuO content is low and copper ion is insufficient and chlorine ion is relatively high, so that the via-filling depth was high during plating. The hole filling depth

Fig. 7. Cross sectional areas after via-filling plating of copper (II) oxide with the amount of NaOH.

were 11.9 mm, 11.0 mm, and 14.5 mm for the usage of hydroxide of 100 g, 120 g, and 160 g, respectively. Those values satisfy the hole filling management range is less than 15.0 mm. On the other hand, when the amount of sodium hydroxide was 200 g, the hole-filling was 16.3 mm. This is because the higher content of CuO and the higher chloride ion concentration lead to an increase in the hole filling value. This is attributed to the impurities that may not be cleaned by using the same amount of wash water under the same conditions due to excessive introduction of sodium hydroxide. Therefore, when using 120 g of sodium hydroxide, the hole filling was the best at 11.0 mm, and the higher the CuO content and the lower the chloride ion, the better the hole filling.

4. Conclusions

In this paper, copper oxide (II) for electrolytic plating was prepared by a two steps of chemical reaction without sintering from a copper chloride etching waste by using sodium chlorate as an etching agent in PCB etching process. The results were as follows:

1. In case of alkali copper carbonate [$m\text{CuCO}_3 \cdot n\text{Cu(OH)}_2$], first reaction product, CuCO_3 is produced more than Cu(OH)_2 when the reaction molar ratio of sodium carbonate is low, since m is larger than n . As the reaction molar ratio of sodium carbonate increased, m is larger than n and Cu(OH)_2 was produced more than CuCO_3 . In the case of m has same values as n , the optimum reaction mole ratio was 1.44 at the reaction temperature of 80°C based on the theoretical copper content of 57.5 wt.%.

2. The optimum amount of sodium hydroxide was 120 g at 80°C for production of copper (II) oxide using alkali copper carbonate, the first reaction product. At this time, the yield of copper (II) oxide was 96.6 wt.%. Also, the chloride ion concentration was 9.7 mg/L. The properties of produced copper (II)

oxide such as mean particle size, dissolution time for sulfuric acid, and repose angle were 19.5 mm, 64 seconds, and 34.8°, respectively.

3. From the hole filling test results, it was found that the copper oxide (II) prepared with 120 g of sodium hydroxide, the optimum amount of basic hydroxide for copper carbonate, has a hole filling of 11.0 mm, which satisfies the general hole filling management range of 15 mm or less.

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