Preparation of Nano-Powders of p-Type Transparent Conductive Copper Aluminum Oxide by Co-Precipitation Method

Hsin-Chun Lu, Jo-Ling Lu, Chun-Lung Chu, Chi-You Lai, Gwo-mei Wu

Department of Chemical Engineering and Materials Engineering, Chang Gung University
259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan, Taiwan, 333, R.O.C

Abstract—Nano-powders of p-type transparent conductive copper aluminum oxide (CAO) have been successfully synthesized by co-precipitation method. By adding sodium hydroxide into the mixed solution of copper chloride and aluminum chloride, co-precipitate precursors of CAO with particle size around 50-60 nm were produced. After washing, filtering, and drying of the co-precipitates, nano-powders of CuAlO2 were produced when the dried co-precipitate precursors were calcined at temperature above 1100 °C. By aging at pH=3.5 for six hours and co-precipitating at pH=8.0, the atomic ratio of Cu/Al of the nano-powders can be maintained throughout the synthesis. After calcining at 1200°C in air for 4 hours, the CAO co-precipitate precursors totally transformed into nano-powders of CuAlO2 with crystal size around 64 nm. Continued calcining at 1200°C above 4 hours led to the decomposition of CuAlO2 into nano-powders of CuAl2O4 and volatile CuO with no significant change in crystal size. Finally, it was found that by calcining under inert atmosphere, the decomposition of CuAlO2 could be suppressed at the expense of decreasing its crystallinity.

I. INTRODUCTION

The development of p-type transparent conducting oxides (TCO) is one of the most crucial technologies for p-n junction-based devices such as transparent solar cells and transparent light emitting diodes. Among various materials, copper aluminum oxide (CAO) with the molar ratio Cu/Al=1, i.e. CuAlO2, and with delafossite structure has been known as one of the p-type TCO materials for potential industrial applications. Since TCO sputtering targets with excellent properties can be prepared, but the characteristics of the sputter-deposited thin films can also be enhanced. Among the different methods that can produce CuAlO2 powders, co-precipitation method is the easiest to scale up for industrial production.

In this article, we report the synthesis of crystalline CuAlO2 nano-powders by co-precipitation method. In addition, the effects of calcination temperature, calcinations time, and calcinations atmosphere on the properties of CuAlO2 nano-powders are also reported.

II. EXPERIMENTAL PROCEDURES

The detailed experimental procedure for the preparation and characterization of CAO nano-powders is shown in Fig. 1. Aluminum chloride (AlCl3) and copper chloride di-hydrate (CuCl2·2H2O) with the molar ratio of Cu/Al=1 were dissolved separately in de-ionized water and the solutions were continuously stirred until they became clear. The two solutions were then mixed thoroughly before the addition of the precipitant, sodium chloride (NaOH). The co-precipitation process was carried out in two steps: the pH of the solution was first adjusted to 3.5 by adding adequate amount of NaOH and the solution was allowed to age for 6 hours; the solution pH was then adjusted again to the final pH value by adding NaOH to obtain the co-precipitate precursors of CAO. The co-precipitates were repeatedly washed and filtered several times before being dried. The dried co-precipitate precursors were then calcined under different conditions. Finally, the calcined powders were pressed to form 1 cm diameter pellets and these pellets were sintered at 1200°C for 8 hours under different atmospheric conditions.

The morphology and the compositions of the co-precipitate precursors, the calcined powders, and the sintered pellets were analyzed by scanning electron microscopy (SEM) (Hitachi S-3000N) and energy dispersive X-ray spectroscopy (EDS) (HORIBA, EMAX-ENERGY, EX-200). The structure and the crystal size of the calcined powders were characterized by X-ray diffractometry (Bruker’s XAS D5005, Kα). Finally, the resistance of the sintered pellets was measured by a four-point probe (Mitsubishi MCP-T600).

CuAlO2 thin films can be prepared by PLD (pulsed laser deposition) [3], spray pyrolysis [4], chemical vapor deposition [5], dip-coating [6], sputtering [7-10]. Due to the advantages of being able to continuously produce high quality thin films at low deposition temperature and the capability for large area coating, sputtering is the main deposition method used in the industry to produce TCO thin films. Therefore, how to improve the properties of the TCO sputtering targets and the sputter-deposited TCO thin films has always been a very important research topic for both the academia and the industry.

The properties of sputtering targets and sputter-deposited thin films are greatly influenced by the characteristics of the powders that are used to prepare the sputtering targets. Therefore, by using high quality powders, not only sputtering targets with excellent properties can be prepared, but the characteristics of the sputter-deposited thin films can also be enhanced. Among the different methods that can produce CuAlO2 powders, co-precipitation method is the easiest to scale up for industrial production.
III. RESULTS DISCUSSION

A. Effect of Calcination Temperature

Fig. 2 shows the XRD patterns of the powders produced by calcining the dried co-precipitate precursors of CAO with molar ratio Cu/Al=1 in air for 4 hours at different temperatures. For the co-precipitates calcined at 1000°C, only diffraction peaks of CuO and CuAl2O4 could be identified in the diffraction pattern (Fig. 2a). However, when the calcination temperature was raised to 1100°C, diffraction peaks of CuAlO2 can also be found in the diffraction pattern (Fig. 2b) in addition to those of CuO and CuAl2O4. Finally, when the calcination temperature was raised to 1200°C, almost all the diffraction peaks from CuO and CuAl2O4 are disappeared and only those of CuAlO2 can be identified in the diffraction pattern (Fig. 2c). Experimental results of Park et. al. [11] indicated that when the mixture of CuO and Al2O3 was heated between 1069°C and 1095°C, the mixture transformed into CuAlO2 powders with Rhombohedral structure. However, when the mixture was heated above 1300°C, significant weight loss and phase separation were observed. From the literature and the experimental results shown above, it can be inferred that when the dried co-precipitates were calcined below 1100°C, the amorphous precursors first transformed into CuO and CuAl2O4. The absence of CuAlO2 from the calcined powders indicates that there was not enough energy to transform CuO and CuAl2O4 into CuAlO2 according to the following reactions:

\[
\text{CuO} + \text{CuAl}_2\text{O}_4 \rightarrow \text{CuAlO}_2 + \frac{1}{2}\text{O}_2
\]  

However, when the calcination temperature was raised above 1100°C, there was enough energy for CuO and CuAl2O4 to react and to transform into CuAlO2 according to (1). When calcined at 1200 for 4 hours in air, almost all the CuO and CuAl2O4 in the calcined powders were transformed into CuAlO2.

Table 1 shows the results of EDS determination of Cu/Al molar ratio and crystallite size estimation of the powders shown in Fig. 2 as well as the resistance measurements of the pellets prepared from these powders. It can be observed from Table 1 that both the Cu/Al molar ratio of the calcined powders and the resistance of the sintered pellet decreased as the calcination temperature increased while the crystallite size increased with the calcination temperature. Because CuO gradually decomposes to Cu2O when heated above 1000°C and the melting point of Cu2O is 1232°C, the Cu/Al molar ratio of the calcined powders decreased when the calcination temperature increased.

![Fig.2. XRD patterns of the nano-powders prepared from calcination of the dried co-precipitates in air for 4 hours at (a) 1000°C, (b) 1100°C, and (c) 1200°C.](image-url)
due to the evaporation of copper [12]. The crystallite sizes estimated from the XRD pattern and the Scherrer formula are between 54 nm and 64 nm with the crystallite size increased with calcination temperature. From the resistance measurements of the pressed and the sintered pellets, it is obvious that pellets made from the CAO powders calcined at 1200°C possess the lowest resistance. This can be attributed to the fact that these pellets were prepared from the calcined CAO nano-powders with the molar ratio Cu/Al=1 and with CuAlO₂ Rhombohedral structure.

### B. Effect of Calcination Time

Fig. 3 shows the XRD patterns of the powders produced by calcining the dried co-precipitate precursors of CAO with molar ratio Cu/Al=1 at 1200°C in air for different time. From these XRD patterns, it is obvious that the intensities of the diffraction peaks for the co-precipitates calcined for 6 hours are most intense, indicating that these powders possess best crystallinity and largest crystallite size (Table 2). However, when the calcination time exceeded 4 hours, diffraction peaks of CuAl₂O₄ can be found in the XRD diffraction patterns. In addition, the intensities of diffraction peaks of CuAl₂O₄ decreased when the calcinations time exceeded 6 hours. When extending the calcination of the co-precipitates at 1200°C, more CuO decomposed and escaped through evaporation from the calcined powders, leading to the decrease of Cu/Al molar ratio (Table 2). According to the Le Chatelier's principle, the equilibrium shifts toward the backward reaction in (1), i.e. CuAl₂O₄ decomposing to CuO and CuAlO₂. This leads to the re-appearance of CuAl₂O₄ in the calcined powders and the decrease in the intensities of the diffraction peaks of CuAl₂O₄. From the resistance measurements of the pressed and the sintered pellets, it is obvious that the pellet sintered for 4 hours possesses the lowest resistance. This can again be attributed to the fact that this pellet possesses the exact stoichiometry of CuAl₂O₄ with the molar ratio of Cu/Al=1.

### C. Effect of Calcination Atmosphere

Fig. 4 shows the XRD patterns of the powders produced by calcining the dried co-precipitate precursors of CAO with molar ratio Cu/Al=1 at 1200°C for 4 hours under different atmospheric conditions. It can be observed from Fig. 4 that the intensities of the diffraction peaks for the co-precipitates calcined at 1200°C in air are most intense, indicating that these powders possess best crystallinity and largest crystallite size (Table 3). However, for the co-precipitates calcined under inert atmosphere (N₂ or Ar), there is no evidence from the XRD patterns indicating the existence of CuAl₂O₄. According to the Le Chatelier's principle, the equilibrium shifts toward the forward reaction in (1), i.e. CuO and CuAl₂O₄ combining to form CuAl₂O₄, under oxygen-deficient or inert atmospheric environment. This explains why there was no CuAl₂O₄ observed in the powders calcined in N₂ or Ar. However, for CuO and CuAl₂O₄ to transform to CuAl₂O₄, these two compounds must first transform from the amorphous co-precipitate precursors to the respective crystalline metal oxides. Under oxygen-deficient inert atmospheric environment such as N₂ or Ar, both the amorphous

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**Table 2**

Properties of CAO powders and pellets prepared from co-precipitates calcined at 1200°C in air for different time

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Cu/Al of ratio calcined powders</th>
<th>FWHM (2θ =38°)</th>
<th>Crystal size (nm)</th>
<th>Pellets resistance before sintering(Ω)</th>
<th>Pellets resistance after sintering(Ω)</th>
<th>Cu/Al of the sintered pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.01</td>
<td>0.217</td>
<td>63.88</td>
<td>1.93×10⁴</td>
<td>2.39×10⁵</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>0.98</td>
<td>0.216</td>
<td>64.18</td>
<td>3.60×10⁴</td>
<td>5.68×10⁵</td>
<td>0.97</td>
</tr>
<tr>
<td>8</td>
<td>0.96</td>
<td>0.219</td>
<td>63.30</td>
<td>3.96×10⁴</td>
<td>7.26×10⁵</td>
<td>0.94</td>
</tr>
</tbody>
</table>

**Table 3**

Properties of CAO powders and pellets prepared from co-precipitates calcined 1200°C for 4 hours under different atmospheric conditions

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Cu/Al of ratio calcined powders</th>
<th>FWHM (2θ =38°)</th>
<th>Crystal size (nm)</th>
<th>Pellets resistance before sintering(Ω)</th>
<th>Pellets resistance after sintering(Ω)</th>
<th>Cu/Al of the sintered pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.01</td>
<td>0.217</td>
<td>63.88</td>
<td>1.93×10⁴</td>
<td>2.39×10⁵</td>
<td>1.00</td>
</tr>
<tr>
<td>Ar</td>
<td>N/A</td>
<td>0.228</td>
<td>60.801</td>
<td>6.58×10⁴</td>
<td>1.15×10⁵</td>
<td>N/A</td>
</tr>
<tr>
<td>N₂</td>
<td>1.26</td>
<td>0.262</td>
<td>52.911</td>
<td>1.40×10⁴</td>
<td>6.04×10⁵</td>
<td>1.01</td>
</tr>
</tbody>
</table>
to crystalline transformation and the CuAlO$_2$ formation will be slow compared to those in air. These probably lead to the observed decrease in both the intensities of the diffraction peaks and the crystallite size of CuAlO$_2$ for the powders calcined in N$_2$ or Ar. From the resistance measurements of the pressed and the sintered pellets, it is obvious that pellets made from the CAO powders calcined in air possess the lowest resistance. This can again be attributed to the fact that this pellet possesses the exact stoichiometry of CuAlO$_2$ with the molar ratio of Cu/Al=1.

IV. CONCLUSIONS

From the experiment results, it is evident that nano-powders of p-type transparent conductive copper aluminum oxide can be synthesized by co-precipitation method. By calcining the dried co-precipitate precursors at temperature above 1100$^\circ$C, nano-powders of CuAlO$_2$ were produced. After calcining at 1200$^\circ$C in air for 4 hours, the CAO co-precipitate precursors totally transformed into nano-powders of CuAlO$_2$ with crystal size around 64 nm. Continued calcining at 1200$^\circ$C above 4 hours led to the decomposition of CuAlO$_2$ into nano-powders of CuAl$_2$O$_4$ and volatile CuO with no significant change in crystal size. Finally, it was found that by calcining under inert atmosphere, the decomposition of CuAlO$_2$ could be suppressed at the expense of decreasing its crystallinity.

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