Growth of delafossite CuAlO\textsubscript{2} single crystals in a reactive crucible

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Abstract

Delafossite oxide CuAlO\textsubscript{2} has received great attention as a promising p-type conducting oxide. In this work, high-quality CuAlO\textsubscript{2} single crystals with a size of several millimeters (mm) are successfully synthesized with a reactive crucible melting method. The crystals are characterized by x-ray diffraction, scanning electron microscopy with energy-dispersive spectroscopy, transport measurement, and magnetic susceptibility measurement. The CuAlO\textsubscript{2} single crystals show semiconducting behavior with hole carriers, which is consistent with other crystals grown by the conventional slow-cooling method. This growth method we reported here eliminates the process of removing the remaining flux, allowing easy access to the high-quality single crystals. This new approach to growing high-quality delafossite oxide CuAlO\textsubscript{2} with a few mm size is important for new technologies that demand p-type semiconductor-based device fabrication.

Keywords: delafossite, growth mechanism, CuAlO\textsubscript{2}

(Some figures may appear in colour only in the online journal)

1. Introduction

Delafossite CuAlO\textsubscript{2} (CAO) is highly attractive as a p-type metal oxide owing to its excellent conductivity compared to other p-type semiconductors [1–3]. Moreover, CAO exhibits high optical transmittance of up to 70\% in a thin regime [2, 4, 5], drawing more attention to its potential application for optoelectronic devices. Mainly, CAO has been synthesized in thin films and polycrystalline powders, where defects and impurities predominantly determine transport and optical properties. The first CAO single crystals were synthesized by Shannon \textit{et al} using a hydrothermal reaction [6], which was widely used to grow delafossite compounds. However, the size of crystals grown in the method was small. To resolve the difficulty, Ishiguro \textit{et al} reported a slow-cooled method used copper oxide as flux [7]. In this method, a complex procedure is required to eliminate the copper oxide Cu\textsubscript{2}O flux; for example, the single crystals are put in HNO\textsubscript{3} at 100 °C for four days to resolve the remaining flux [7]. Therefore, the development of a simple method to grow high-quality and large-sized CAO single crystals is needed for further investigation of its intrinsic properties as well as their application to electronic and optical devices.

According to the literature that reports on the Cu–Al–O phase diagram, a CuAlO\textsubscript{2} phase would be obtained from mixed starting reagents of Cu\textsubscript{2}O with Al\textsubscript{2}O\textsubscript{3} at high temperature (>1100 °C) [8]. Furthermore, Cu\textsubscript{2}O powders are easily evaporated at high temperatures, which may promote the reaction between the vaporized Cu\textsubscript{2}O flux and the Al\textsubscript{2}O\textsubscript{3} crucible. In this context, the vaporized (or melted) Cu\textsubscript{2}O flux can react to the surface of the alumina crucible, producing the CAO phase through the following reactions: Cu\textsubscript{2}O (flux) + Al\textsubscript{2}O\textsubscript{3} (crucible) → 2 CuAlO\textsubscript{2} (crystal). In this study, we report a
unique method to synthesize high-quality CAO single crystals on the millimeter (mm) scale. Cu$_2$O powders are solely heated in the alumina crumble at high temperatures; then, Cu$_2$O powders react with Al$_2$O$_3$ crucible, resulting in mm-sized CAO single crystals. We confirmed that the CAO single crystals are p-type semiconductors showing paramagnetic behavior, which is in good agreement with other crystals grown by the conventional slow-cooling method.

2. Experiments

High-quality mm-sized CAO single crystals were grown by the deliberate reaction between Cu$_2$O flux and Al$_2$O$_3$ crucible. Only Cu$_2$O powder (0.5–2.5 g) was put into the alumina crucible (99.9% purity), which was not covered by a lid. The lidless crucible allows the supersaturation state of CAO in the evaporating Cu$_2$O flux. The crucible was located inside a box furnace and heated to 1225 °C. After holding the temperature at 1225 °C for 12 h, the furnace was cooled at a rate of 0.5–1 °C h$^{-1}$ to 1150 °C, then cooled to room temperature at a rate of 150 °C h$^{-1}$. Many shiny and thin hexagonal plate-like CAO crystals were obtained. The obtained crystals were mechanically isolated from the alumina crucible. CAO single crystals are usually 1 mm × 1 mm. The crystal structure of CAO was examined by x-ray diffraction (XRD) with Cu Kα radiation (Bruker D8 Discover x-ray Diffractometer installed in Quantum Matter Core-Facility of Pusan National University). The structural analysis was performed with the help of Full-Prof Suite software. The chemical composition was obtained by scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS). Temperature dependence of the resistivity and magnetic susceptibility were measured with a vacuum probe station and a magnetic properties measurement system at Pusan National University. For the Hall measurement, surface of CAO single crystal was polished to reduce the thickness down to 81.9 μm. To make an ohmic contact, 10 nm-thick Ti and 200 nm-thick Au contact electrons were deposited and thermally annealed in vacuum (<10$^{-4}$ Torr) at 400 °C for 30 min. Hall measurement have carried out in HMS-3000 Hall measurement system under magnetic field of 0.5 T at 300 K.

3. Results & discussions

Figures 1(a)–(d) illustrate the single crystal growth process. At high temperatures, CAO phases were synthesized at the interface of Cu$_2$O flux and alumina crucible by the chemical reaction. At the same time, some of the flux is evaporated, generating a supersaturated solution of CAO and Cu$_2$O. Figures 1(a) and (b) describe the process of supersaturation, in which the concentration of CAO (black) increases. Since supersaturation is the driving force of the crystallization process, the reacted surface of the crucible provides direct evidence that the Cu$_2$O flux reacts with the alumina crucible from the CAO phase.

In order to obtain large-sized CAO single crystals, we optimized the growth conditions as summarized in table 1. First, crystal growth using various amounts of Cu$_2$O flux has been attempted (growths A & B). Substantial size single crystals of CAO were obtained when a sizable amount of Cu$_2$O flux was employed. However, it was difficult to separate the crystals in this case due to a massive amount of remaining flux. Another critical parameter we discovered is the size of the alumina crucible. We utilized two crucibles with different areas (growths B & C). The CAO crystals grown in the crucible with a small area are larger than those grown in a wide crucible. The Cu$_2$O flux evaporates rapidly in a wide crucible, so the crystal cannot be large enough. On the other hand, in the narrow crucible, the evaporation of the Cu$_2$O flux is significantly suppressed, allowing the flux and the crucible to react sufficiently to create large-sized crystals. Cu$_2$O residues, however, were found particularly in the narrow crucible as a
The mm-sized CAO single crystals were successfully obtained in the optimized growth condition (growth D). The thermal process was repeated twice to ensure sufficient time for the CAO crystals to make mm-size. The macroscopic size of the grown CAO single crystals is as large as ~1 mm × 1 mm with shiny black color, as shown in the optical image (see inset of figure 2(a)). The crystals have triangular or hexagonal plate shapes, unlike cubic like Cu$_2$O single crystals [9], supporting that CAO single crystals were successfully obtained from the Cu$_2$O flux. The XRD result supports the single crystalline quality of the CAO single crystal, as shown in figure 2(a). The XRD shows only (00L) reflections, implying that the growth direction of the CAO crystal is along the c-axis. Figure 2(b) shows XRD in-plane azimuthal φ scans of CAO 012 peaks. The CAO 012 peak revealed only six peaks with similar intensities, suggesting that CAO single crystal has good crystallinity. The six-fold peak is due to the intrinsic twin domains as discussed in delafossite thin films [10].

The crystal structure of the CAO single crystal was determined by the powder XRD and Rietveld refinement, as shown in figure 2(c). The CAO powder was prepared by grinding single crystals. The experimentally obtained XRD patterns (red dots) agree well with the calculated XRD pattern (solid black line). The lattice parameters, a, b, and c estimated from the Rietveld refinement are a = b = 2.861 (7)Å, c = 16.974 (4)Å, in good agreement with [11]. The elemental stoichiometric composition of the obtained single crystal was determined by SEM/EDS technique. Only Cu, Al and O are detected, confirming absence of impurities. The chemical composition is uniform with a ratio of Cu:Al = 1.06:1, which shows a good agreement with obtained ratio from the stoichiometric powder [12]. We noted that copper is widely used as component in many parts of the measurement system, thus it tends to be detected in higher amounts than it actually exists in the sample. Taking into account the accuracy of Scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX) (typical error ± 5%), this results show that nearly stoichiometric crystals can be synthesized by growth in the reactive crucible.

Figure 3(a) displays the temperature dependence of resistivity $\rho(T)$ measured in the temperature range from 300 to 450 K. It is worth noting that reliable and reproducible measurements with low contact resistance were particularly limited to the high-temperature range (T > 300 K). The CAO crystal exhibits semiconductor behavior. The resistivity drops from ~123 Ω cm at 300 K to ~1 Ω cm at 450 K. Figure 3(b) shows that the plot of log($\rho$) versus 1000 T$^{-1}$ is linearly dependent. Such a linear dependence can fit an Arrhenius-type formula $\rho = \rho_0 e^{U/kT}$, where $\rho_0$ is the prefactor of resistivity, $U$ is the activation energy, and $k$ is the Boltzmann constant [13]. The activation energy is estimated to be $U = 340$ meV, which is consistent with that expected from the temperature dependence of the carrier density [14]. The activation energy is smaller than the bandgap $E_g \sim 3.5$ eV [4, 14], confirming that CAO is an extrinsic semiconductor with shallow electron acceptors; Cu vacancies are reported to act as shallow electron acceptors in CAO [2]. The Hall coefficient $R_H \sim 8 \pm 2 \times 10$ cm$^3$ C$^{-1}$ was positive, suggesting that grown CAO crystal is p-type semiconductor. The carrier density

| Sample | Cu$_2$O g | Bottom area mm$^2$ | Number of thermal process | Size of the crystals mm |
|--------|-----------|-------------------|---------------------------|-------------------------|
| A      | 2.5       | 1485              | 1                         | 0.4                     |
| B      | 0.5       | 1485              | 1                         | 0.2                     |
| C      | 0.5       | 50                | 1                         | 0.5                     |
| D      | 2.5       | 227               | 2                         | 1.9                     |

Table 1. Summary of growth conditions.
is estimated to be $1.1 \pm 0.3 \times 10^{17}$ cm$^{-3}$, which shows a good agreement with those value obtained from previous report [14].

Figure 4 presents the temperature dependence of magnetic susceptibility $\chi(T)$ measured under magnetic field $H = 1$ kOe along a-axis. The CAO single crystals show a paramagnetic behavior, as reported in early studies [14–16]. Stoichiometric CAO without point defects is supposed to exhibit diamagnetism because the electrons in Cu$^+$, Al$^{3+}$, and O$^2-$ are all paired [14]. In reality, CAO exhibits weak paramagnetism, which could be attributed to Cu$^{2+}$ with $d^0$ orbital occupations. As the valence-band top of CAO consist of Cu $d$ orbitals, hole carriers directly influence the oxidation state of Cu$^+$. It is worth noting that the magnetic susceptibility of grown crystals ($\chi$ (5 K) = $8.5 \times 10^{-6}$ emu g$^{-1}$ Oe) is lower than that of polycrystalline powders ($\chi$ (5 K) = $2 \times 10^{-5}$ emu g$^{-1}$ Oe) [17], suggesting that the density of Cu vacancy in this sample is lowered than that in previously synthesized samples (see figure 4(b) for comparison).

For further understanding, $\chi(T)$ was fitted to the modified Curie–Weiss law: $\chi = \chi_0 + \frac{C}{T + \theta}$ [18]. Here $\chi_0$ is the temperature independent contribution from diamagnetism and Van Vleck (VV) susceptibility, $\theta$ is the Curie–Weiss temperature, $C = N g^2 \mu_B^2 S(5 + 1)/3k_B$ is the Curie constant with number of magnetic ions per gram $N$, Boltzmann constant $k_B$, Lande g-factor $g$, magnitude of electron spin $S$, and Bohr magneton $\mu_B$. The best-fit values to $\chi_0$, $\theta$, $C$ are $1.07 \times 10^{-6}$ emu Oe$^{-1}$ cm$^{-3}$, $-0.31$ K, and $2.25 \times 10^{-3}$ emu K Oe$^{-1}$ cm$^{-3}$, respectively. These values are coherent with those obtained for single crystals grown by the slow-cooling method [14]. Assuming that the paramagnetic moment emanates from the Cu$^{2+}$ defect states with $S = 1/2$, the density of paramagnetic defect is estimated to be $N = 3.58 \times 10^{20}$ cm$^{-3}$, which is about 1.4% of that of Cu sites in CAO ($2.5 \times 10^{22}$ cm$^{-3}$). We note that the estimated ratio of defect states is smaller than the polycrystalline powders ($\sim 2.8\%–3.1\%$) [16] and comparable to single crystals synthesized by a slow-cooled method ($\sim 1.3\%$) [14]. The $\chi_0$ also arises presumably due to Cu$^{2+}$ ions. While the core electron shells of Cu$^{1+}$, Al$^{3+}$, and O$^2-$ contribute to diamagnetic susceptibility, as discussed in a previous report [14], VV contribution can arise from the open shells of Cu$^{2+}$ ions [19].

4. Conclusion

In summary, we have reported the growth of mm-sized CAO single crystals in a reactive alumina crucible. Unlike the conventional flux growth, in which the flux acts as a solvent to dissolve the desired substance, in the method reported in this paper, the flux also plays the role of the starting material that reacts with reactive crucible [20]. High-quality single crystals...
of CAO without the remaining flux were successfully obtained by the reaction between the Cu$_2$O flux and alumina crucible. The structural, transport, and magnetic properties of CAO single crystals were investigated. CAO single crystals show semiconducting and weak paramagnetic behavior, which is in good agreement with other crystals grown by the conventional slow-cooling method.

This work may offer interesting possibilities for the synthesis of the other delafossite single crystals. For example, the CuFeO$_2$ phase can be obtained under Cu$_2$O-rich condition at phase diagram of Cu–Fe–O system [21]. Thus, CuFeO$_2$ single crystal might be synthesized by the reactive crucible method with iron crucible and Cu$_2$O powders. Furthermore, obtaining high-quality delafossite single crystal in mm-size may advance the growth of delafossite thin films [22–25]. As recently demonstrated, CAO can be a good substrate for the growth of delafossite thin films [26]. Therefore, this growth method we reported here can eliminate the process of removing residuals, which can solve many problems caused by the residuals, thus facilitating relevant studies on the high-performance p-type conducting oxides.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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