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Cu_2O single crystal growth using CuCl flux and bandgap evaluation

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A R T I C L E I N F O

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A B S T R A C T

High-quality Cu_2O single crystals were grown in CuCl flux, utilizing an Al_2O_3 or MgO crucible and a slow-cooling technique. The resultant crystals exhibited a well-faceted cubic morphology, each with dimensions in the order of a few micrometers. The bandgap of Cu_2O was evaluated by diffuse reflectance spectroscopy and photoluminescence measurement using single crystals. The measured bandgap (Eg ≒ 1.95 eV) was marginally lower than the widely reported value. However, this measured value could be reasonably asserted to be representative of the intrinsic bandgap because the single crystals experienced minimal strain from the substrate, and the optical absorbance data displayed no arbitrariness.

1. Introduction

Cu_2O semiconductor has recently garnered considerable attention owing to the realization of high-efficiency solar cells [1–3]. Tandem solar cells comprising a Cu_2O top cell theoretically indicate a total efficiency exceeding 30 % [2]. Furthermore, Cu_2O is devoid of toxic elements and exhibits long-term stability. Therefore, the prospective application of next-generation tandem solar cells with Cu_2O top cells holds the potential to significantly reduce carbon emissions. Accurate determination of the bandgap of Cu_2O is crucial for maximizing the efficiency of the tandem solar cell. The selection of material for the n-type layer and the calculation of theoretical efficiency in the tandem solar cell using a p-Cu_2O layer depend on a precise understanding of the bandgap of the Cu_2O absorption layer [4]. However, the reported values of the Cu_2O bandgap demonstrate a lack of consensus [5–9]. A potential contributing factor to this inconsistency may be the susceptibility of Cu_2O to incorporating CuO or metal-Cu that affects the physical properties [10]. The growth of high-quality Cu_2O single crystal is deemed the most effective approach to obtaining a bandgap closer to the intrinsic value than those previously reported. Although various methods for the growth of Cu_2O single crystals have already been reported, none have been specifically tailored for obtaining high-quality Cu_2O single crystals of a specific size. Many existing techniques necessitate specialized equipment, such as floating-zone (FZ) furnaces (including analogous apparatus) [11–13] or high-pressure vessels [14] and have not been utilized for precise bandgap estimation. The use of a flux containing monovalent Cu is promising for growing pure Cu_2O single crystals, since Cu_2O predominantly grows in the presence of monovalent Cu. In fact, $Cu_2Ta_4O_{11}$, $Cu_5Ta_{11}O_{30}$, and $Cu_3Ta_7O_{19}$, wherein Cu adopts the monovalent state, have been recovered using CuCl flux [15,16].

2. Experimental section

Cu_2O (Fujifilm Wako, >99.5 %) and CuCl powders (Fujifilm Wako, >99.9 %) (Cu_2O/CuCl = 5.0 (mol%)) were mixed in mortar and placed in Al_2O_3, MgO, and Si_3N_4 crucibles (1 cm^3). Each crucible was covered with a lid to avoid evaporation during heating. Thereafter, the crucibles containing the staring materials were introduced into an electric furnace. The temperature was increased to 500 °C and maintained for 1 h. Subsequently, the temperature was gradually decreased to room temperature at a rate of 50 °C/h. Upon removal from the furnace, each crucible was immersed in boiling distilled water for a full day to facilitate the dissolution of CuCl. The obtained crystals were subjected to X-ray diffraction (XRD) analysis (MiniFlex 600c, RIGAKU) and scanning electron microscopy (S-4300, Hitachi). To determine the optical properties, Photoluminescence (PL) measurement was conducted (532 nm, 10 mW (beam diameter: 0.5 mm), Matrix, COHERENT). Additionally, the diffuse reflectance spectrum was measured using a spectrophotometer (Solid Spec 3700 DUV, SHIMADZU).

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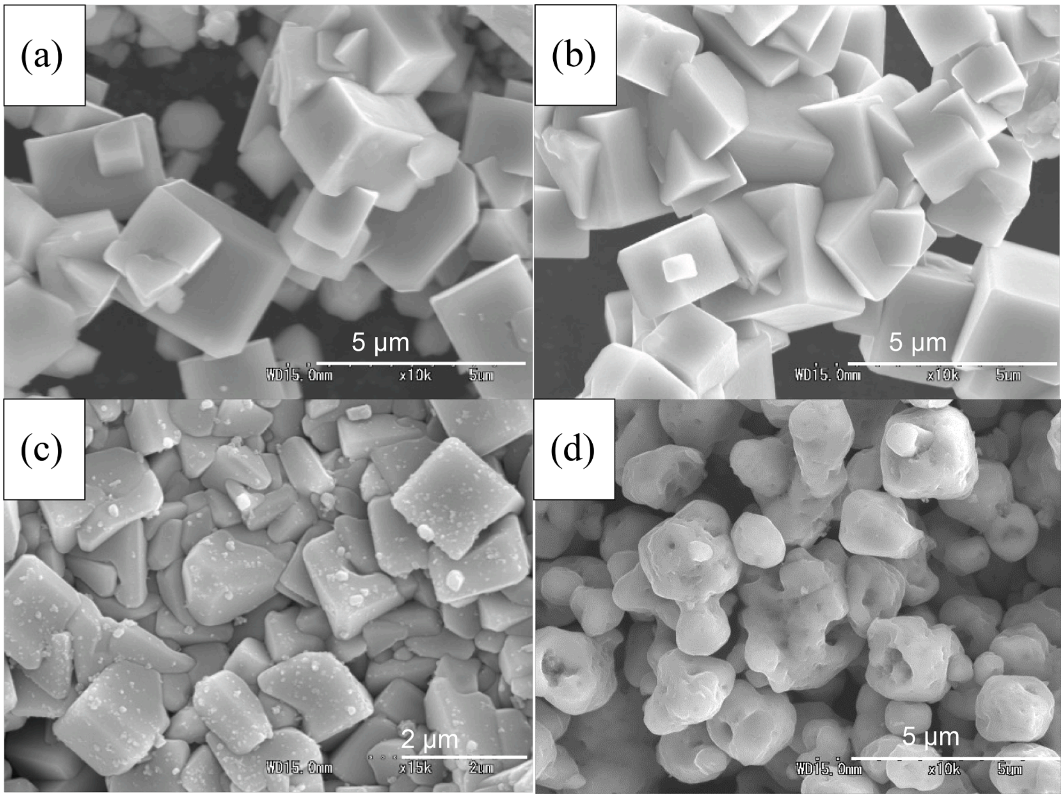

Fig. 1. SEM photographs of Cu_2O single crystals grown in CuCl flux with slow cooling. (a), (b), (c), and (d) show the crystals grown in Al_2O_3, MgO, and Si_3N_4 crucibles and the .
Source Cu_2O powder, respectively

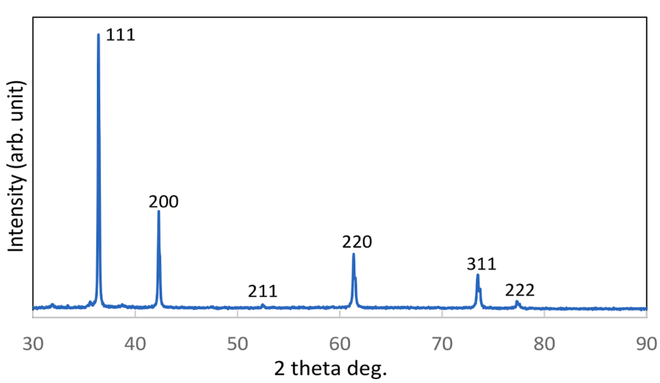

Fig. 2. XRD pattern of Cu_2O crystals recovered from MgO crucible with CuCl flux.

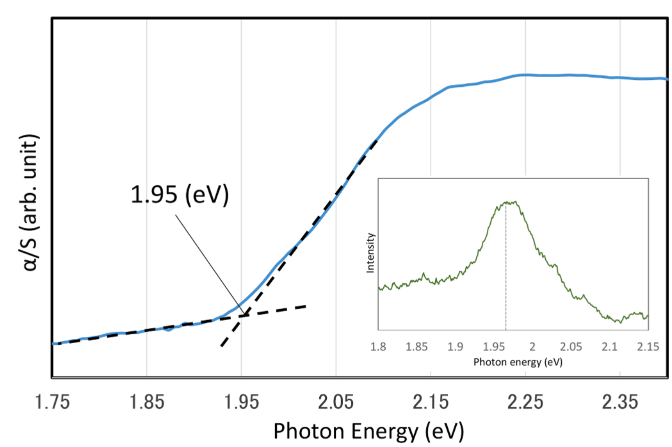

Fig. 3. Optical absorbance (α/S) and PL measurement (inset) with 500 nm excitation wavelength on Cu_2O single crystals. Each result indicates agreement at 1.95 eV. The optical absorbance spectrum was calculated from the diffuse reflectance spectrum using the Kubelka–Munk equation: $\alpha/S = (1 - R)^2/2R$, where α, R, and S are the absorption, reflectance, and scattering coefficient, respectively.

3. Results and discussion

Fig. 1 shows the SEM images of the recovered samples. The crystals grown in Al_2O_3, MgO, and Si_3N_4 crucibles and the source Cu_2O powder are marked as (a), (b), (c), and (d), respectively.

In all cases, the crystals exhibited growth with a {1 0 0} face. However, the sample grown in Si_3N_4 crucible showed a slightly rounded shape and unremovable contaminations, indicating corrosion of the Si_3N_4 crucible via reaction with CuCl flux during the crystal growth process. Conversely, crystals recovered from Al_2O_3 and MgO crucibles showed a well-faceted cubic morphology. Twins were observed (Fig. 1 (a–c)). Cu_2O has been reported to easily form twins during growth [17]. Typically, twins arise when the growing crystals encounter sufficiently high supersaturation to overcome the energy barrier for twin formation, or when adhesive impurities reduce this energy barrier. At this stage, pinpointing the predominant factors in twin formation is difficult. However, it appears that twins do not adversely affect this study because they do not significantly impact the optical properties or crystal bandgap. Therefore, crystals obtained from Al_2O_3 and MgO crucibles (Fig. 1(a, b)) are suitable for investigating their properties.

Fig. 2 illustrates the XRD measurement of Cu_2O crystals grown in MgO crucible. Sharp peaks, consistent with Cu_2O, were confirmed. The peak sharpness can be attributed to the excellent crystallinity.

Before the measurement of PL and diffuse reflectance spectrum, an elemental analysis was conducted to specify the recovered crystals to be Cu_2O and determine if the crystals contained foreign impurities. Energy-dispersive X-ray (EDX) spectroscopy revealed that recovered crystals comprise of Cu and O and show no signals from chlorine or elements constituting the crucible. Nonetheless, the EDX analysis may not be highly sensitive and might not detect trace amounts of foreign elements.

Fig. 3 depicts the diffuse reflectance spectrum, with the inset displaying the results of PL measurement.

The bandgap values obtained from both PL and diffuse reflectance spectrum measurements are in good agreement, indicating Eg ≒ 1.95 eV; this value is notably lower than the commonly accepted range of Eg of 2.1–2.2 eV. In most papers reporting the bandgap of Cu_2O, film samples are employed for measurements, and the bandgap is determined using the Tauc plot. The bandgap measured using film samples often deviate from the intrinsic value owing to substrate-induced strain, as changes in the cell volume caused by the substrates can influence the bandgap [18]. Moreover, the bandgap calculated from Tauc plots may exhibit a degree of arbitrariness based on how the vertical scale is set. In contrast, the optical absorbance (α/S) defines the bandgap without any arbitrariness because the value is determined by intersections with an extrapolation of the background. Furthermore, the bandgap obtained from α/S is further substantiated by the peak position observed in the PL measurements. Thus, we conclude that the Cu_2O bandgap value of Eg ≒ 1.95 eV is closer to the intrinsic value than those previously reported.

4. Conclusions

Cu_2O single crystals were grown using CuCl flux via a slow-cooling method; the resulting crystals exhibited a well-faceted cubic morphology. PL and diffuse reflectance spectrum measurements revealed the bandgap of Cu_2O: Eg = 1.95 eV. This value is marginally smaller than the commonly accepted one. We propose a reasonable adjustment to the recognized bandgap of Cu_2O, setting it at Eg = 1.95 eV. This adjustment is substantiated by using single crystals grown in the flux system in the evaluation and further supported by the peak position observed in the PL measurements. Based on this refined understanding of the bandgap, we suggest that the design of a Cu_2O solar cell could be optimized, potentially leading to enhanced efficiency.

CRediT authorship contribution statement

Fumio Kawamura: Writing – review & editing, Writing – original draft, Project administration, Methodology, Funding acquisition, Conceptualization. **Takehiko Nagai:** Investigation, Formal analysis, Data curation. **Hitoshi Tampo:** Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.136428.

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