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Synthesis of CIGS absorber layers via a paste coating

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ABSTRACT

$CuIn_xGa_{1-x}Se_2$ (CIGS) thin films were prepared by a paste coating with the aim of developing a simpler and the lower cost method for fabricating the absorber layers of thin film solar cells. In particular, a paste of a Cu, In, Ga, and Se precursor mixture was first prepared, followed by a reaction between them at elevated temperatures after depositing the paste onto a glass substrate. No apparent change in composition was observed during thermal annealing at 450 °C in the absence of a gas-phase selenium source. A pre-annealing process at 250 °C under ambient conditions performed before annealing (450 °C) under reduction conditions reduced the level of carbon deposition in/on the films without perturbing the stoichiometry of the CIGS thin films.

1. Introduction

Among the various thin film solar cells in the market, $CuIn_xGa_{1-x}Se_2$ (CIGS) thin film solar cells have been considered the most promising alternatives to crystalline silicon solar cells on account of their potential high solar to electricity-conversion efficiency, reliability, and stability [1–4]. The CIGS thin film solar cells fabricated by conventional vacuum-based routes, such as co-evaporation and sputtering techniques, have already achieved comparable efficiency (~19%) to polycrystalline silicon solar cells, which is much higher than that of other thin film solar cells [2–4]. However, as noted by many other researchers, the current methods for fabricating CIGS thin film solar cells need considerable improvements considering the manufacturing cost and scale as well as environmental issues [1,5–8]. Since the current methods for manufacturing CIGS thin film solar cells are based on vacuum processes, they require initial high capital investment as well as maintenance of capital expense arising from the necessity of vacuum equipment. Moreover, there is significant loss of resource material (20–50%), which again increases the manufacturing cost [5]. In addition, the large-scale production of photovoltaic (PV) panels would be restricted due to the limiting size of vacuum equipment.

Non-vacuum processes have been suggested to solve the problems of the current CIGS solar cell fabrication methods, such as printing, electroplating, spraying, etc. [5–13]. In particular, precursor-based printing methods, e.g. screen printing and doctor-blade, would be competitive in terms of processing capital costs, efficiency of resource material usage, and processing speed [5–8]. In addition, these methods can be applied to continuous roll-to-roll deposition processes as well as to large-scale panel fabrication. In precursor-based printing methods, various types of elemental sources have been applied. For example, metal nitrates, metal chlorides, metal iodides, or elemental metals have been used as Cu, In, and Ga precursors. In most cases, the cationic form of the metals is generated from these precursors [5–11]. In contrast, gas-phase Se precursors, such as H_2Se or Se vapor, are generally used as Se sources instead of the salt-type of precursors.

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Although the salt-type of precursors (e.g. Na_2Se) have been used to synthesize of CIGS alloys, a selenization process using H_2Se or Se vapor is subsequently applied [9,10].

Selenization may be an essential process in the synthesis of a CIGS absorber layer. It was reported that selenization helps to increase the grain size of CIGS crystal and compensates for the loss of Se during high-temperature annealing process [1]. However, despite these beneficial effects of selenization for CIGS thin film synthesis, there are several drawbacks [1]. First, the representative Se precursor, H_2Se, which is a very toxic chemical, is unavoidably released into the atmosphere during the selenization process. Second, it may be a barrier for the overall cost-effective fabrication process of CIGS solar cells because it requires separate facilities from the synthesis of Cu-In-Ga alloy layers.

To produce CIGS thin film solar cells in a cost-effective manner, we have been carrying out a long-term research plan in that all the fabrication processes of CIGS are accomplished using precursor-based non-vacuum processes. Furthermore, we are aiming to develop processes that can replace some environmental unfriendly ones, such as selenization with hazardous gases, in the synthesis of the CIGS absorber layer. In this study, as a first step of this project, we suggest a new method for fabricating the CIGS absorber layer using a paste coating. With this method, a cationic Se precursor rather than elemental or anionic Se was used to prepare the paste, and no further selenization using gas-phase precursors was employed to synthesize the CIGS absorber layer.

2. Experimental

A precursor mixture was prepared by dissolving the appropriate amounts of $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%, Kanto, 0.50 g), $Ga(NO_3)_3 \cdot xH_2O$ (99.9%, Alfa Aesar, 0.27 g), $In(NO_3)_3 \cdot xH_2O$ (99.9%, Alfa Aesar, 0.31 g), and $SeCl_4$ (99.5%, Alfa Aesar, 0.92 g) in anhydrous ethanol (60 mL), followed by the addition into a solution of terpineol (Fruka, 10.0 g) and ethyl cellulose (Alfa aesar, 0.75 g) in ethanol (20 mL). After condensing the solution at 40 °C under reduced pressure, a viscose paste with rheological properties suitable for a doctor-blade coating was prepared.

After printing the paste on the glass substrates, the film thickness was adjusted to ~2 μm using two stripes of a 3 M scotch tape, applied to both sides of the glass substrates. The samples were then placed into a wind blower (Leister) for pre-annealing and/or a furnace for high-temperature annealing. Pre-annealing was performed below 250 °C for 1 h under ambient conditions, and high-temperature annealing was carried out at 300–500 °C for 40 min in a H_2(5%)/Ar gas mixture at a flow rate of 80 mL/min.

Structural characterization of the films was performed by scanning electron microscopy (SEM, Hitachi, S-4200) and X-ray diffraction (XRD, Shimadzu, XRD-6000). Composition analysis was carried out using energy dispersive X-ray spectroscopy (EDX, Horiba) and ICP–AES (Perkin-elmer). Thermogravimetric analysis (TGA, Ta Instruments Inc.) was also performed to determine appropriate annealing conditions as well as to determine the thermal stability of the films.

3. Results and discussion

The use of a cationic Se precursor, $SeCl_4$, is unusual since the final product, $CuIn_xGa_{1-x}Se_2$, is a chalcogenide compound where Se has an oxidation state of −2. Na_2Se is most frequently used as a Se source for precursor-based CIGS thin film synthesis [6]. A reduction process is necessary to change the oxidation state of Se from +4 to −2. Alcohols, e.g. ethanol and/or terpineol in this synthetic method may play a role as reducing agents at elevated temperatures similar to the polyol process, which is well known in metal nanoparticle synthesis [14,15].

Cu, In, and Ga nitrates and $SeCl_4$ were dissolved completely in ethanol at room temperature to generate the precursor mixture. An ethanol solution of terpineol and ethyl cellulose was also prepared and combined with the precursor mixture. It should be noted that the pH of the mixture was approximately 1, indicating proton generation from alcohols Eq. (2). This suggests that Se^{4+} ions coordinate with alkoxy species to form $Se(OR)_4$ Eq. (2).

$$SeCl_4 \rightarrow Se^{4+} + 4Cl^- \quad (1)$$

$$Se^{4+} + 4ROH \rightarrow Se(OR)_4 + 4H^+ \quad (2)$$

$$4H^+ + 4Cl^- \rightarrow 4HCl\uparrow \quad (3)$$

$$Cu^{2+} + xIn^{3+} + (1-x)Ga^{3+} + Se(OR)_4 + ROH \rightarrow CuIn_xGa_{(1-x)}Se_2 + \text{residual organics}\uparrow \quad (4)$$

Although a viscous paste with suitable rheological properties was prepared by condensing the mixture solution under reduced pressure, the reaction between the precursors to the CIGS alloy particles does not occur in this stage. However, some HCl gas was generated, resulting in an increase in pH to ~3 Eq. (3).

A reaction Eq. (4) between the metal ions in the precursor mixture occurred during heat treatment of the printed paste above 100 °C. The temperature effects on the compositional change were examined by carrying out the heat treatments under ambient conditions using a hot wind blower for 1 h. As shown in Fig. 1, heat treatment at 100 °C resulted in the appearance of an XRD peak at 28.1° 2θ with a weak peak at 46.5° 2θ . At higher temperatures (200 °C), the intensity of the XRD peak at 28.1° 2θ increased with the appearance of new peaks at 29.2°, 47.8°, and 55.8° 2θ. Heat treatment at 300 °C resulted in another new intense peak at 31.1° 2θ with a weak peak at 49.9° 2θ. Simultaneously, weak peaks at 26.5° and 45.5° 2θ were observed. However, a significantly different XRD pattern was observed when the printed films were annealed at 400 °C, showing only weak peaks at 30.6° and 35.5° 2θ. The color of the films also changed from black to grey.

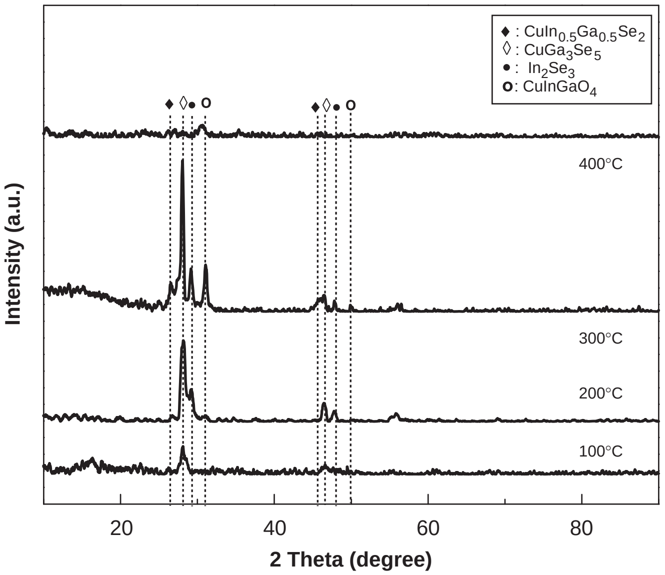

Fig. 1. X-ray diffraction (XRD) data of the various films prepared from the Cu–In–Ga–Se precursor paste with respect to the annealing temperatures under ambient conditions.