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Three-stage growth of Cu–In–Se polycrystalline thin films by chemical spray pyrolysis

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Abstract

Structural, optical and electrical properties of polycrystalline Cu–In–Se films, such as $CuInSe_2$ and ordered vacancy compounds (OVC), prepared by three-stage process of sequential chemical spray pyrolysis (CSP) of In–Se (first stage), Cu–Se (second stage) and In–Se (third stage) solutions have been studied in terms of substrate temperature at the second stage (T_{S2}). The films grown at $T_{S2} \leqslant 420\,°C$ exhibited larger grains in comparison with the Cu–In–Se films grown by the usual CSP method. Optical gap energy was approximately 1.06 eV for $360\,°C \leqslant T_{S2} \leqslant 420\,°C$, but increased dramatically from 1.06 to 1.35 eV when the T_{S2} rose from 420 to 500 °C. Conductivity type was p-type for $T_{S2} < 420\,°C$, but n-type for $T_{S2} > 420\,°C$.

Keywords: $CuInSe_2$; Ordered vacancy compound; Chemical spray pyrolysis; Three-stage growth

1. Introduction

Copper indium diselenide ($CuInSe_2$) has a direct band gap of about 1.03 eV [1,2] and high absorption coefficient up to a value of $6\times10^5\,cm^{-1}$ [3]. Therefore, it is expected to be a promising material for photovoltaic applications, usually as a form of solar cell composed of polycrystalline thin films. Recently, thin film solar cells with the quaternary $Cu(In,Ga)Se_2$ (CIGS) absorber layers, formed by physical vapor deposition (PVD) with the "three-stage" process, attained a very high conversion efficiency of over 19% [4]. In the three-stage process, the first stage consists of the formation of an $(In,Ga)Se_3$ layer. At the second stage, deposition of Cu and Se leads to the formation of a Cu-rich CIGS. Liquid-phase Cu–Se acts as a flux for the growth of CIGS, yielding large and columnar grains. In the third stage, deposition of In, Ga and Se results in a slightly (In,Ga)-rich CIGS, which can be used for the solar cell.

Chemical spray pyrolysis (CSP) is an attractive method because large-area films with good uniformity can be grown at low cost. So far, the authors have studied the preparation of polycrystalline films of $CuInSe_2$ and related compounds by CSP, and published the preparation and properties of $CuInSe_2$ [5–7], CIGS [8,9] and $CuIn(S,Se)_2$ films [10,11]. Recently, we have reported that the CSP deposition and structural and optical properties of In-rich Cu–In–Se films involving ordered vacancy compounds (OVC), such as $Cu_2In_4Se_7$ and $CuIn_3Se_5$, by the CSP method [12].

In this paper, the three-stage CSP method has been examined for the first time for the deposition of CIS films. The Cu–In–Se polycrystalline films with In-rich compositions have been deposited on the glass substrate by the sequential spraying of the In–Se, Cu–Se and In–Se spray solutions. The grown films have been characterized with respect to composition, surface morphology, X-ray diffraction (XRD), optical absorption and resistivity.

2. Experimental

2.1. Film preparation

The CSP apparatus used for the three-stage growth of $CuInSe_2$ films is the same as previously reported one [5]. As

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the In–Se spray solution, 20 vol% aqueous ethanol solution of $InCl_3$ and *N*, *N*-dimethylselenourea (DMSeU) was used. The molar ratio, In:Se, in the In–Se spray solution was 2:4.95. As the Cu–Se spray solution, 20 vol% aqueous ethanol solution containing $CuCl_2$ and DMSeU was used. The molar ratio, Cu:Se, was 2:1.65. The pH value for both the In–Se and Cu–Se spray solutions were kept at 4.0 by adding NH_4OH. Both the spray solutions were sprayed with N_2 gas at a constant rate of 5 ml/min. The conventional slide glass for the optical microscope (Matsunami, S-111, 0.8–1.0 mm in thickness) was used as the substrate ($25 \times 25\,mm^2$).

In this study, three kinds of time sequential spray program were examined. Fig. 1 shows such three kinds of sequences: sequence I, sequence II and sequence III. At the first-stage (①), the In–Se spray solution was sprayed at substrate temperature (T_{S1}) of 360 °C. The spray deposition time for the sequences I, II and III was 25, 50 and 25 min, respectively, corresponding to the volume of the In–Se spray solution of 125, 250 and 125 ml, respectively.

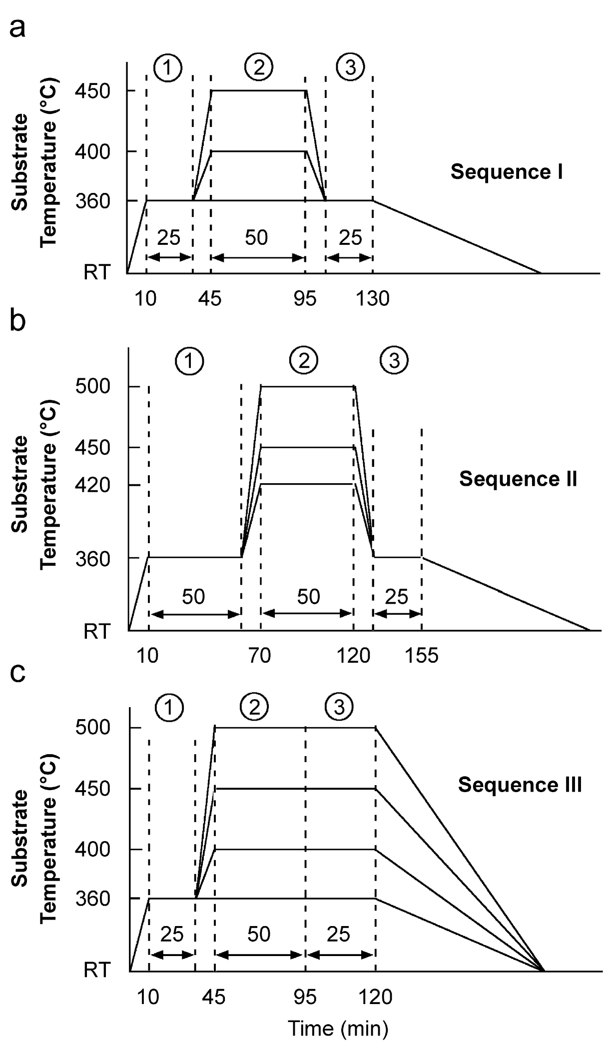

Fig. 1. Three kinds of substrate temperature sequences: ① first stage (In–Se solution supply), ② second stage (Cu–In solution supply) and ③ third stage (In–Se solution supply).

The amount of the solution in the sequence II is twice of that in the sequences I and III. At the second-stage (②), the Cu–Se solution of 250 ml was sprayed at substrate temperature (T_{S2}) of 360 °C for 50 min. At the third-stage (③), the substrate temperature (T_{S3}) was reduced to 360 °C for the sequences I and II. For the sequence III, substrate temperature was kept constant during the second and the third stages. The volume of the In–Se spray solution for the third stage was 125 ml. In order to distinguish between the film deposited by the sequential spraying of In–Se, Cu–Se and In–Se spray solutions and the film deposited the usual CSP method, the former and the latter are denoted hereafter by 'the three-stage CSP film' and 'the usual CSP film', respectively.

2.2. Characterization

The film structure was characterized by XRD method using Cu–K_α radiation. An XRD diffractometer equipped with a goniometer with a fixed small-angle X-ray incidence (5° incidence) and 2θ scanning mechanism with sample rotation within the plane was used. Film composition was determined by an electron probe microanalyzer (EPMA: JEOL, JXA-8600MX) using an L line with an acceleration voltage of 7 kV and a beam diameter of 10 μm. A single crystal of $CuInSe_2$ was used as the standard. Penetration depth of the electron beam (EB) with the acceleration voltage of 7 kV is estimated to be approximately 0.5 μm. Observation of surface morphology was performed using a scanning electron microscope (SEM: Hitachi, S-3100H). The conduction type was determined by a hot probe method. Resistivity was measured by a van der Pauw method. The optical transmission was measured using single-beam monochromator (Ritsu Oyo Kougaku, MC-20L) in combination with a lock-in amplifier (NF Circuit Design Block, LI-572B). Monochromatized light was detected by photomultipliers (Hamamatsu, R-7102 and R-7696) and a PbS photoconductive detector.

3. Results and discussion

3.1. Film thickness and composition

Fig. 2 shows film thickness as a function of T_{S2}. It can be seen that the film thickness decreases almost linearly with T_{S2}. Large difference in thickness between the sequences I and II by a factor of 2 may reflect the difference in the amount of the In–Se solution for the first stage between both the sequences.

Fig. 3 shows the In/(Cu + In) ratio in the three-stage CSP film as a function of second-stage substrate temperature. In the figure, the In/(Cu + In) ratios corresponding to $CuInSe_2$, $CuIn_3Se_5$ and $Cu_2In_4Se_7$ are indicated by the broken lines. It is noted that all the points are in one curve as shown in Fig. 3, independent of the difference in the temperature sequence. This result suggests that the In/(Cu + In) ratio in the film can be controlled by adjusting