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Influence of process parameters on the gallium composition of a $CuIn_{1-x}Ga_xSe_2$ solar cell on the efficiency of non-vacuum blade coating stacking

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ABSTRACT

The distribution of an energy gap gradient can influence photovoltaic conversion, which in turn influences the performance of solar cells. On the other hand, controlling the energy gap gradient can influence the range of the absorption spectrum, and thus the overall solar photovoltaic conversion efficiency is affected. To control the energy gap of a $CuIn_{1-x}Ga_xSe_2$ (CIGS) solar cell, this study employs a non-vacuum stack coating technique. The chemical composition of the ink is regulated and a multilayer stack is coated to investigate (1) the distribution range of the energy gap and (2) the variability of conversion efficiency in multilayer stack and single-layer composition conditions, in order to determine the feasibility of using a coating stack design to change and control an energy gap. The effect of film composition on crystallinity is tested through high-temperature selenylation. Finally, a miniature solar module is prepared and the conversion efficiency is found to improve from 5.02% to 7.08%, and the feasibility of energy gap control is demonstrated.

1. Introduction

In recent research on solar cells, following the success of the crystalline silicon thin-film solar cell, the I-III-VII compound family has been studied most extensively for application in thin-film solar cells. For example, $CuIn_{1-x}Ga_xSe_2$ (CIGS) has a direct band gap, a wide energy-gap range, and a very high photoabsorption coefficient, as well as good radioresistance and thermal stability properties. Different characteristics of p-n junctions can be formed by modulating the composition ratio. Thus, it can serve as the main absorption layer material for improving thin-film solar cells.

A CIGS absorption layer for a thin-film solar cell can be created using the co-evaporation method, and the maximum efficiency is currently reported to be 22.8% (Kamada et al., 2016). This absorption layer is prepared using the "three-stage co-evaporation method", where the distribution of Ga content in CIGS is controlled by the evaporation method in order to obtain high solar energy conversion efficiency. The Ga distribution gradient determines the width and shape of the thin-film energy band, and the increase in the surface and back energy gaps can inhibit the composition of the cell absorption layer. Furthermore, the open-circuit voltage V_{oc} is effectively increased, and the middle narrow energy gap prevents the spectral response of a cell in a long-wave band from decreasing, so that the J_{sc} loss is reduced (Huang, 2008; Voorwinden et al., 2003).

The other processes used a series of vacuum and non-vacuum process operations, such as sputtering, evaporation, printing, electroplating, and spraying (Dhage et al., 2014; Li et al., 2015; Liu et al., 2012; Park et al., 2009; Wang et al., 2011). However, the process and equipment both have high costs and are toxic (Mitzi et al., 2009). The Ga content distribution can be controlled by using process conditions to control the diffusivity (Zhang et al., 2014). If this CIGS quaternary compound nano-powder is made into a coating using a dispersion technique, the powder will be coated on the substrate uniformly, the Ga distribution will be controlled, the nano-powder will be grown via short annealing, and an absorption layer will be prepared. The high photovoltaic conversion efficiency of CIGS will be maintained, and process and equipment costs can be greatly reduced.

This study proposes using a nano-precursor "stack" coating, where the problems of the diffusion process are avoided, to ensure that the absorption layer has Ga gradient variation.

2. Materials and methods

Optimum CIGS nano-powder preparation conditions can be found by using the solvothermal method, and the nano-sized CIGS

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precursor paste is prepared using a grinding dispersion machine. The paste forms a thin-film precursor layer on the substrate by using stack coating.

The CIGS powder is synthesized using hydrothermal synthesis. The preparation procedure is described as follows. (1) Prepare Cu powder, 0.951 g; In powder, 1.337 g; gallium (III) nitrate hydrate, 1.977 g; Se powder, 2.364 g powders mixed with ethylenediamine, 50 ml, and place in a 100-ml Teflon container. (2) Place the prepared solution in a magnetic stirrer and stir uniformly for 30 min. (3) Place the Teflon container in a pressure pan, close completely, and heat at 200 °C in an oven. (4) When the reaction is finished, remove the CIGS compound and place in a funnel for separation. (5) Two liquids are used to filter the CIGS compound in the funnel separation process. First, the organic solvent is removed with ethanol, and cleaned with deionized water until there is no color change in the filtered solution. (6) Place the separated precipitate in a high-temperature vacuum oven (120 °C, 10^{-3} Torr) for 24-h drying, and the CIGS quaternary compound powder for this experiment is obtained. (7) Test the fourteen different proportions of synthesized CIGS powder according to the conditions.

The I-III-VI CIGS crystalline nano-powder is prepared, and the CIGS powder dispersed in n-propanol is mixed with a small amount of ionic dispersant. The ion-type surfactants can generate electrical repulsion between solid particles in close proximity, and thus the solid particles are mutually exclusive to achieve a dispersion effect. They are ground by a grinder at 2000 rpm to obtain CIGS ink with a secondary particle size (D50) of 50–100 nm. The solid content is 10–20 g/100 ml.

Afterwards, nano-ink of 3–5 centipoise (cP) is coated using a knife. The $CuIn_{(1-x)}Ga_{(x)}Se_2$ inks with Ga/(In + Ga) ratios of 0.25, 0.5, and 0.9 are coated on 5 × 5-cm Mo glass at 150 rpm.

After coating, the sample is baked in a 100 °C oven for 5 min. This step is repeated 2–5 times (where the increment of dry film thickness is approximately 0.25 μm at each time). The sample and 0.5 g of selenium powder are placed in a quartz tube and in an inert nitrogen gas atmosphere. The furnace body is heated to 350 °C for 5 min to remove the solvent and dispersant, and then heated to 540 °C for 20-min selenylation. After this, the thin-film CIGS absorption layer film is formed. The selenized film is treated with Potassium cyanide (KCN) to remove Cu-Se binary phases, and the solar module is made according to the previous structure (Mo/CIGS/CdS/i-ZnO/n-ZnO:Al) (Archbold et al., 2007; Bhattacharya and Ramanathan, 2004; Islam et al., 2011; Meng et al., 2014; Salman et al., 2012; Wang et al., 2009; Jeong et al., 2005).

In experimental measurements, the crystal structure is analyzed using an X-ray diffraction (XRD) instrument (PANalytical, X'Pert). It uses Cu as the Pd material and has a wavelength of $\lambda = 1.5405$ Å, an operating voltage of 45 kV, and a current of 40 mA. The XRD diffraction angle is 2θ, scanning from $2\theta = 20°$ to 60° at a rate of 0.083° per second for analysis. For morphological and composition analyses, a scanning electron microscope (SEM; Jeol, JSM 6400) and Oxford Link ISIS EDS system are used for the qualitative and quantitative analyses of composition. The quantum efficiency (QE) is measured using (QE-3000) equipment. The solar cell analysis light source (I-V) for simulated measurement (PV Measurement Inc., PVM 415) uses a standard simulated light source at AM1.5 and 1000 W/m^2 at 25 °C for measurement.

3. Results and discussion

3.1. Material properties and characteristics

Fig. 1(a) shows the results of XRD analysis after 36-h synthesis at 160, 180, and 200 °C. The results show that the crystal structure varies with temperature; when the temperatures are 160 °C and 180 °C, three noticeable peaks are produced, namely CIGS(1 1 2), (2 2 0), and (3 1 2). There are also secondary phases, such as Se and $CuSe_2$(2 1 0)/(2 1 1). This may be because the ethylenediamine chelating agent has low chelating ability for In^{3+} and Ga^{3+}, forming In_2Se_3 and Ga_2Se_3, respectively. When the temperature and pressure are increased, the In_2Se_3 and Ga_2Se_3 dissolve and react with $[Cu(en)_2]^+$. According to the XRD data, a temperature higher than 180 °C is favorable for $[Cu(en)_2]^+$ to react with In_2Se_3 and Ga_2Se_3 to form CIGS.

When the temperature rises to 200 °C and is maintained for 36 h, the crystal structure exhibits a chalcopyrite single structure, as shown in Fig. 1. The diffraction peak position of the (1 1 2) crystal face is located at $2\theta = 26.89°$, that of the (2 2 0)/(2 0 4) crystal face is at $2\theta = 44.64°$, and that of the (3 1 2)/(1 1 6) crystal face is at $2\theta = 52.94°$. In Fig. 1(a), the reaction result after 36-h synthesis at 200 °C is consistent with JCPDS card no. 35-1102. In Fig. 1(b), the three points are the full-widths at half-maximums (FWHM) of the CIGS (1 1 2) peaks for the samples with synthesis temperatures of 160, 180, and 200 °C. The FWHM corresponds to the point defects and grain growth (Schlenker et al., 2004). For the sample with 36-h synthesis at a heating temperature of 200 °C, the crystal has a preferred orientation of [1 1 2]. For the sample with 36-h synthesis at 200 °C, the peak has a smaller FWHM (0.818°) and a larger grain size than the other samples. According to the analysis of the

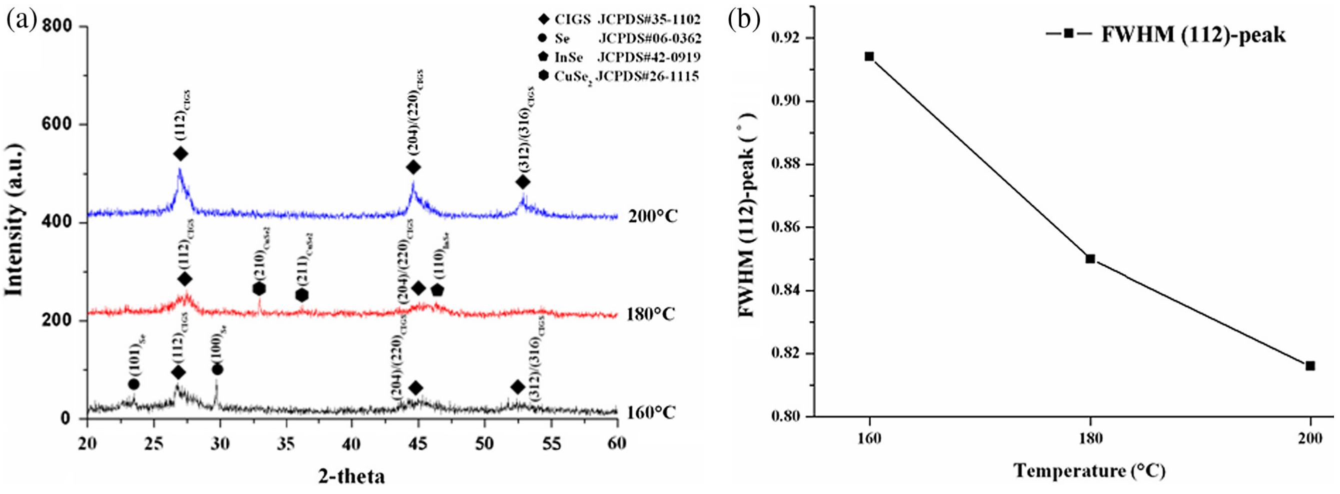

Fig. 1. XRD analysis of CIGS compound powder crystals.