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GROWTH OF $CuInSe_2$ THIN FILMS BY TRIPLE-IONIZED BEAM TECHNIQUE

ABSTRACT

$CuInSe_2$ thin films were prepared on the soda-lime glass substrate by the triple-ionized beam technique (IBT), in which Cu, In, and Se vapors were ionized and accelerated. The substrate temperature was as low as 300℃. The films were characterized by X-ray diffraction, SEM, EPMA and ICP. As a result, we were able to obtain films with improved grain size and the crystallinity by ionization of Se-vapor. Those films showed a nearly stoichiometric composition with apparent grain size of more than 2μm. Thus, IBT turned out to be an appropriate technology for low temperature deposition of high quality $CuInSe_2$ thin films.

1. INTRODUCTION

The chalcopyrite type ternary semiconductor $CuInSe_2$ has been attracting much attention as a polycrystalline thin film material for high efficiency solar cells application, since the material has a direct energy gap of around 1.04eV and the highest absorption coefficient reported to date for any semiconductors (COUTTS et al.). Recently, a conversion efficiency of more than 17% was reported for solar cells based on thin films of $CuInSe_2$ (BODEGARD et al.).

However, most of the deposition techniques reported to date require high processing temperatures higher than 450 ℃ in order to obtain high quality films. To realize superstrate-type solar cells suitable for mass production, the substrate temperature for deposition of $CuInSe_2$ is required to be lower than 300℃ in order to prevent interdiffusion between the window layer and $CuInSe_2$. The IBT (ionized beam technique) has been known to be an excellent technique for preparing high-quality thin films at a relatively low temperature, since it utilizes the effect of bombardment of ionized beam and the charge of ionized particles (TAKAGI et al.). In our previous publications, we reported the deposition of $CuInSe_2$, in which Cu- and In-vapor were ionized (Se vapor was not ionized) to provide superstrate-type solar cells at a low temperature. This technique will be referred to as "dual-IBT" in the following text. The best cell made of these films obtained (Cu/In=0.88) had an efficiency of 2.08% (USHIKI et al. ; SANO et al.). However, in this method we failed to obtain films with a grain size as large as 2 μm, which is required for good performance solar cells with nearly- stoichiometric composition of Cu/In=0.95~0.99.

In the present paper are reported the preparation of $CuInSe_2$ thin films by the triple IBT-deposition in which Cu-, In- and Se-vapor for $CuInSe_2$ were ionized and accelerated and the characterization of the films by X-ray diffraction, scanning electron microscope (SEM) ,electron-probe micro-analysis (EPMA) and inductively-coupled plasma (ICP) technique.

2. EXPERIMENT

$CuInSe_2$ thin films were grown on the soda-lime glass substrates by the ionized beam technique. Cu-, In- and Se-vapor were ionized separately and accelerated in the an apparatus shown schematically in Fig. 1. We name this method "triple-IBT". During the film-deposition, the acceleration voltages for Cu-, In- and Se-beams were maintained at 2kV and the electron currents for ionization of the Cu-, In- or Se-beams were varied between 0 mA and 150 mA. Source materials employed were Cu, In and Se of 99.999% purity. Source temperatures of the three crucibles for Cu, In and Se were 1420 ℃, 980 ℃ and 320 ℃, respectively. The substrate temperature was kept at 300℃ by an infrared lamp, and the pressure in the vacuum chamber was maintained at less than 1×10^{-5} Torr during deposition. The typical thickness of the films obtained were approximately 2μm for deposition period of 90 minutes.

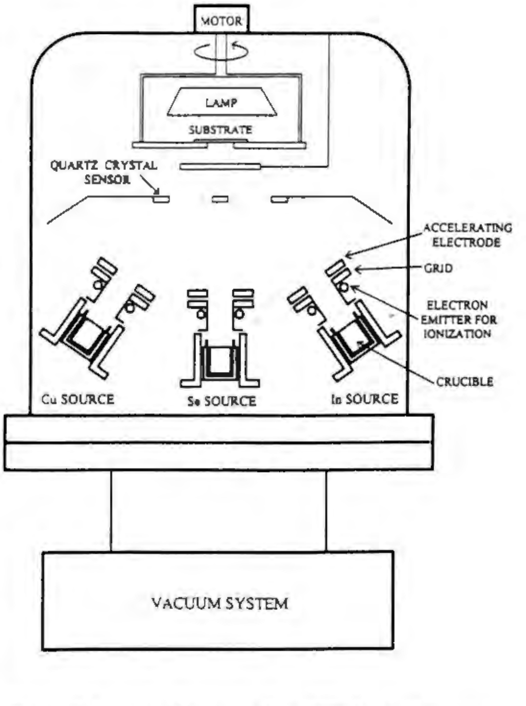

Fig. 1 Schematic diagram of an IBT deposition system.

Characterization of the $CuInSe_2$ films were performed by X-ray diffraction for structural analyses, and scanning electron microscope (SEM) for surface morphology observation. The chemical composition of the samples were determined through the electron-probe micro-analysis (EPMA:JEOL,JXA-840) and the inductively-coupled plasma (ICP) technique.

3. RESULTS AND DISCUSSION

A typical X-ray (Cu Kα) diffraction pattern of $CuInSe_2$ films prepared on bare soda-lime glass substrates by the triple-IBT is shown in Fig. 2. The 112, 211, 105 and other diffraction lines characteristic of chalcopyrite structure were observed, the relative intensity suggesting that the ⟨112⟩ axis is preferentially oriented perpendicularly to the film surface. No impurity phase such as $Cu_{2-x}Se$ and In_2Se_3 was observed .

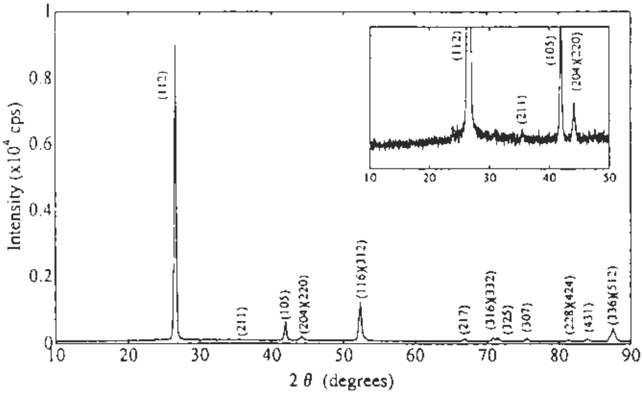

Fig 2. X-ray diffraction pattern of $CuInSe_2$ film prepared by the triple-IBT.

Figure 3 (a) shows the surface morphologies and the cross sections of the $CuInSe_2$ films which were prepared by the triple-IBT. For comparison, those of films prepared by the dual-IBT are also shown in (b). As shown in Fig. 3 (a), a remarkable increase of grain size which amounted to 2~3 μm for nearly stoichiometric composition (Cu/In=0.98) was observed in $CuInSe_2$ films prepared by the triple-IBT. The cross sectional micrograph showed that the crystals were perfectly columnar with densely packed structure and tightly adhered to the substrate. On the other hand, the $CuInSe_2$ films prepared by the dual-IBT showed much smaller grain size of about 0.8 μm for composition of Cu/In=1.01. The cross sectional micrograph showed crystal grains with less perfect columnar structures. It is surprising that the triple-IBT films showed large grain size than the dual-IBT films even though the composition of the former film is more In-rich than the latter.

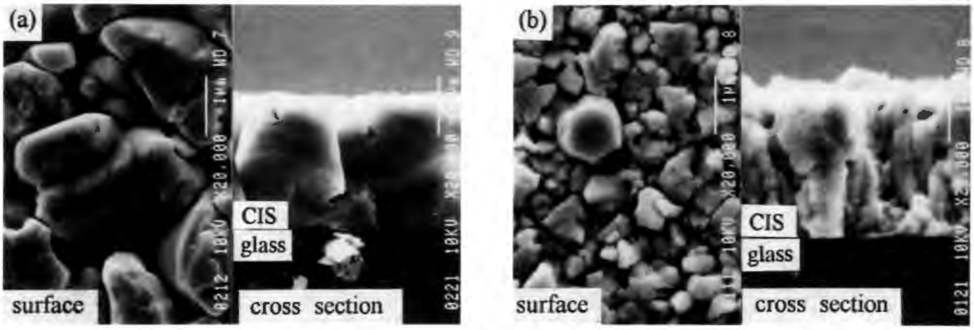

Fig. 3 SEM micrographs of $CuInSe_2$ films prepared by (a) the triple-IBT and (b) the dual-IBT.

These results indicate that ionization of Se is crucial for improvement of crystallinity of IBT-grown films. We believe that the triple-IBT plays an important role not only in migration of atoms and in improvement of adhesion, but also in formation of the ternary compound during the crystal growth by active Se ions.

4. CONCLUSION

We succeeded in improving substantially the grain size and the crystallinity of $CuInSe_2$ thin films deposited at low temperatures by using IBT, in which Cu-, In- and Se-vapors were ionized and accelerated. It is therefore suggested that the triple-IBT is a promising technique for fabrication of superstrate-type solar cells at low temperatures.

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