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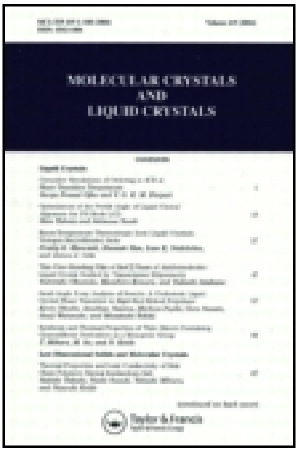

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Surface Morphology of Cu(Zn, Sn) Metal Precursor for Solar Cell Applications

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Version of record first published: 30 Aug 2012.

To cite this article: Sungwook Hong (2012): Surface Morphology of Cu(Zn, Sn) Metal Precursor for Solar Cell Applications, Molecular Crystals and Liquid Crystals, 565:1, 153-158

To link to this article: http://dx.doi.org/10.1080/15421406.2012.693320

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Mol. Cryst. Liq. Cryst., Vol. 565: pp. 153–158, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.693320

Surface Morphology of Cu(Zn, Sn) Metal Precursor for Solar Cell Applications

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Cu(Zn, Sn)(CZT) metal precursors were deposited on glass substrates by an RF-magnetron sputtering method for use in CZT-based solar cells. Recently, researches have shown that CZT-based solar cell films prepared with a metal precursor with a rough surface morphology produce a low conversion efficiency. A single layer of tin (Sn) grown on a substrate has a rough surface morphology. In this study, the co-sputtering method was used, wherein Zn, Cu, and Sn layers were deposited on co-sputtered layers of Cu-Sn, Zn-Sn, and Cu-Zn, respectively. From an atomic force microscopy analysis, the root-mean-square surface roughness of the Zn/Cu-Sn layer was found to be 12.3∼14.3 times smaller than that of the other layers precursors, Cu/Zn-Sn, and Sn/Cu-Zn.

Keywords CZTS; CZTSe; metal precursor; solar cell; surface morphology

Introduction

Recently, Cu(Zn, Sn)(CZT)-based optical absorbers have attracted increased attention for use in solar cell applications. An ideal solar cell absorber material should have a direct band gap of around 1.3∼1.5 eV and be composed of abundant, inexpensive, and nontoxic elements [1]. Quaternary compounds of Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have been considered because they contain abundant and nontoxic elements: Cu, Zn, Sn, S, and Se. The energy band gap of this materials has been theoretically calculated to be 0.96 eV (CZTSe) and 1.50 eV (CZTS) [1] and experimentally to range from 0.98 eV for selenide to 1.5 eV for sulfide [2–3]. Using a vacuum process, the highest efficiency in the case of CZTS has been reported to be 6.7% by Katagiri et al. and that in the case of CZTSe has been reported to be 3.2% by Zoppi et al. [4–5]. The properties of CZT-based solar cells have been shown to be considerably affected by the quality of the metal precursor [3]. H. Araki et al. have explained the efficiency of CZTS thin films in terms of its surface morphology; the films were grown with various metallic layers [6]. In these researches [3,6], the effect of surface morphology was not considered in the fabrication process. However, the characteristics of the solar cells were discussed in terms of the surface morphology of the metal precursors. Further, there are no reports on the improved surface morphology of metal precursors. In the present study, a cause for deciding rough surface morphology and a method for improving the surface morphology of the metal precursor were researched.

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Experimental

Two types of metal precursors were deposited by an RF-sputtering method on a glass substrate without heating. Specifically, one metal precursor was grown by the co-sputtering method, and the other was grown sequentially. First, three samples were produced by the co-sputtering method, wherein Zn, Cu, and Sn layers were deposited on co-sputtered layers of Cu-Sn, Zn-Sn, and Cu-Zn, respectively. These samples were designated CZT-A, CZT-B, and CZT-C, respectively. Second, two samples, designated CZT-D and CZT-E, were prepared by sequentially depositing the metals. The order of the stacked layers in CZT-D and CZT-E was Cu/Zn/Sn/glass and Cu/Zn/Sn/Cu/glass, respectively.

The background pressure in the deposition chamber was 1.6×10^{-6} Torr. The metal precursor was deposited in argon gas at room temperature. The argon flow rate was 10 sccm, and the working pressure was 5.5×10^{-3} Torr. The substrate holder was rotated at 10 rpm to induce uniformity in the thin film.

The surface morphology was analyzed using a scanning electron microscope (SEM, Hitachi S-4200) and an atomic force microscope (AFM, Nanoscope IIIa). The chemical composition of the metal precursor was found by using an inductively coupled plasma spectrometer (ICP, Optima 7300DV). The crystalline properties of the metal precursors were analyzed by X-ray diffraction (XRD, PANalytical X'pert Pro-MPD goniometer).

Results and Discussion

The stoichiometry of the metal precursor films is listed in Table 1. The table indicates that CZT-A, CZT-D, and CZT-E were slightly Cu rich, and CZT-B and CZT-C were Cu poor, but all the samples were Zn rich.

Figure 1 shows SEM images of the co-sputtered layers, Cu-Sn (Fig. 1a), Zn-Sn (Fig. 1b), and Cu-Zn (Fig. 1c). The surfaces of the Cu-Sn and Cu-Zn layers were flat, but Zn-Sn layer was rough, as shown in Fig. 1. This result agrees with previous observation that Sn and Zn react preferentially with Cu [7,8].

Figure 2 shows SEM images of the metal precursor films. The smoothest top surface was that of sample CZT-A. The roughness of the top layer of sample CZT-B was caused by the roughness of the first layer, which was co-sputtered with Zn and Sn, as shown in Fig. 1b. The roughness of the top layer of sample CZT-C was caused by the crystal growth of Sn on the Cu-Zn layer. The grain size on the surface of the CZT-E films was smaller than that on the surface of CZT-B and CZT-C. Sn crystallized independently in CZT-B and CZT-C but was bonded with Cu on CZT-E. This was confirmed by XRD analysis.

Table 1. Elemental compositions and ratios of metal precursors measured by ICP

	Atomic Ratio(%)			Compositional Ratio (%)	
Sample name	Cu	Zn	Sn	Cu/(Zn+Sn)	Zn/Sn
CZT-A	51.6	22.9	25.5	1.07	0.90
CZT-B	42.4	27.6	30.0	0.75	0.92
CZT-C	49.2	22.3	28.5	0.97	0.78
CZT-D	50.9	20.2	28.8	1.04	0.70
CZT-E	52.3	21.0	26.7	1.10	0.79

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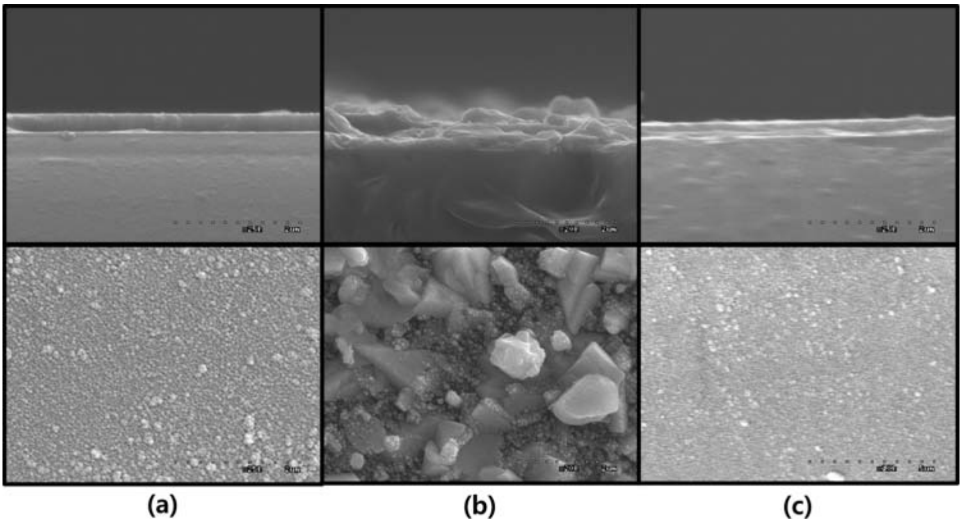

Figure 1. SEM images of co-sputtered layers of (a) Cu-Sn, (b) Zn-Sn, and (c) Cu-Zn

As shown in Fig. 3, the main peaks ($2\theta = 30.64^\circ$ and $2\theta = 32.02^\circ$) of Sn on samples CZT-B and CZT-C were relatively higher than those of other samples. This result shows that Sn in CZT-B and CZT-C had the tendency to grow by itself. However, Sn in the CZT-A sample was bonded with Cu as Cu_6Sn_5, CuSn, and $Cu_{81}Sn_{22}$. CuZn and CuSn phases were shown on samples CZT-D and CZT-E, which were deposited sequentially and had multiple layers. These phases were induced by the interface between Cu and Zn or Cu and Sn.

The size of the Cu, Zn, and Sn crystals formed within a single layer is shown as a function of growing time in Fig. 4. Using the data obtained from the XRD patterns, which were obtained from a single layer of Cu, Zn, and Sn, the crystalline size was determined by the Scherrer formula [9], which is given as

$$D = \left(\frac{0.9\lambda}{\beta \cos\theta} \right) \tag{1}$$

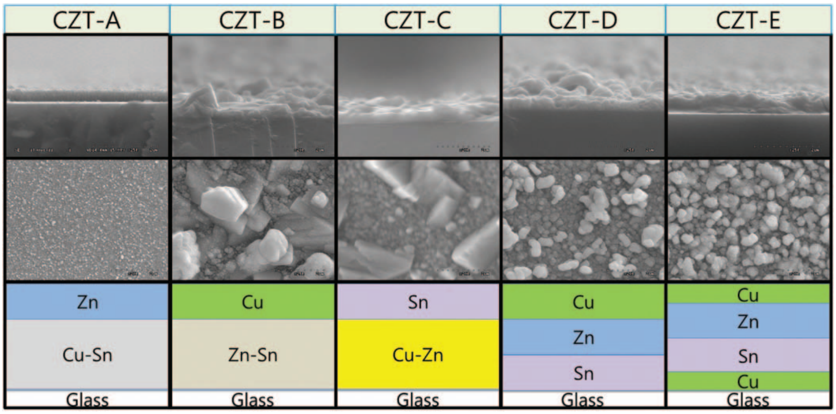

Figure 2. SEM images and stacking order of metal precursors.

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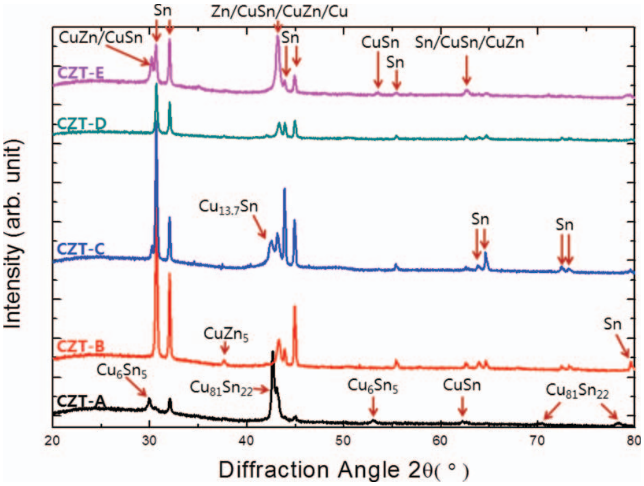

Figure 3. XRD patterns of metal precursors.

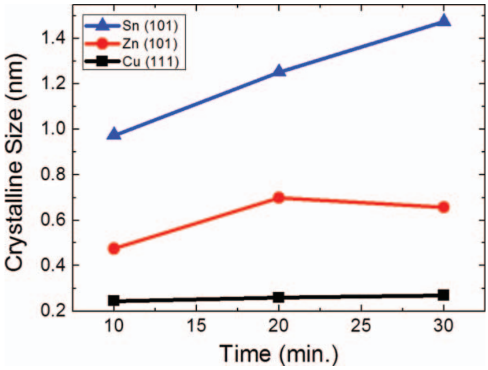

Figure 4. Change in crystalline size for Cu, Zn, and Sn single layers as a function of growing time.

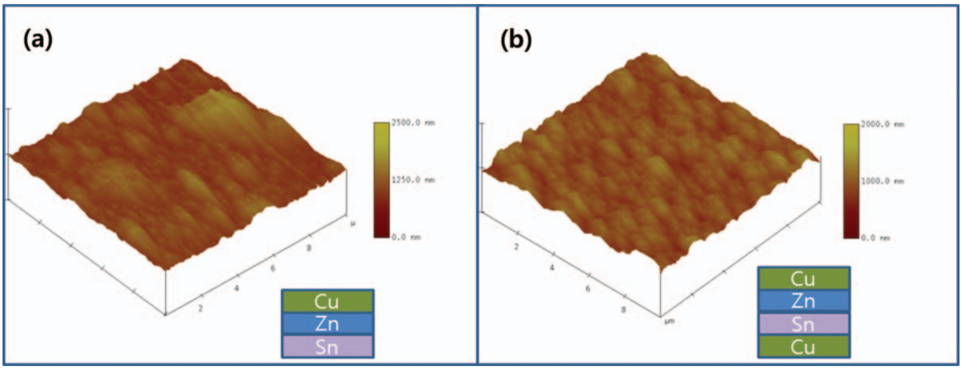

Figure 5. AFM images of (a) CZT-D and (b) CZT-E metal precursors, Cu, Zn, and Sn, grown sequentially.

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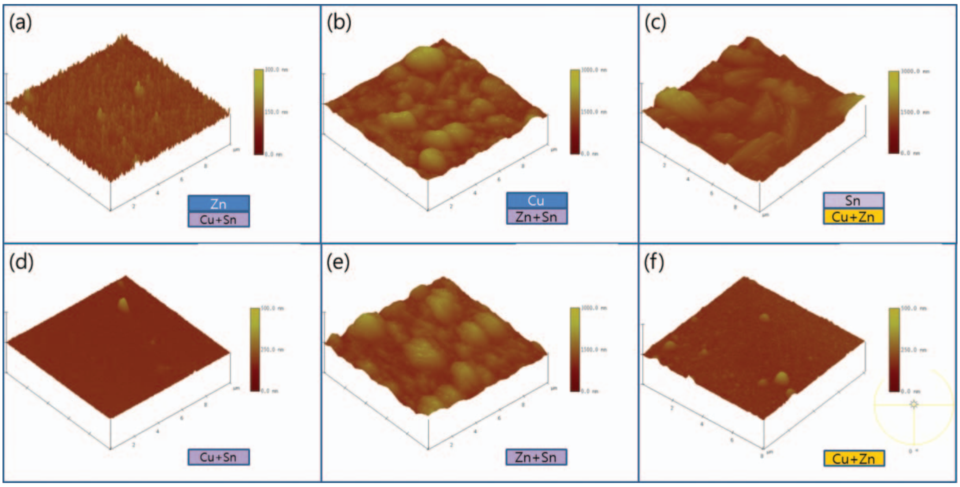

Figure 6. AFM images of metal precursors, (a) CZT-A, (b) CZT-B, (c) CZT-C, and of first layer co-sputtered with (d) Cu-Sn, (e) Zn-Sn, and (f) Cu-Zn of CZT-A, CZT-B, and CZT-C, respectively.

where λ is the wavelength of the CuKα line, β is the full width at half maximum(FWHM) in radians, and θ is the Bragg angle. As the deposition time of the elements was increased, the crystalline size of Sn increased more than that of Cu and Zn. This result shows that crystallization of Sn occurred more easily than that of Cu and Zn during the growing process.

Figure 5 shows AFM images of the metal precursors on samples CZT-D and CZT-E. The root-mean-square (rms) value of the surface roughness was determined to be 217.1 and 94.5 nm for CZT-D and CZT-E, respectively. The rough surface of CZT-D (Fig. 5a) was caused by the independent growth of Sn at the Sn layer. The AFM images of the metal precursors for samples CZT-A, CZT-B, and CZT-C are shown in Fig. 6. The surface roughness values of CZT-A, CZT-B, and CZT-C were determined to be 16.2, 199.7, and 232.3 nm, respectively. The roughness value of CZT-A was 12.3∼14.3 times smaller than that of CZT-B and CZT-C. As shown in Figs. 5 and 6, the independent growth of Sn increased the surface roughness of the metal precursor.

Conclusions

A metal precursor for solar cell application was fabricated using the RF-magnetron sputtering method. The surface roughness of the metal precursors, which were grown both sequentially and co-sputtered, was determined by AFM analysis. Sn was preferentially bound with Cu, and CuSn, Cu_6Sn_5, and $Cu_{81}Sn_{22}$ phases were found at the metal precursor. The increase in the surface roughness of the metal precursors was caused by the independent growth of Sn. From AFM analysis, the surface roughness value of the CZT-A film, in which the first layer was co-sputtered with Cu and Sn, was determined to be 16.2 nm; this value was 12.3∼14.3 times smaller than that for the films. When a metal precursor is fabricated with Cu and Sn by the co-sputtering method, it is expected that the surface morphology and conversion efficiency of CZT-based solar cells will be enhanced.

Acknowledgment

This research was supported by the Daegu University Research Grant, 2011

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