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Investigation of Cu_2SnSe_3 Preparation by Simultaneous Electrodeposition as Precursor of $Cu_2ZnSnSe_4$ Thin Film Solar Cell

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Abstract. Chalcogenide material of multinary metals are of interest in relation as optoelectronic devices such as laser and solar cell. Cu_2SnSe_3, ternary chalcogenide, is semiconductor with low bandgap. Beside that Cu_2SnSe_3 is important precursor for the growth of a promising $Cu_2ZnSnSe_4$ thin film solar cell since it contains elements that is abundance in the earth crust. The aim of this work is to synthesis Cu_2SnSe_3 thin film compound by using simultaneous electrodeposition. The product then was characterized using EDX, XRD, RAMAN and SEM. The result showed that Cu_2SnSe_3 can be prepared by electrodeposition at a potential of -0.6V *vs.* Ag/AgCl for 20 min. Annnealing can cause the increase of Cu_2SnSe_3 sample crystalinity. Annealing in argon atmosphere at 500 ºC affected selenium evaporation in the film, therefore it improved Cu/Sn ratio. Further, annealing in selenium atmosphere at temperature of 500 ºC can increase the intensity of Cu_2SnSe_3 crystal much better and also improve the Se/(Cu+Sn) ratio close to ideal value. Spectra of XRD and raman also proved the presence of Cu_2SnSe_3 in the prepared thin film.

INTRODUCTION

Now a days there are a great interest on multinary metal chalgenides [1,2]. The materials are used in optoelectronic devices such as laser and solar cell [3]. Ternary chalcogenides I-IV-VI, including Cu-Sn-X (X = S, Se), are semiconductors with narrow and intermediate bandgaps. These materials are suitable for solid lubricant due to the utmost mechanical and thermal properties.

In group I_2-IV-VI_3, Cu_2SnS_3 semiconductor compound is known very suitable for lithium battery electodes [4], photovotaic devices [5], thin film wave guides and light emitting diodes [6]. Cu_2SnSe_3 with a low boiling point and mass density and a high average atomic weight and refraction index is a candidate to be applied as acousto-optic in infrared area [7,8]. Cu_2SnSe_3 is also considered as thermoelectric material with high efficiency [9] as well as utmost precursor for the growth of a promising thin film solar cell of $Cu_2ZnSnSe_4$ through solid state reaction from Cu_2SnSe_3 with ZnSe [10,11]. There are a some techniques for Cu_2SnSe_3 preparation, but to obtain its single crystal is not easy. Reports on Cu_2SnSe_3 preparation works are few either for bulk [12,13,14] or thin film materials [15].

Techniques of evaporation, sputtering, and stack electrodeposition had been developed for preparation of Cu_2SnSe_3 [15,16,17]. Electrodeposition techniques for preparation of semiconductors had been done by two ways, namely stack electrodeposition and codeposition or simultanoeus electrodeposition. In this paper we worked on Cu_2SnSe_3 preparation through simultaneous electrodeposition. Structure is very important in determining the physical properties of the materials. Therefore for characterizations of the film were done using EDX, XRD, Raman and SEM.

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EXPERIMENTAL

Preparation of Cu_2SnS_3

Preparation of working electrodes. Before used for electrodeposition, the working electrodes of Mo-glass was cut with a size of 0.7 cm x 1.0 cm and then the electrodes were immersed in acetone with sonification for 10 min, after that were immersed in aquadest for 10 min with sonification. Finally they were immersed again in aceton and they were ready for used as working electrodes.

Preparation of electrodeposition solution. Electrodeposition solution was prepared by the succession of 1 mM $CuSO_4$, 20 mM $SnCl_4$, 7 mM Na_2SeO_3, 500 mM lactic acid and 500 mM KCl. Then the volume was made 50 mL using aquadest and all the solids were dissoved with slow stirring. Finally the pH was set to 2.5.

Electrodeposition. We used potentiostat Hokuto dento HSV-100 for electrodeposition. The electrodeposition of Cu_2SnSe_3 was done using regulated potential was set at -0.6 V for certain time. As usual the Mo-glass was positioned as working electrode, while platinum and Ag/AgCl as counter and reference electrodes. The distance between working and counter electrodes was 1 cm.

Annealing of as-deposited films. The film was subjected to argon atmosphere annealing at temperatures of 300, 400 and 500 ^oC for 20 min and to selenium atmosphere annealing at temperature of 500 ^oC, the annealing was done for 10 min.

Characterizations

Atomic compositions were determined by energy-diffuse X-ray (EDX) analysis using a Hitachi S-2250N EDX analyzer. Crystal structures of the Cu_2SnSe_3 films were analyzed by X-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer (Cu Kα, Ni filter). Crystalline phase compositions were determined by Raman spectroscopy using a JASCO NRS-3100 Laser Raman Spectrophotometer with a laser wavelength of 532 nm. Morphology of the films was examined using a Hitachi S-5000 FEG field emission scanning electron microscope (FE-SEM) at a voltage of 20 kV.

RESULTS AND DISCUSSION

Composition of Metal Analysis

Electrodeposition to prepare Cu_2SnSe_3 was done using the solution containing 1 mM Cu, 20 mM Sn, 7 mM Se, 500 mM lactic acid and KCl 500 mM. Electrodeposition was conducted at potential of -0.6 V vs Ag/AgCl for 20 min and the distance of counter and working elekctrodes is 1 cm. Addition of lactic acid as complexing agent functions to make the deposition potentials of the three metals, copper, selenium and tin were as close as possible so that the three metals can deposit together simultaneously [18]. After that the molybdenum-glass covered with Cu_2SnSe_3 was annealed with argon and selenium atmospheres for 10 min. Argon annealing was done at 300, 400 and 500 ^oC, while annealing using selenium atmosphere was conducted at temperature of 500 ^oC, the results can be seen in Table 1 and Figure 1.

TABLE 1. Composition of metals of Cu_2SnSe_3 thin film (as-deposited) and after annealing in argon and selenium atmosphere.

Metal	As-deposited	Annealed (^oC)			
		in argon			in selenium
		300	400	500	500
Cu	31.2	33.3	33.2	35.7	27.2
Sn	22.0	21.3	22.3	19.1	20.5
Se	46.8	45.4	45.5	45.2	52.2

Table 1 shows that initial sample (as-deposited Cu_2SnSe_3, without annealing) rich in tin but poor in selenium. With annealing using argon until temperature of 500 ^oC did not improve the precentage of selenium even almost similar, while tin tends to evaporate that causes the precentage reduction at temperature of 500 ^oC. Annealing at temperature of 300 and 400 ^oC did not inflence significantly to evaporate either selenium or tin. The presence of

selenium in annealing of Cu_2SnSe_3 is enough to increase percentage of selenium that causes selenium rich (little bit higher than its ideal composition). Tin also decresed with annealing at the temperature of 500 °C. However copper and tin are still not in the ideal composition.

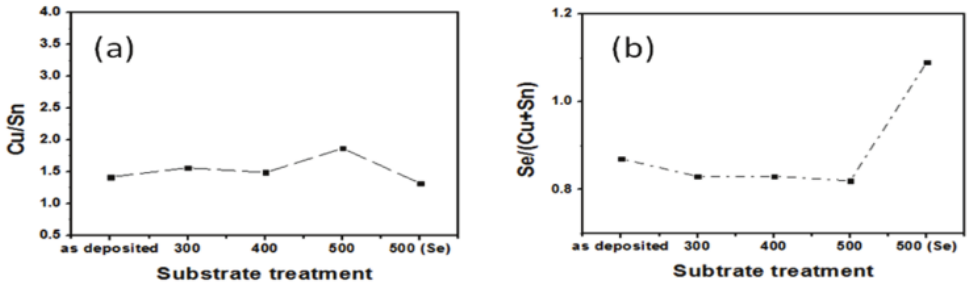

FIGURE 1. Atomic ratio (a) Cu/Sn and (b) Se/(Cu+Sn) of Cu_2SnSe_3 thin film for as-deposited, annealed for 20 min in argon atmosphere at temperatures of 300, 400 and 500 °C as well as in selenium atmosphere at temperature of 500 °C for 10 min.

Figure 1 shows (a) atomic ratio of Cu/Sn and (b) atomic ratio of Se/(Cu+Sn) of as deposited and annealed Cu_2SnSe_3 at temperatures of 300, 400 and 500 °C for 20 min in argon atmosphere as well as the sample annealed at 500 °C for 10 min in selenium atmosphere. Figure 1(a) shows the increase of annealing temperature, increase the ratio of Cu/Sn, although the increase is not so significant as compared with initial sample (as-deposited) that are 1.6 and 1.4 for the thin film annealed at 300, and 400 °C in argon atmosphere and as-deposited one, respectively. But with the following annealing at 500 °C will increase the atomic ratio of Cu/Se around 1.9 due to the evaporation of tin while annealing at 500 °C. However with selenium atmosphere will reduce ratio of Cu/Sn as much as 1.3 compared with as-deposited thin fim due to the reduction of tin evaporation and also the increase of selenium percentage in Cu_2SnSe_3. Over all the obtained thin film of Cu_2SnSe_3 is poor copper that is not suitable for *p*-type semicondutor because there is no copper that places crystal lattice from tin to form *p*-type defect anticite.

Figure 1(b) depicts all obtained film had ratio of Se/(Cu+Sn) above 0.8. Annealing of Cu_2SnSe_3 thin film at temperatures of 300, 400 and 500 °C with argon atmosphere showed the decrease of the ratio, although it is not so significant as compared with as-deposited thin film, the values reduced from 0.87 to 0.82. The presence of selenium atmosphere for the annealing at temperature of 500 °C shows the increase of the ratio of Se/(Cu+Sn) until 1.09 or a little bit selenium rich and this is the ideal ratio that is expected for thin film of Cu_2SnSe_3. Cu_2SnSe_3 has both monoclinic [6,13,14] and sphalerite structures [15] that is suitable for the variation of atomic ratios of Cu/Sn and Se/(Cu+Se) of 1.743-2.03 and 1.075-1.275, respectively. Next, characterization of Cu_2SnSe_3 thin film was done using spectrometer of XRD, raman and SEM.

XRD Analysis

Analysis of XRD (Figure 2) of Cu_2SnSe_3 thin film has polycrystal properties and containing SnSe as second phase as shown with the peak (400) at its diffraction profile. The presence of Cu_2SnSe_3 was comfirmed at 2θ between 27-28°, near 45° and 53° each of which for (111), (220) and (311). Figure 2(a) is the XRD pattern of the initial thin film sample (as-deposited film) resulted from electrodeposition can not be seen the growth of Cu_2SnSe_3 dominantly. It seemed to be dominated by SnSe crystal. The Cu_2SnSe_3 crystal began to grow after annealed at the temperatures of 300, 400 and 500 °C both for the atmospheres of argon and selenium. Although, it still has SnSe crystal in the thin film (figure 2(b)-(e)). Annealing at 400 °C in argon atmosphere (Figure 2(c)) shows the growth of Cu_2SnSe_3 (111) greater than at the temperatures of 300 °C and 500 °C in argon atmosphere (Figure 2(b) and (d)). Meanwhile the annealing at temperture of 500 °C in argon caused the decrease of Cu_2SnSe_3 peak, this is due to evaporation of tin when the annealing at that temperature. Figure 2(e) shows the greatest increase Cu_2SnSe_3 (111) peak, even also occurs at the peaks of Cu_2SnSe_3 crystals (220) and (311). Since the as-deposited thin film is poor selenium, therefore by annealing at temperature of 500 °C at selenium atmosphere caused the increase of selenium composition in the formed

Cu_2SnSe_3. Part of unreacted tin to form Cu_2SnSe_3 will form SnSe, that increases the signal of SnSe at the annealing condition. Meanwhile 2θ around 40° is the signal for the moybdenum crystal where the thin film adheres on it.

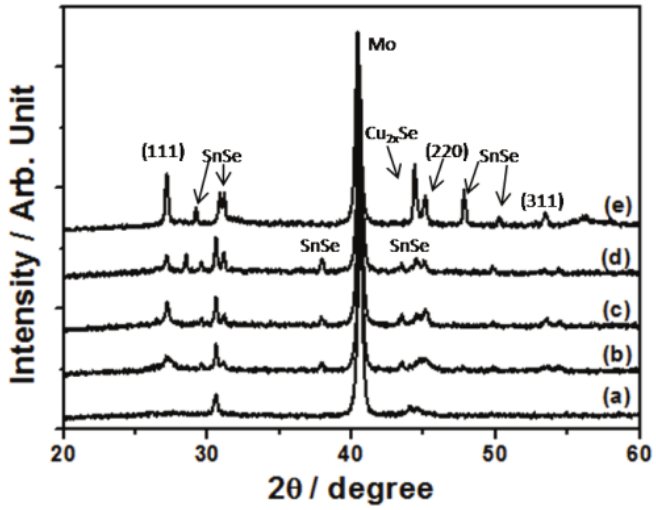

FIGURE 2. Profiles of X-ray diffraction of Cu_2SnSe_3 thin films (a) initial sample (as-deposited), annealed in argon atmosphere at (b) 300 °C, (c) 400 °C and (d) 500 °C as well as (e) annealed in selenium atmosphre at temperature of 500 °C.

Raman Analysis

Raman spectra of Cu_2SnSe_3 is shown in Figure 3, the dash line shows the peaks of mentioned selenide, for Cu_2SnSe_3 was affirmed at wave numbers of 177 and 231 cm^{-1}, this result is almost similar with the works of Li *et al* [19] that gave at the wave numbers of 178 and 230 cm^{-1}. The presence of annealing increases crystal growth of Cu_2SnSe_3, that is seen the increase of peak intensity (Figure 3(b)-(e). The peak in Figure 3(b) shows the presence of peak widening due to low annealing temperature that caused Cu_2SnSe_3 formed unperfectly, while for annealing in argon at 400 °C gave narrower and higher peak compared to the annealing in argon at 300 °C. Finally the intensity reduced again caused by the evaporation of tin at the annealing in argon at 500 °C as shown in Figure 3(d). Selenium atmosphere gave the highest peak intensity of Cu_2SnSe_3 crystal as seen in Figure 3(e). Meanwhile the peak at 255 cm^{-1} is SnSe, since from that XRD data before there is no Cu_2SnSe_3 crystal for initial sample. However other researcher mentioned 251 cm^{-1} is Cu_2SnSe_3 [19].

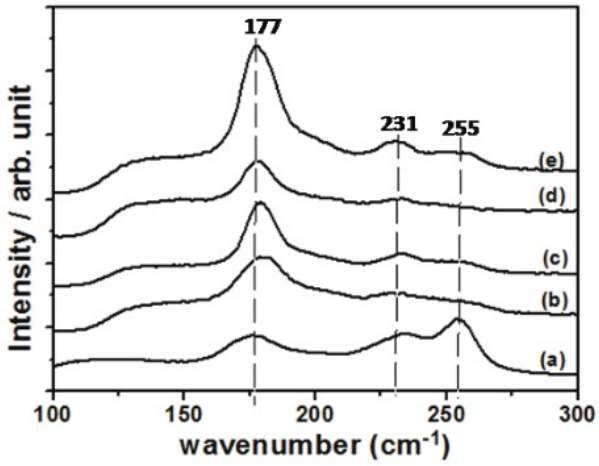

FIGURE 3 Raman spectra of Cu_2SnSe_3 thin films (a) initial sample (as-deposited), annealed in argon atmosphere at temperature of (b) 300 °C, (c) 400 °C and (d) 500 °C as well as (e) annealed in selenium atmosphere at temperature of 500 °C.

SEM Analysis

SEM imanges of Cu_2SnSe_3 thin film for as-deposited and treated samples annealed with argon or selenium atmopheres are given in Figure 4. As-deposited thin film (Figure 4(a)) shows the spheric grains with diameter around 0.5 mm. Since the solution was not stirred, the grains were bigger than strirred one.

The annealing in argon at temperatures of 300 and 400 °C (Figure 4(b) and (c)) caused the spherical grains became thinner compared to as-deposited one. The further heating caused the grains seen as melting due to the evaporation of tin partly (Figure 4(d)). In selenium atmosphere at temperature of 500 °C gave the different result than previous one. To make the better result SEM of the sample annealed in selenium atmosphere in 500 °C can be seen in Figure 5. The figure shows the spherical grains ca. 1 μm characterized for Cu_2SnSe_3, although the grains were covered by small SnSe above them.

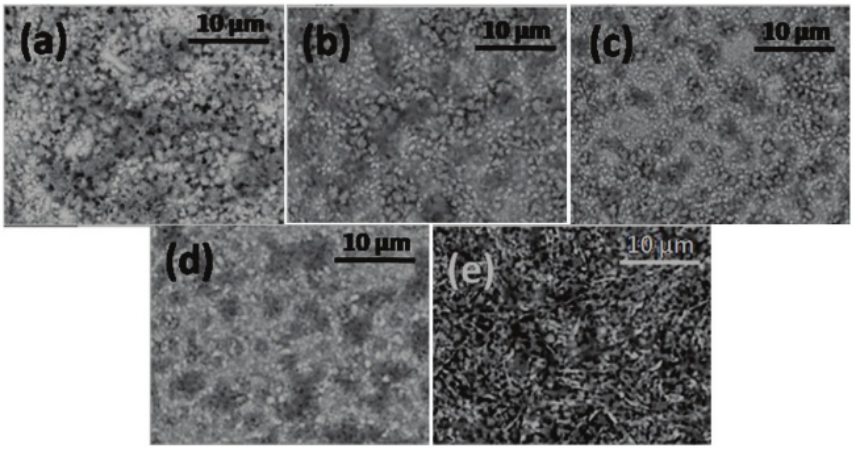

FIGURE 4 SEM image of Cu_2SnSe_3 thin film (a) inital sample (as-deposited), annealed in argon atmosphere at temperature of (b) 300 °C, (c) 400 °C and (d) 500 °C as well as (e) annealed in selenium atmosphere at temperature of 500 °C.

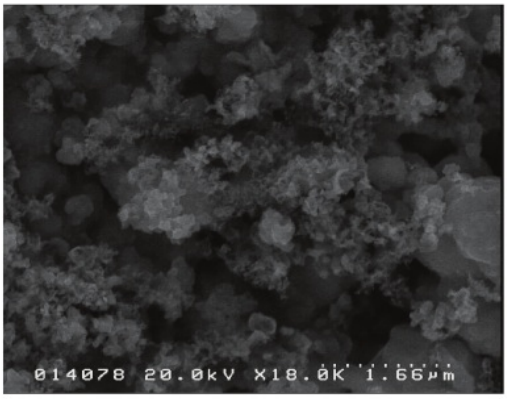

FIGURE 5 SEM image of Cu_2SnSe_3 thin film annealed in selenium atmosphere at temperature of 500 °C with a higher magnification.

CONCLUSION

Synthesis of Cu_2SnSe_3 thin film using simultaneous eletrodeposition had been done. Annealing of the thin film improve the crystalinity of Cu_2SnSe_3 formed. Annealing with the presence of argon atmosphere gave tin in the film partly evaporated at temperature of 500 °C. However, annealing with the presence of selenium atmosphere to the as-deposited Cu_2SnSe_3 thin film produced a better result with the composition percentage close to ideal. The Cu_2SnS_3 thin film resulted was copper poor, that reduced the *p*-type semiconductor properties. Over all Cu_2SnSe_3 resulted still had impurieties such as SnSe, Therefore for the need of $Cu_2ZnSnSe_4$ preparation treatment the film should be done.

ACKNOWLEDGMENT

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