Re-crystallization of CZTS prepared by galvanostat electro-deposition

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Abstract

Cu_2ZnSnS_4 (CZTS) with large absorption coefficients of over 10^4 cm^{-1} in the visible band is a suitable absorption layer for applications in thin film solar cells [1]. Nowadays, Cu(In,Ga)Se_2 (CIGS) based solar cells with higher than 20 % converting efficiency are available, but indium and gallium constituents of the CIGS are both rare elements, and the selenium is toxic[2-3]. CZTS is considered to be competitive to CIGS, due to its high amount constituents of zinc and tin (Zn, Sn) in the earth for replacing indium and gallium [4].

Cu_2ZnSnS_4 (CZTS) films had been successfully obtained on Mo/SLG substrates by one-step electro-deposition. The electrolytic aqueous for CZTS electro-deposition was prepared using $CuSO_4$, $ZnSO_4$, $SnSO_4$ and $Na_2S_2O_3$ mixed at 2:1:2:2 mol ratio. The electro-deposition was carried on using galvanostat method through double electrodes at a current of 3 mA. After electro-deposition, the obtained CZTS was re-crystallized in vacuum and then treated with sulfurization using sulfur vapor in nitrogen ambience. The re-crystallization was executed at 200, 240, 280 °C, respectively, for 30 min, and the sulfurization at 400 °C for 5 min. The effects of the re-crystallization process on the electro-deposition films were investigated through x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), raman spectroscopy, and uv-vis spectra. As shown in Fig. 1, from XRD examination, it is obvious that CZTS crystallite with kesterite structures identified from XRD JCPD card with peaks at 28.3, 47.2, and 56 (2θdegree) from (112), (220), and (312) reflected plane, respectively, is successfully obtained through the one-step electro-deposition. Besides, CuS and/or SnS binary phases were also found in the film. The binary phases seem to decreased with increasing the re-crystallization temperature. From SEM as shown in Fig. 2, two kinds of grain features which may result from different phases are found in the sample (a) and (b). The different grain featues will be further identified using EDS. The as-prepared CZTS optical energy gap was derived from uv-vis spectra. All of the as-prepared samples of have an average absorption coeifficient over 10^4 cm^{-1} in the visible range from 400 to 750 nm. The square absorption coefficient versus photon energy spectra depicts that the obtained samples have the energy of 1.09 ~1.22 eV. The optical energy my result from CZTS and binary phases, and found to be decreased with re-crystallization temperature. The optical properties depict that the CZTS is suitable for thin film solar cell application.

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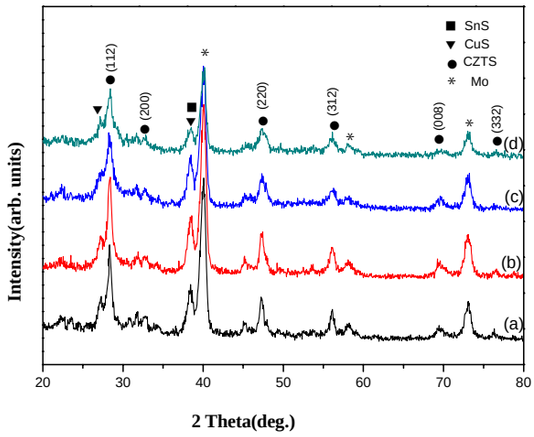

Fig. 1. CZTS XRD spectra of (a) as-electro-deposited, and re-crystallized at (b) 200 (b) 240 (b) 280℃.

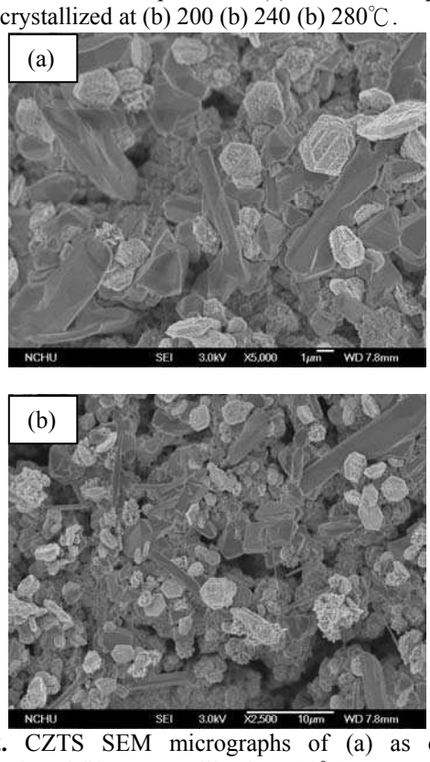

Fig. 2. CZTS SEM micrographs of (a) as electro-deposited, and (b) re-crystallized at 200℃.

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