



Optical and surface probe investigation of secondary phases in $\text{Cu}_2\text{ZnSnS}_4$ films grown by electrochemical deposition

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ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films were grown by electrochemical deposition, and we measured the work function of the as-grown and of the KCN-etched CZTS surfaces by using Kelvin probe force microscopy (KPFM) and micro-Raman scattering spectroscopy with incident laser wavelengths of 488.0 and 632.8 nm, respectively, and the results indicate that a secondary phase formed at different depths. The KPFM measurements can discriminate phase uniformity at the nano-scale. Secondary phases, such as Cu_{2-x}S ($0 < x < 1$), ZnS , and MoS_2 , were identified on the as-grown surface while Cu_{2-x}S was removed from the KCN-etched surface. The KCN-etched CZTS absorption layer was measured to have a 5.0% conversion efficiency. Owing to the low cost of electrochemical deposition, it is desirable to obtain high tailored CZTS films can be obtained with the robust surface characteristics of a uniform work function with a single phase.

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1. Introduction

Kesterite ($\text{Cu}_2\text{ZnSnS}_4$; CZTS) is one of the most promising materials for use in thin-film solar cells since its characteristics can give desirable properties to solar cell devices that are competitive in the market. Solar cells need to convert photons into electrical energy with high efficiency at a low cost, and the advantages of using CZTS are that it has a high absorption coefficient, a band gap near 1.5 eV, and *p*-type conductivity [1–4]. Pure CZTS thin-films have a band gap of ~ 1.4 eV, which is higher than that of CZTSe thin-films (~ 1.0 eV), possibly as a result of the technical benefits of having an absorber layer [2,5]. At present, CZTSSe thin-film solar cells have produced the highest conversion efficiency, at 12.6% [6], and pure CZTS thin-film solar cells can achieve a conversion efficiency of 9.2% [7]. Furthermore, solution or electrochemical deposition is an easy and inexpensive method that can be used to fabricate these films at room temperature without a vacuum, and the highest conversion efficiency of an electrochemically-deposited CZTS thin-film solar cell has been recorded at 8.0% while that for CZTSe thin-film solar cells was at 7.0% [8–10].

The composition of a material made from a quaternary compound can be rather complex, and the number of metallic elements can be adjusted in order to simplify the compound material from quaternary to ternary. A ternary phase diagram can be used to understand the phase formation of a Cu–Zn–Sn system [11] in order to categorize specific compositions where secondary phases are clearly shown. The final formation of a CZTS film with its secondary phases is influenced by its composition which depends on the precursor used and on the conditions of sulfurization [12,13].

Secondary phases have significant effects on the performance of the solar cell. For example, Katagiri et al. reported that CZTS absorber layer etching technique that used deionized water improved the efficiency of the solar cell to over 6.7% [14]. Many prior studies have used different techniques, such as Raman scattering spectroscopy, to characterize the secondary phases of such materials [15], and potassium cyanide (KCN) etching is widely used to remove secondary phases. The secondary phases exist in different locations in the absorber layer [16]. In previous studies, Bär et al. characterized the CZTS surface using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) and found changes in the surface composition where KCN etching had removed the Cu- and Sn-related secondary phases [17]. A Cu-poor CZTS film presents that Cu and Sn concentrations of the surface were reduced

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by XPS measurement. However, the bulk composition (EDS) is similar to that prior to etching. Therefore, KCN etching changed the surface composition of the CZTS thin-films, resulting in a widening of the surface band gap.

Therefore, we need to perform optical and local electrical observations to carefully characterize the composition and secondary phases of CZTS thin-films after KCN etching. We observed the composition difference of surface and bulk with EDS and XPS, before and after KCN etching respectively. Raman spectroscopy and KPFM can characterize the distribution of the secondary phase with varying thickness and surface uniformity. Furthermore, the work function of the CZTS layers is one of the most important things that can be used to determine the open circuit voltage (V_{OC}). CZTS thin-film solar cells are known to have a lower V_{OC} , even though they have a band gap of about 1.4 eV, which is high when compared to that of CIGS thin-film solar cells. Therefore, it is critical to understand the work function distribution of the CZTS layer in order to be able to optimize the V_{OC} of the CZTS thin-film solar cells. We also demonstrated an etching method for a single phase surface of CZTS, which might affect the interfaces of the PN-junction of the CZTS solar cells. Moreover, identification of the surface phases leads to improving the device performances and conversion efficiency as well as understanding the phase growth mechanism of the CZTS layers with electro-plating deposition.

2. Experimental

A potentiostat (WPG100, Won-A tech, Korea) was used to electrochemically deposit Cu–Zn–Sn metallic precursor films from an aqueous solution containing Cu, Zn, and Sn ions. The mole ratios of the materials were 0.02 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.035 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.014 M SnCl_2 with 0.5 M Tri-sodium citrate as a mixing agent [18]. The raw materials were deposited at a constant current density of 1.3 mA/cm^2 for 2000 s, and the three electrode systems used for the electrochemical deposition included a Mo-coated soda-lime glass substrate (working), a Pt plate (counter), and a saturated Ag/AgCl reference electrode. The metallic precursor films were annealed in a quartz tube furnace under a sulfur atmosphere (vaporized elemental sulfur with high-purity Ar carrier gas) [18], and the films were sulfurized at various temperatures at around 550 °C. KCN etching was performed with a 10% KCN solution with distilled water for 3 min. Lee et al. reported that CZTS thin-film solar cells could achieve a 2% conversion efficiency [19] when soaked in an aqueous KCN solution, and we had improved the efficiency to higher than 5%. We use the same process with the CZTS samples, and very recently, we had achieved a conversion efficiency of 8% for CZTSe solar cells by applying selenization via KCN etching [20].

The room temperature micro-Raman scattering spectra were measured using a McPherson 207 spectrometer equipped with a nitrogen-cooled charge-coupled device (CCD) array detector. The

films were excited with a coherent 488-nm wavelength sapphire laser operating at a power of 1.5 mW and with a 632.8-nm He–Ne laser focused to a spot of 1 μm in diameter. The surface and the cross-sectional morphology, as well as the composition of the films, were examined using a field-emission scanning electron microscope (FESEM, JSM-6700F) and an energy dispersive spectrometer (EDS, Link system OXFORD analyzer). We also measured the core-level spectra of the related elements using XPS manufactured by VG Microtech to obtain surface composition. The non-monochromatic Al $K\alpha$ line ($h\nu=1486.6$ eV) was used as an excitation source with a pressure lower than 10^{-9} Torr in the analytical chamber. The binding energy was referenced by using C 1s of absorbed hydro-carbon (284.5 eV).

The KPFM measurements were performed with a commercial AFM (Nanofocus Inc., n-Tracer) with a Pt/Ir coated cantilever. The KPFM measurements confirmed that the surface potential was the same as the contact potential difference (CPD) between the metallic AFM tip and the sample, and this quantity was denoted as V_{CPD} . V_{CPD} can be defined as in Eq. (1), and it is identical to the work function difference between the tip and the sample as long as there are no defect states on the surface of the sample [21]. The Pt/Ir-coated tips were calibrated with highly oriented pyrolytic graphite (HOPG) ($\Phi=4.6 \pm 0.1$ eV) in order to convert the potential difference to a work function [22], and the absolute work function of the tip can be calculated from Eq. (1), which is determined by means of the distribution of each point, which in turn produces the surface potential of the sample. The topographical images were obtained at a resonant frequency of the probe of about 78.35 kHz, and the surface potential was measured under a non-contact mode by applying an AC voltage with an amplitude of 1.0 V and a frequency of 74.5 kHz to optimize for clear images at a sufficient sensitivity. The scan area had a size of $10 \times 10 \mu\text{m}^2$, and the scanning rate was set to 0.5 Hz to minimize the topological signal while the lock-in amplifier was operated at a sensitivity of 100 mV/nA. The samples were not damaged while carrying out these measurements.

$$V_{CPD} = \frac{\phi_{sample} - \phi_{tip}}{-e} \quad (1)$$

3. Results and discussion

3.1. Bulk and surface composition of CZTS thin-films

Table 1 summarizes the typical Cu/(Zn+Sn) and Zn/Sn ratios of the bare and of the KCN-etched CZTS samples studied in this paper. The bulk composition is measured by using EDS, and the surface composition is obtained through XPS.

The A sample is Cu-rich, and the B sample is Cu-poor. Fig. 1 indicates the composition of the bulk and of the surface of CZTS

Table 1

The composition of the Cu, Zn, Sn, and S in the CZTS thin films was measured by EDS and XPS. The bulk composition of A sample is Cu-poor and the B sample is Cu-rich by EDS measurement. The surface compositions of A and B samples are Cu-poor by XPS measurement.

Composition	EDS				XPS			
	Before etching		After etching		Before etching		After etching	
	(A)	(B)	(A')	(B')	(A)	(B)	(A')	(B')
Cu (%)	35.04	24.18	22.53	26.80	28.3	8.2	21.6	23.5
Zn (%)	11.33	13.78	17.21	13.81	15.8	19.6	19.8	16.2
Sn (%)	7.24	12.70	11.75	11.74	20.1	26.4	18.3	15.8
S (%)	46.39	50.98	48.5	47.65	35.8	45.9	40.3	44.4
Cu/(Zn+Sn)	1.89	0.91	0.78	1.05	0.79	0.17	0.57	0.73
Zn/Sn	1.56	1.09	1.46	1.18	0.78	0.74	1.08	1.03

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