Synthesis and physical properties of $Cu(In,Ga)Se_2$ nanoparticles and $CuGaSe_2$ thin-films for tandem cell photovoltaic applications

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ABSTRACT

For tandem cell photovoltaic applications, we have investigated $Cu(In,Ga)Se_2$ (CIGS) nanoparticles and $CuGaSe_2$ (CGS) thin-films. Alternative structures with metal Mo and transparent conductive oxide (TCO) back contacts were also studied.
The CIGS nanoparticles were synthesized by pulsed laser ablation (PLA) and treated in a Se annealing process after deposition. Topography, optical and other analysis results revealed that they show unique morphology, bandgap shift, and high absorption coefficient. Electrical characteristics of the *pn*-junction structures showed photovoltaic properties with J_{sc} of 31.7 nA/cm^2 and V_{oc} of 0.17 V in case of nanopaticles.
The CGS thin-films were grown via a single step by co-evaporation. Various processes for CGS films have been proposed such as bi-layer and three stage processes [3,4]. Although the so-called three-stage process has recorded the best efficiency until now, we have prepared CGS thin-films by a single process to make sure reproducibility. In order to use CGS thin films as a top cell of tandem devices, we investigated optical bandgap and photovoltaic properties. Properties of the CGS thin-films on TCO will be compared those of the films on Mo.

INTRODUCTION

Chalcopyrite $CuInSe_2$ (CIS)-based materials are most promising for thin-film photovoltaic devices owing to their high absorption coefficient, tunable band gap as Ga content is changed, and higher efficiency than other thin-film solar cells [1,2]. Although studies for improving the performance and decreasing production cost of CIS-based solar cell devices have been progressed, fundamental understanding of the CIS-based materials, especially nano-scale, is insufficient. To improve solar cell technology in the next generation, it is indispensible to investigate physical mechanisms in nano-scale. Moreover, we searched possibility of nanoparticles for tandem cell applications because bandgap is generally changed in nano-scale.
CGS thin-films are also one of the ideal compounds with a band gap of 1.7 eV. A variety of processes for CGS films have been proposed such as the bi-layer and three stage processes [3,4]. Although the three-stage process has recorded the best efficiency until now, we have prepared the CGS thin films by single process to make sure reproducibility.

EXPERIMENTS

We have studied CIGS nanoparticles synthesized by PLA and characterized to know their behaviors. The synthesis details described a previous report [5]. Meanwhile, CGS thin-films were grown by a co-evaporation method.
In case of the nanoparticles, Se atoms was deficient as treatment temperature was increased. To improve the defects, they were thermally treated under Se atmosphere called a selenization process. Meanwhile, for CGS thin-films, Cu, Ga, and Se source were simultaneously evaporated by e-beam or thermal power and the substrate temperature was ~~at~~ 530°C.
The prepared samples were examined by X-ray diffraction (XRD) with Cu *Kα* radiation, atomic force microscope (AFM), field emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray spectroscopy (EDS).
Electrical properties were examined with *pn*-junction structure consisting of *n*-type CdS layer through chemical bath deposition (CBD). The CBD process were performed with $CdSO_4$ (0.015 M), thiourea (1.5 M), and NH_4OH aqueous solution at 75°C for 15 minutes.
The nanoparticles and thin-films were synthesized on indium tin oxide (ITO) as well as Mo substrate to examine the potential for tandem cell applications. The *J-V* and photovoltaic properties were investigated under dark or white light illumination.

RESULTS AND DISCUSSIONS

EDS analysis revealed that the particles had different chemical composition as post heat treatment process was changed. Among them, nanoparticles treated at higher temperatures showed deficiency of Se atoms, which means decreased nanoparticle size due to the loss. Process for adding Se atoms, selenization, were performed to be stoichiometric even though high temperature. According to XRD patterns, all the nanoparticles after Se-incorporation have chalcopyrite structures. The EDS results also revealed Se atoms are recovered.
Figures 1 (a) and (b) are AFM images of CIGS nanoparticles treated at 400°C and CGS thin-films grown at 530°C, respectively. The stacked particles on Mo clump together, while the grain of CGS thin-films is longish and not particularly rough. Each RMS roughness is 8.00 and 11.05 nm on Mo substrate before deposition of CdS. After CdS deposition, the roughness of CGS thin-films is slightly decreased, but that of CIGS nanoparticles is increased. It may result from sweeping of the particles when CdS was grown on the nanoparticles by CBD.

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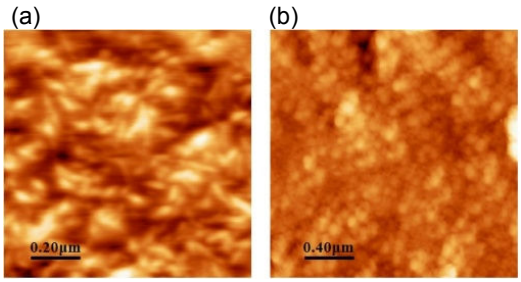

Figure 1 AFM images of (a) CGS thin-film and (b) CIGS nanoparticles before CdS deposition.

Surface chemical analysis of the nanoparticles was investigated by x-ray photoelectron spectra (XPS) as shown Figure 2 for more accurate composition analysis. Apart from C1s and O1s peak, the Cu, In, and Se peaks are identified in the spectrum. A Ga peak is screened since low content of the particles. C and O peaks were founded on nanoparticle surfaces because the intensity diminished after sputtering.

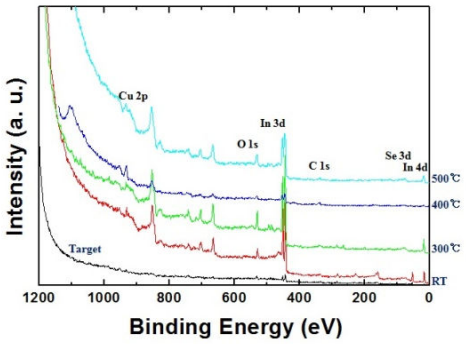

Figure 2 XPS survey spectrum of the nanoparticles.

The optical characteristics analyzed from transmission and reflectance data through Eq. 1 indicate slightly different properties of the nanoparticles.

$$\alpha h\nu = [B(h\nu - E_g)^{1/2}] \quad (1)$$

where B is constant, and E_g is the bandgap energy.
Figure 3 (a) shows higher absorption coefficient over ~10^5 and higher optical bandgap than thin-films. As their treatment temperature was increased, the bandgap tends to be increased as shown in Figure 3 (b).
When we analyzed transmission and reflectance of CGS thin-films in the same manner, the optical bandgap of 1.7 eV was obtained. According to our previous work, the bandgap is shifted as Ga content is increased such as 1.1 eV of CIS, 1.24 eV of CIGS (Ga/(Ga+In) = 0.3), and 1.7 eV of CGS. These values are consistent with the energy bandgap values as reported elsewhere [6].

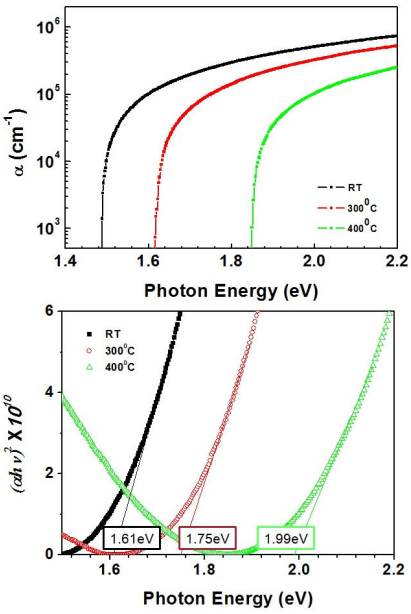

Figure 3 (a) High absorption coefficient of CIGS nanoparticles and (b) Optical bandgap of CIGS nanoparticles with different annealing temperature.

All the cells including the selenized nanoparticles and CGS thin-films showed photovoltaic properties when white light was illuminated. In case of the particles on Mo substrate, the cell reveals a short-circuit current density (J_{sc}) of 72.69 μA/cm^2 and open-circuit voltage (V_{oc}) of 3.55 mV under white light illumination with 8 mW/cm^2. Meanwhile, the J_{sc} and V_{oc} of the CGS thin-films are 0.3 V and 1.06 mA/cm^2, as shown in Figure 4. When light of 500-600 nm is irradiated with a Xe-lamp, V_{oc} and J_{sc} decrease by 0.2 V and 9.4 μA. It results from very weak irradiated light such as 20 μW/cm^2 of average power and limited incident wavelength. It is a good agreement with general property of solar cells, so it can prove prospect of solar cell applications with only CdS/CGS structure. Although CdS/CGS is enough to make *pn*-junction, *n*-type electrodes are needed for more stable junction formation. Table 1 shows photovoltaic properties of CdS/CGS structure from our experimental conditions. The photovoltaic characteristics of them on ITO are demonstrated but somewhat reduced.

Table 1. Electrical characteristics of CdS/CGS thin-film illuminated by 8 mW/cm^2.

	Mo substrate	ITO substrate
V_{oc} (V)	0.3	0.36
J_{sc} (mA/cm^2)	1.06	0.56
FF	0.47	0.47
η (%)	1.9	1.2

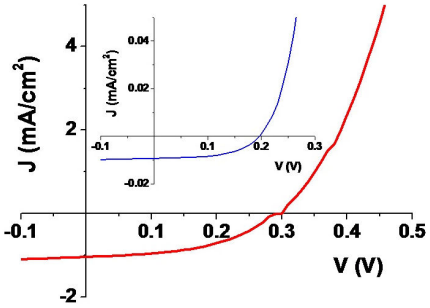

Figure 4 *J-V* characteristics CdS/CGS thin-films on Mo substrate with light power of 8 mW/cm^2 (inset : 20 μA/cm^2 of incident power and 500-600 nm of wave length).

SAMMARY AND CONCLUSIONS

CIGS nanoparticles and CGS thin-films as absorber layers for tandem solar cell applications in photovoltaic devices were synthesized by pulsed laser ablation and co-evaporation, respectively. To enhance the properties of nanoparticles, a process to add Se atoms was also performed. XRD and EDS results revealed that the structure and chemical composition were changed due to the change of synthesis processes, thermal treatment, Se annealing process. Surface chemical analysis results were support that CIGS nanoparticles were well synthesized by PLA.

The optical bandgap of the nanoparticles is increased when they were grown at high temperature. On the other hand, that of the CGS thin-films is 1.7 eV since high Ga composition.

To understand electrical properties and examine possibility for tandem cell applications, the cells including CIGS nanoparticles or CGS thin-films have been fabricated. From the cells, we found out electrical and photovoltaic properties by measuring *J-V* characteristics under dark and illumination, which reveals J_{sc} of 72.69 μA/cm^2 and V_{oc} of 3.55 mV and 0.3V and 1.06 mA/cm^2 of CIGS nanoparticles and CGS thin-films on Mo substrate, respectively. The CdS/CGS thin-film structure also indicates sufficient properties for tandem cell applications. Judging from the results, CIGS nanoparticles and CGS thin-films have possibility for top cells in tandem solar cell applications.

ACKNOWLEDGEMENT

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