Synthesized Cu (In, Ga) Se$_2$ (CIGS) thin films and implementation as the active light absorbing material in photovoltaic devices (PVs)

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ABSTRACT

This review article summarizes our research focused on Cu(In, Ga)Se$_2$ (CIGS) nanocrystals, including their synthesis and implementation as the active light absorbing material in photovoltaic devices (PVs). CIGS thin films were prepared by arrested precipitation from molecular precursors consisting of CuCl, InCl$_3$, GaCl$_3$ and Se metal onto Mo/soda-lime glass (SLG) substrates. We have sought to use CIGS nanocrystals synthesized with the desired stoichiometry to deposit PV device layers without high temperature processing. This approach, using spray deposition of the CIGS light absorber layers, without high temperature selenization, has enabled up to 1.5 % power conversion efficiency under AM 1.5 solar illumination. The composition and morphology of CIGS thin films were studied using energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM), respectively. X-ray diffraction (XRD) studies show that the structural formation of CIGS chalcopyrite structure.

Keywords: CuInGaSe$_2$ (CIGS); photovoltaic; solar cells, nanoink, spray-coating.

تحضير الغشاء (CIGS) CuInGaSe$_2$ كطبقة إمتصاص الضوء لنبائط الفولطاضوئية
الخلاصه

حضر الحبر النانوي (CIGS) CuInGaSe$_2$ ليكون طبقة إمتصاص الضوء لخلية شمسية وذلك بتفاعل عناصر النحاس والأنديوم والكاليوم والسلينيوم ذات النقاوة العالية في درجة حرارة 240 C^o لمدة 30 دقيقة في بيئة من غاز النتروجين ومفرغة من الهواء، بعد ذلك تم ترسيب الأغشية على أرضيات من زجاج الـ SLG مغطاة بطبقة من الموليبدينوم ،عملية الترسيب تمت بطريقة (Coating – Spray)). اظهرت دراسة خواص تيار- جهد للمفرق (Mo/CIGS/CdS/ ZnO/ITO) بان الكفاءة 1.561% بسمك 500 نانومتر وتركيز 30 mg/ml .

الكلمات المرشدة: خلية شمسية، نبائط فولطا ضوئية، الحبر النانوي CIGS ، الترسيب بالرش.

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INTRODUCTION

Cu(In,Ga)Se$_2$ (CIGS)-based solar cells have emerged as one of the most promising candidates for high-efficiency low-cost thin film solar cells[1], it is a strong light absorber[2],and high efficiencies of as high as $\eta=20.0\%$ have been reported [3,4]. Our research has primarily focused on Cu(In,Ga)Se$_2$ (CIGS) nanocrystals. Of the thin film semiconductors (i.e., CdTe and amorphous Si), CIGS has yielded the highest efficiency of more than 20% PCE [5]. CIGS has a direct band gap that is tunable in energy from 1.0 to 1.6 eV, depending on the Ga concentration [6], it tolerates relatively large concentrations of grain boundaries and has good photostability [7,8]. The many elements in CIGS solar cells can form a great variety of compounds during cell processing [9]; therefore, the CIGS system is very complicated. On the other hand, it is very tolerant to defects and impurities because the chemistry, as well as the structure, can adjust itself in many possible ways[10,11].

Thin film PVs with lower manufacturing cost, like amorphous Si, copper indium gallium diselenide (CIGS) and CdTe, are gaining marketshare, but still require significant cost reductions to enable widespread adoption[2,12].

Experimental

HDA, ODE, copper(I) chloride (CuCl; 99.995+%), indium(III) chloride (InCl$_3$; anyhydrous 99.99%), Galium(III) chloride (GaCl$_3$; anyhydrous 99.99%) elemental selenium (99.99%), cadmium sulfate (CdSO$_4$, 99.999%) from Aldrich Chemical Co.; ammonium hydroxide (18M NH$_3$, ACS certified), toluene (99.99%), ethanol (absolute), from Fisher Scientific; and thiourea (99.999%) from Fluka. Copper (I) chloride, indium (III) chloride, Gallium (III) chloride, HDA and ODE were stored in a nitrogen-filled glovebox to prevent degradation.

CIGS nanocrystals were synthesized as previously described [2, 13]. 1 mmol of CuCl, 0.5 mmol of InCl$_3$ and 0.5 mmol of GaCl$_3$ was combined with 10 ml of HDA and 20 ml of ODE, then a magnetic stir bar in a 100-mL three neck flask in a nitrogen-filled glovebox. The flask was sealed by a condenser-stop cock setup and two septa; the flask was removed from the glovebox and mounted on a Schlenk line. The reaction mixture was heated up to 110 °C, degassed for 30 minutes by pulling vacuum on the vessel and purged with clean nitrogen and heat to 200 °C for 30 minutes. While maintaining the nitrogen environment, the reaction vessel was heated to 180 °C and 10 ml solution of 1 M Se in TBP was injected into the reaction vessel. The reaction mixture temperature was raised to 240 °C as quickly as possible and the reaction was allowed to proceed for 30 minutes. The heating mantle was removed and the reaction was cooled slowly to room temperature. After cooling, the reaction mixture was transferred to a glass centrifuge tube. 10 ml of ethanol was added to the centrifuge tube and the mixture was centrifuged at 4500 RPM for 10 minutes. The supernatant was discarded and the solid precipitate was dissolved in 10 ml of toluene. The new solution was centrifuged at 4500 RPM for 10 minutes to remove larger and poorly capped nanocrystals. The supernatant was transferred to a new glass centrifuge tube and the solid precipitate discarded. Ethanol was added drop-wise to the particle solution until a turbid mixture was achieved. The reaction was centrifuged again at 4500 RPM for 10 minutes. The supernatant was discarded and the precipitate dissolved in toluene to achieve a 20 mg/ml solution.

For morphological structure studies, transmission electron microscopy (TEM) was performed using a JEOL 2010F TEM at 200 kV accelerating voltage. TEM samples

were prepared by drop casting from chloroform onto a 200 mesh nickel grid with a carbon film (Electron Microscopy Sciences). Energy dispersive X-ray spectroscopy (EDS) was carried out using an Oxford INCA EDS detector on the JEOL 2010F TEM. Scanning electron microscopy (SEM) was performed on a Zeiss Supra 40 VP SEM operated at 5 keV accelerating voltage through an In- lens detector with samples grounded using copper tape.

For structural study X-ray diffraction (XRD) was performed using a Rigaku R-Axis Spider diffractometer with an image-plate detector and Cu Kα (λ = 1.54 Å) radiation operated at 40 kV and 40 mA. XRD samples were prepared by drying a drop of concentrated nanoparticle dispersion onto a glass slide in a glovebox. The nanocrystal powder was then suspended on a 0.5 mm nylon loop using mineral oil for analysis. Samples were scanned for 15 min while rotating at 2°/s. The 2D diffraction patterns were integrated using the Rigaku 2DP powder processing suite with subtraction of the background scattering from the nylon loop and mineral oil.

UV–vis–NIR absorbance spectroscopy was performed at room temperature using a Varian Cary 500 UV–vis–NIR spectrophotometer in ordr to study the optical properties. Nanocrystals were dispersed in toluene in quartz cuvettes. Absorbance was also measured for thin, optically transparent nanocrystal films deposited by spray-coating on a quartz substrate.

Conductive back contacts Mo were deposited separately on sodalime glass (Delta Technologies, 25 mm x25 mm x 1.1 mm) after cleaned by sonication in an acetone/isopropanol mixture, followed by rinse with (DI) water, and drying under nitrogen. Molybdenum of 500 nm thick (99.999% Lesker) was deposited by RF sputtered. 10 mg mL^{-1} solutions of nanoparticles were prepared for the spray-deposition. CIS nanocrystal layers were spray-coated with an airbrush (SONOTEK) operated at 1.6 psig of head pressure. A CdS buffer layer was deposited by chemical bath deposition following procedures described by McCandless and Shafarman [13]. Briefly, A CdS buffer layer was deposited by dropping 0.7 mL of a CdS precursor solution (1.25 mL of 15 mM CdSO$_4$, 2.2 mL of 1.5 M thiourea, and 2.8 mL of 18 M NH$_4$OH in water) onto the CIS nanocrystal film heated to 95 °C on a hot plate and covered with an inverted crystallization dish for 2 min. The substrate was removed from the hot plate, rinsed with DI water, and dried with a stream of compressed air. Top layers of ZnO and ITO were deposited by RF sputtering from a 40 nm ZnO target (Lesker, 99.9%) in a 0.5% O2 in Ar atmosphere (Praxair, 99.95%) and a 300 nm of ITO target (Lesker, 99.99% In$_2$O$_3$:SnO$_2$ 90:10) in Ar atmosphere (Praxair, research grade). ZnO and ITO are deposited selectively onto 8 rectangular regions with active device areas of 0.08 cm^2 (8 mm^2 a 4mm x 2mm rectangle). Silver paint was applied for electrical contact to the devices.

PV device response was measured using a Keithley 2400 General Purpose Sourcemeter under solar simulation using a Newport Xenon Lamp Solar Simulator with an AM1.5 filter (100 mW/cm^2). Intensity of the light source was calibrated using a NIST calibrated Si photodiode (Hamamatsu, S1787-08). Different fractions of solar spectrum were generated by placing colored glass cutoff filters (Newport) directly in the path of light beam emanating from the solar simulator. Incident photon conversion efficiency (IPCE) was measured using a home-built device with lock-in amplifier (Stanford Research Systems, model SR830) and monochromator (Newport Cornerstone 260 1/4M). IPCE was calibrated with Si and Ge photodiodes (Hamamatsu).

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Results and discussion

Figure 1 displays the EDS spectrum of film. From the spectrum, energy response of the four elements including copper, indium, gallium and selenium can be easily recognized. Table 1 summarizes the composition of CIGS nanoink determined by EDS; we know the film is approximately equal to the ideal stoichiometric ratio of chalcopyrite CIGS films with the Cu, In, Ga, and Se atomic ratio of 1:0.65:0.35:1.86. The result may suggest producing a film with higher selenium content.
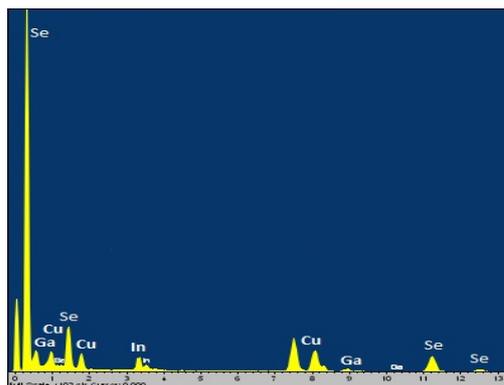
Figure (1): EDS spectrum of CIGS films.

Figure 2 shows TEM images for the CIGS nanocrystals. The nanocrystals are composed of chalcopyrite CIGS. TEM images of CIGS nanocrystals shows the nanocrystals are irregularly shaped and rather polydisperse.
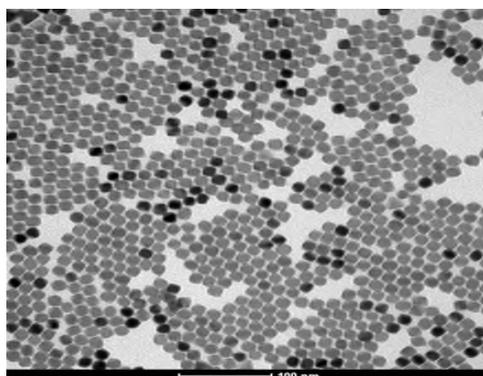
Figure (2) :PTEM images of CIGS.

Table (1) The Composition of CuInGaSe$_2$ Nano ink Determined by EDS

Nano ink	Element	Weight %	Atomic %
CIGS	Cu	26.14	32.96
	Ga	1.17	1.34
	In	25.43	17.75
	Se	47.26	47.95

Figure 3 shows all the diffraction peaks in the XRD pattern can be indexed to phase of CIGS films deposited on SLG substrates with chalcopyrite tetragonal structure, which are in good agreement with the standard values of the reported data (JCPDS No.40-1488) as the major phase and no secondary phase with a preferred orientation along (112) direction. The two weak peaks including (211), and (400) at ($2\theta = 35^{\circ}$ and 64°) emerge here that distinguishes the chalcopyrite phase from the sphalerite phase. In addition, no peaks of other impurities, indicating the high phase purity of CIGS sample. From the figures one can observed that CIGS films are polycrystalline structure where many peaks appeared.A typical feature is that, in all the range of compositions obtained, the samples exhibit a strong preferential orientation, The most intense peak is situated at approximately 26.50° which is belong to Miller indices (112). As could be seen from the XRD patterns, the three main diffraction peaks due to (112), (220) and (312) planes which are belong to ($2\theta = 26.58°$, $44.18°$ and $52.34°$) correspond to CIGS.
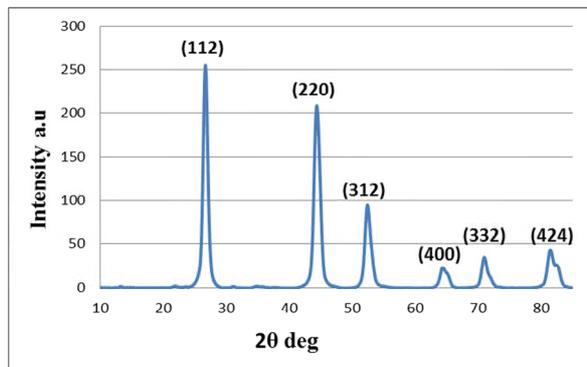
Figure (3): XRD pattern of CIGS.

The morphology of the CIGS synthesized at 240 $^{\circ}$C for 30 min. shown in Figure 4,the film has uniform thickness and is nearly free of drying cracks.
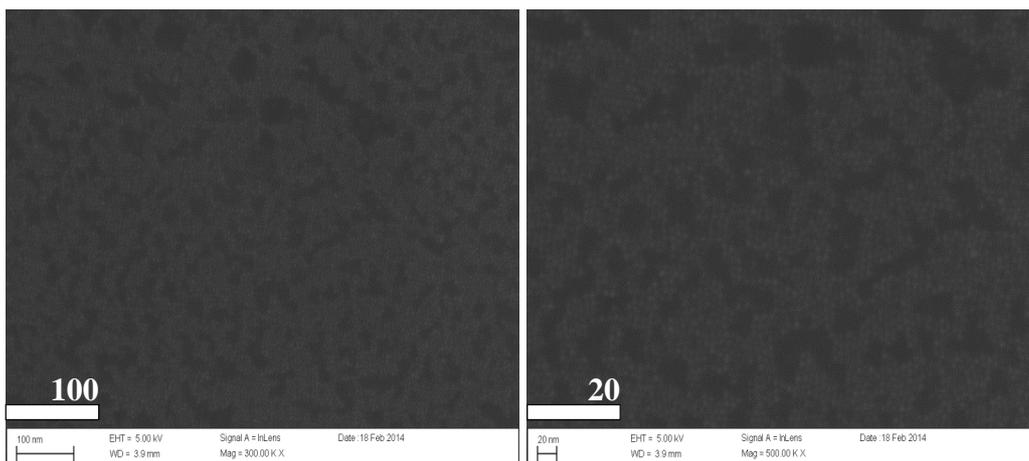
Figure 4: SEM Images of CIGS 500 nm layer deposited with 30 mg/ml by spray-coating.

Figure 5(A) shows Illustration of PV device that could be prepared by spray-casting CIGS nanocrystal absorber layers. And (B) a cross-sectioned PV device with a layer of CIGS thickness was obtained using this method.
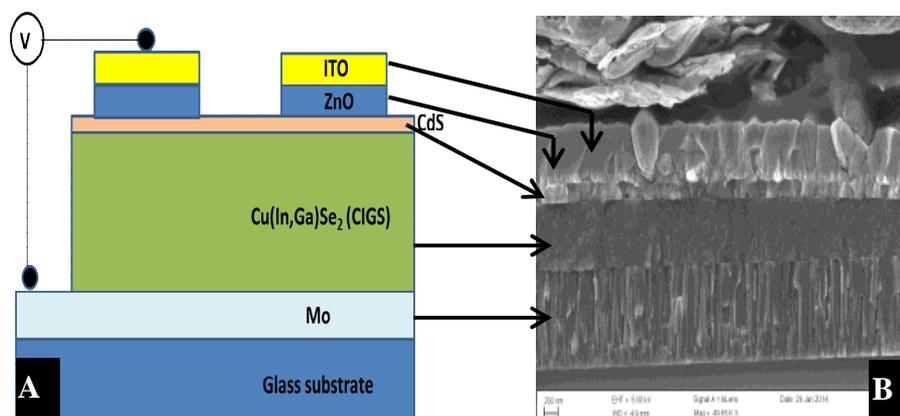
Figure (5) (A) Illustration of the device layer structure. (B) Cross-sectional SEM image of a PV device made by spray-coating of CIGS.

PV devices were fabricated by spray-casting of the CuInGaSe$_2$ nanocrystal ink onto Mo back contacts on glass substrates. Nanocrystal films with of CIGS Nanocrystal layer uniform Fig. 6 dark and light I-V curves for the device with highest power conversion efficiency (PCE). Devices have been made using this approach with power conversion efficiencies under AM1.5 illumination of up to 1.5%.

The device has an architecture consisting of layers of glass/Mo /CIGS(nc)/CdS/ZnO/ITO. No high-temperature annealing or selenization of this device was carried out. This particular device had a power conversion efficiency under AM 1.5 simulated sunlight of 1.5%. Since the absorber layers are not processed at high temperature, alternative substrates and contacts can be used, including transparent conductive ITO or mechanically flexible plastic.

The devices generally consist of a sandwiched construction of the p-type light-absorbing nanocrystal layer interfaced with an n-type semiconductor (CdS, ZnO) positioned between two planar conducting contacts. The thin CdS layer (5–10 nm) also helps protect the CIS nanocrystal layer during sputtering of the window layer.
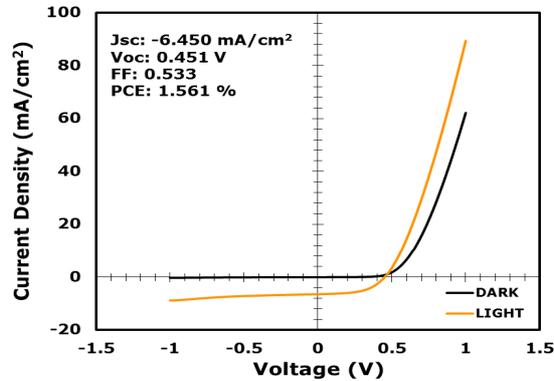
Figure (6): I-V characteristics for Mo/CIGS/CdS/ZnO/ITO heterojunction solar cell at thickness layer of 500 nm deposited by spray-coating.

CONCLUSIONS

PV devices with reproducible and reliable power output were fabricated by spray-casting. CIGS nanocrystals without postdeposition annealing. Layered Mo/CIGS/CdS/ZnO/ITO PV device exhibited power conversion efficiencies of up to 1.5% under AM 1.5 illumination. The device efficiency still requires significant improvement. A nanocrystals ink that could be used to fabricate high efficiency PVs without needing for high-temperature processing.

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