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Abstract: In this paper, we report a novel and simple solution-based approach for the fabrication of chalcopyrite Cu(In,Ga)Se2 thin film solar cells. A novel aqueous co-precipitation method based on metal selenites, M2(SeO3)x (M= Cu, In, Ga) precursors, was investigated. The resulting powder, dispersed in a binder to form an ink, was coated on a substrate by doctor blade technique. A soft annealing treatment enabled the reduction into the corresponding metal selenides leading after rapid thermal processing (RTP) to crystalline chalcopyrite absorber. The obtained layer provides good compositional control and adequate morphology for solar cell applications. Doctor blade printing in atmospheric environment offers an opportunity for direct application of the absorber material at large-scale. The water-based synthesis is a sustainable and simple procedure, and together with doctor blade printing, provides a potential cost- effective advantage over conventional fabrication processes (vacuum-based deposition techniques).The short circuit current (Jsc), open circuit voltage (Voc), fill factor (FF), and total area power conversion efficiency (Eff.) of the device are 26 mA/cm2, 450 mV, 62%, and 7.2 %, respectively. The effective band gap of 1.12 eV confirmed the Ga-incorporation in the CIGS crystal lattice.

Preparation of $Cu(In,Ga)Se_2$ photovoltaic absorbers by an aqueous metal selenite co-precipitation route

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Abstract

In this paper, we report a novel and simple solution-based approach for the fabrication of chalcopyrite $Cu(In,Ga)Se_2$ thin film solar cells. An aqueous co-precipitation method based on metal selenites, $M_2(SeO_3)_x$ (M= Cu, In, Ga) precursors was investigated. The resulting powder, dispersed in a binder to form an ink, was coated on a substrate by doctor blade technique. A soft annealing treatment allowed the reduction of metal selenites into selenides. Further rapid thermal processing (RTP) achieved crystalline chalcopyrite absorber. The obtained layer provides good compositional control and adequate morphology for solar cell applications. The water-based synthesis is a sustainable and simple procedure, and together with doctor blade printing, provides a potential cost- effective advantage over conventional fabrication processes (vacuum-based deposition techniques).The short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and total area power conversion efficiency (Eff.) of the device are 26 mA/cm^2, 450 mV, 62%, and 7.2 %, respectively. The effective band gap of 1.12 eV confirmed Ga-incorporation in the CIGS crystal lattice.

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1. Introduction

Chalcogenide-based solar cells are considered one of the most promising technologies on the market. It has been already attained a record efficiency conversion rate of 21.7% in $Cu(In_{0,7}Ga_{0,3})Se_2$ (CIGS) thin film cells [1]. These devices also exhibit an excellent long-term stability and durability [2]. In addition, CIGS devices are versatile for deposition on different substrates like glass [1], steel [3], flexible polymeric modules [4] and have been already produced on large scale [5]. High vacuum-based processes like co-evaporation or magnetic sputtering usually deposit CIGS high efficiency devices [6-8]. However, compositional

heterogeneities issues over large areas are posing challenges for commercial manufacturing [9]. In addition, these methods typically use expensive raw materials and accomplish relatively low materials-utilization efficiency of 70-80% that limits the potential for cost reductions [10]. Materials utilization efficiency close to 100% are achievable by non-vacuum processes that deposited the material precisely on the substrate surface [11]. Non-vacuum techniques do not reach the same high efficiencies as the vacuum processes, but they provide lower costs, better large area homogeneity and this would make them highly competitive for future applications [12]. Many non-vacuum routes for chalcogenide-based absorber deposition had already been tested: electrodeposition [13], spin-coating solutions [14, 15] and suspensions of metals [16], oxides [17] and chalcogenides [18].

Above all, the solution-based processes are potentially less energy consuming than the vacuum-based approaches that require significantly energy to evaporate or sputter materials from a source onto a heated substrate. Many solution–based methods can deposit precursor layers at room temperature and apply a short treatment technique such as rapid thermal processing (RTP) to form CIGS. This fact will reduce drastically the energy necessities for preparing the solar cells. Solution-based direct printing of inorganic materials offers the possibility of depositing high quality thin films at low temperature under atmospheric conditions for the fabrication of high-performance and ultra-low-cost electronics. Commonly, metal salts (e.g. chlorides and nitrates) are used as direct precursors for CIGS preparation as they have good solubility in water and alcohol. However, these salts are mainly applied in spray-derived processes (e.g. spray pyrolysis) due to their low viscosity solutions formation. The record efficiency of this process is 10.5% [19]. By mixing salts with binders, the viscosity of the solutions may be increased and then sprayed can be employed. In this concept, several solution methods have already been reported. CIGS films made by spin coating using hydrazine as reducing agent have achieved a high efficiency of 12.2% [20]. However, the toxic and explosive nature of hydrazine might limit the large-scale industrial implementation of this exciting approach. Latest, 12% of power conversion efficiency has been obtained on sulfide nanocrystal inks deposited by drop-casting [21]. This is a significant improvement in the non-vacuum technology. But, the hot-injection CIGS synthesis is non-water based. The procedure uses organic solvent (i.e. triethanolamine) and expensive raw materials as metal acetylacetonates.

Up to now, there are no reports for using selenites as precursors for CIGS preparation by means of solution-based approaches. Copper, indium and gallium selenites (i.e. $CuSeO_3.2H_2O$[22], $Ga_2(SeO_3)_3.6H_2O$ and $In_2(SeO_3)_3.6H_2O$[23]) with well-defined crystal structures exist. These compounds associate elements with selenium containing molecules, without direct oxide bonds with the metal atoms. This could be a key advantage for preparing selenides under easier conditions. Thus, chalcogenites could be converted into chalcogenides in presence of amine compounds [24] and during heating in reducing atmosphere [25]. In addition, aqueous and simple way of precursor preparation is essential for future cheap and large-scale manufacturing.

Doctor blade deposition technique seems to be the best way for industrial fabrication due to it simplicity and availability at many industrial units. ISET technology developed a doctor blade metallic oxides deposition route [26, 27]. This process is based on a metallic hydroxides

precipitation followed by thermal treatment that transforms hydroxide into oxide. Further, the oxides are reduced and selenized according to the reaction (1):

$$Cu, In, Ga\ (precursors) \xrightarrow[2)\ Base\ precipitation]{1) Acid\ disolution} Cu, In, Ga\ (hydroxides) \xrightarrow[3)\ Reduction\ (N_2/H_2(5\%))]{1)\ Deposition\ (Dr\ Blade)\ 2)\ Heating:\ OH^- \rightarrow O^{2-}} Cu, In, Ga\ (Film) \xrightarrow{Selenization\ (H_sSe)} Cu, In, Ga\ (selenides) \quad (1)$$

Good results with efficiencies above 13% were obtained using this route. However, the process is relatively slow. Critical points are metallic oxides attainment from metallic hydroxides (usually requires several hours of heating treatment) and metallic oxides reduction to elemental metals (near of one hour of treatment) [27]. Selenites as precursors simplify the process thanks to their easy reduction to selenides thereby decreasing production time of absorber layer.

In the present work, which follows a preliminary study by T. Todorov [28], we propose an easy solution-based chemistry route as aqueous co-precipitation of metal selenites for precursor preparation. Further, deposition of ink using doctor blade techniques was applied in order to develop CIGS absorbing layer. The water- based synthesis is a safety, sustainable and simple procedure. The precursor powders and the developed layers have been detailed characterized in terms of structural, microstructural, and electrical properties.

2. Materials and methods

- Sample Preparation

All chemicals were used as received without further purification. Cu(NO3)23H2O (99%, Fluka), In(NO3)3xH2O (99.99%, Aldrich), Ga(NO3)3xH2O (99.9%, Aldrich), SeO2 (99.8%, Aldrich) and ammonia solution NH4OH (25%, Panreac). Precursor solution was obtained by dissolving copper (2.52 mmol), indium (1.96 mmol) and gallium (0.84 mmol) nitrates in 125 mL of distilled water with a final metal ratio of [Cu]/([In]+[Ga])= 0.9 and [Ga]/([In]+[Ga])=0.3 [7]. Separately, 10 mmol SeO2 was dissolved in distilled water, resulting in a colorless transparent solution. Ammonia was added in one single batch to obtain the desired precipitate. The powder was washed with water and ethanol and then centrifuged. No additional purification was needed.

To make the ink, triethanolamine (C6H15NO3 puriss., Riedel-de Haën, as surfactant and reducer) and ethanol (C2H5OH Abs., Scharlau, abbreviated as EtOH,) were used. The obtained paste was deposited by a simplified doctor blade method (knife coating) on Mo-coated (~500 nm-thick layer) glass substrates. The substrate was heated at 400 ^{o}C for 1 minute on a hot plate in order to obtain partial decomposition of organic components and selenite reduction. Then a crystallization treatment is carried out in a rapid thermal processing (RTP) furnace (Jetfirst 100, JIPELEC) formed by a sealed annealing zone water cooled and a heating element which consists of 12 infrared halogen lamps with individual power of 1200 W. At 550 ^{o}C during

5 minutes under 5% H_2/N_2 stationary atmosphere with a heat rate of 500 ^{o}C/min. Elemental selenium powder (Se, 99.5%, Merck) was introduced separately into the furnace as selenium source.

Solar cells assemblies were completed by adding of chemically-bath deposited CdS and sputtered i-ZnO/ZnO:Al coatings.

- Characterization

The crystal structure of the materials was characterized by X-ray powder diffraction (XRD) with a SIEMENS D5000D diffractometer with a copper anticathode. The data were collected by step-scanning from 20 to 70º 2 with a step size of 0.05o 2 and 1s counting time per step. The X-ray photoelectron spectra (XPS) of the samples were recorded with a SPECS apparatus equipped with a Phoibos 100 analyzer and a 5MCD detector. The morphology of powders and films were determined by Scanning Electron Microscopy (SEM), using a Leica Leo 440i microscope, and Transmission Electron Microscopy (TEM) applying a JEOL 2100 microscope. Both instruments were equipped with a spectrometer for Energy dispersive X-ray energy spectroscopy (EDS). Current-voltage (I-V) characteristics of the solar cells were carried out using a solar simulator in standard illumination conditions: AM 1.5 and 100 mW/cm2, with a cell size of 0.1 cm2.

3. Results and discussion

The CIGS absorber layers were obtained after a three stage process:

1) Metal-selenites formation by obtaining precipitated mixed powder.

2) Doctor-blade deposition and pre-heating of precipitated selenites.

3) Thermal crystallization process (RTP).

The metal selenite powder was obtained by reaction of the metal nitrate salts with selenium oxide solutions according to reaction (2):

$$M(NO_3)x + SeO_2 \xrightarrow{H_2O} M_2(SeO_3)x.nH_2O + by - products\ (2),$$

Where M= Cu, In and Ga. The nature of the by-products is still unclear.

It is noticeable that the selenite precipitate associates the metal and the chalcogene element, because metal-selenium (selenite) bond allows a rapid reduction to metal-selenide. The TEM micrograph of the precipitated powder (Fig. 1a) shows nanocrystal agglomerates with average size of ~0.5 µm. The agglomerates are formed by small particles with dimensions close to 35 nm. Several regions of the sample were analyzed by EDS. The results describe average elemental composition of the powder (more than 30 areas had been analyzed) closed to the initial stoichiometry (1:0.78:0.33 atomic ratio of Cu/In/Ga). The values of Cu (25.6%), In (21.3%), Ga (7.6%) and Se (45.6%) correspond to the 1:0.83:0.3 (Cu/In/Ga) atomic metal ratios. It can be concluded that the developed method reach a homogeneous compound. As shown by the X-Ray diffraction pattern (Fig. 2, curve 1), the powder displays an amorphous structure.

Fig. 3 displays the XPS spectrum of the as-prepared precipitate. The binding energy of XPS peaks corresponding to levels In3d ($In3d_{3/2}$ at 444.4 eV, $In3d_{1/2}$ at 452.2 eV) and $Ga2p_{3/2}$ (at 1117.7 eV) indicates that the oxidation states of the group 3 metallic cations are In^{3+} and Ga^{3+} [29], the same oxidation state as the initial salts. Also, the peak observed at 58.64 eV is related to Se3d, indicating that selenium oxidation state is 4+ (i.e. selenite species SeO_3^{2-}) [29]. The peaks at 932 eV and 952 eV represent the levels $Cu2p_{3/2}$ and $Cu2p_{1/2}$, respectively. However, these reflections do not establish unambiguously the oxidation state of Cu. The Cu^{1+} and Cu^{2+} have a very similar response [29]. The XPS spectrum of Cu^{2+} should show a very wide additional peak centered at 942.5 eV with similar intensity to the $Cu2p_{1/2}$ [30]. However, this peak is not detected even at the zoomed in-set view (**Fig. 3** in-set) that suggests only the presence of Cu^{1+} species. This is a surprising result since no deliberate reducing agent is added in the solution. A possible explanation would be the effect of the addition of ammonia for the precipitation according to some papers that show the reducing properties of NH3 [31, 32]. The presence of Cu1+ avoids extra reduction procedures.

Then the powder is dispersed into the binder and deposited as a layer on the Mo covered glass substrate. Afterward, the layer is submitted to a soft annealing treatment on a hot plate at 400°C for 1 min in air. The XRD pattern reveals three main peaks that may be associated with chalcopyrite-type material (**Fig. 2** curve 2). The appearance of these peaks is associated with a reduction reaction provoked by the amines nature [24]. The results show accordance to the reaction (3):

$$M_2(SeO_3)x.nH_2O + C_6H_{15}NO_3 \xrightarrow{EtOH} M_2Se_x + by - products \quad (3)$$

Since triethanolamine have been added for the ink preparation, the selenites, for which selenium is tetravalent, have been reduced into selenides where selenium is at oxidation state -2, leading to CIGS compound, although not complete Ga-insertion was achieved. **Fig. 1b** shows the SEM cross section of the pre-treated at 400°C film. It displays that the CIGS layer is compact and adherent with a uniform thickness close to 3 µm.

A crystallization heat treatment is then carried out in N_2/H_2 (5%) atmosphere together with a selenium source at 550°C in a RTP furnace. **Fig. 2** curve 3 shows that the CIGS chalcopyrite phase is obtained as a main crystalline phase. The diffraction peaks labeled with *hkl* could be assigned to the $CuIn_{0,7}Ga_{0,3}Se_2$ (JCPDS card No. 35-1102). Additional peaks at 40.5° and 73.6° (2θ) can be attributed to molybdenum (Mo) from the layer behind. Reflections centered at 31.8° (2θ) and 55.9° (2θ) (labeled as star *) could be associated to a formation of molybdenum selenide at the interface CIGS/Mo ($MoSe_2$ JCPDS card No. 40-0908). The chemical reaction between selenium and Mo layer is very common in CIGS devices, due to interdiffusion processes [33]. Nevertheless, the presence of $MoSe_2$ does not harm the electrical properties of the cell. The zoomed area in **Fig. 2** displays a comparison of reflection (112) in the curves 2 and 3. It can be observed that on the curve 2 appears a small shoulder (+) next to the principal peak. The reflections (220) and (312) in curve 2 also demonstrate additional peaks. The presence of these shoulders and peaks at higher angles are related to gallium partial insertion (presence of gallium-rich phase). The heating applied (curve 3) decreases the shoulder and displace the peak (112) toward higher angles. This is a demonstration of unit cell volume

reduction that is consistence with $rGa^{3+} < rIn^{3+}$.This is a confirmation of the gallium incorporation in the crystal lattice [34].

Fig. 1c shows the cross section of a finished cell. The assembly of the solar cell was completed by adding CdS buffer and i-ZnO/ZnO:Al window layers. It shows that the thickness of the CIGS layer is decreased to 1.2 µm, due to decomposition of organic components coming from the binder. Although carbon presence decreased after annealing treatment, it was still possible to observe it by EDX analysis of CIGS layer located mostly near of interface $MoSe_2$-CIGS. The presence of a carbon layer is usually reported when organic compounds are used in order to deposit absorber layers [35, 36]. Formation of $MoSe_2$ layer with similar to Mo columnar morphology located at the interface CIGS/Mo is also observed. This is in agreement with the DRX results previously discussed (**Fig. 2**). Unclear separation between the CdS buffer (~ 40 nm) and the window films i-ZnO/ZnO:Al is observed. Only EDS analysis confirms the presence of these elements in the cell (data not shown).

The current-voltage (I-V) characteristics for the optimal CIGS solar cell measured under standard AM 1.5 illumination are shown in **Fig. 4**. The as-fabricated device shows an efficiency of 7.2% and good cell parameters (V_{OC} = 450 mV, J_{SC} = 26 mA/cm^2 and FF = 62%). The current density values of the record efficiency sample were determined by quantum efficiency measurements (**Fig. 5**) and the J_{SC} value obtained in J-V curve were close to each other (24.5 and 26 mA/cm^2 respectively). The quantum efficiency showed a good collection of photogenerated electron-hole pairs, yielding values close to 75% in the short wavelength range. Towards longer wavelengths, the quantum efficiency decreases, which indicates low collection length (space charge width plus diffusion length of electrons) values. This result (quantum efficiency showed high carrier collection at short wavelengths) indicates that collection length can be further improved. The effective band gap determined from the spectral response was 1.12 eV indicating gallium incorporation in the chalcopyrite lattice. To compare, the effective values of record performance devices exhibit band gap value of 1.14 eV for composition Ga/(In+Ga) = 0.3 [7] .

4. Conclusions

A novel soft chemistry route is developed based on the formation of metal selenite-based precursor powders for CIGS preparation by aqueous co-precipitation. Doctor blade technique was used as an easy and cheap way of paste deposition. A key point of the process is the internal reduction of the selenites into selenides through a mild annealing technique. The formation of crystalline CIGS layer with good morphological properties confirms the effectiveness of the developed method of preparation. The coatings are dense, well adhered and uniform. The electrical response of the CIGS cell yielded an efficiency of 7.2%. The effective band gap of 1.12 eV confirmed the Ga-incorporation in the CIGS crystal lattice. Further studies of ink composition and thermal crystallization treatment could remove or decrease carbon on the absorber layer and improve CIGS crystallinity thus getting better electric parameters.

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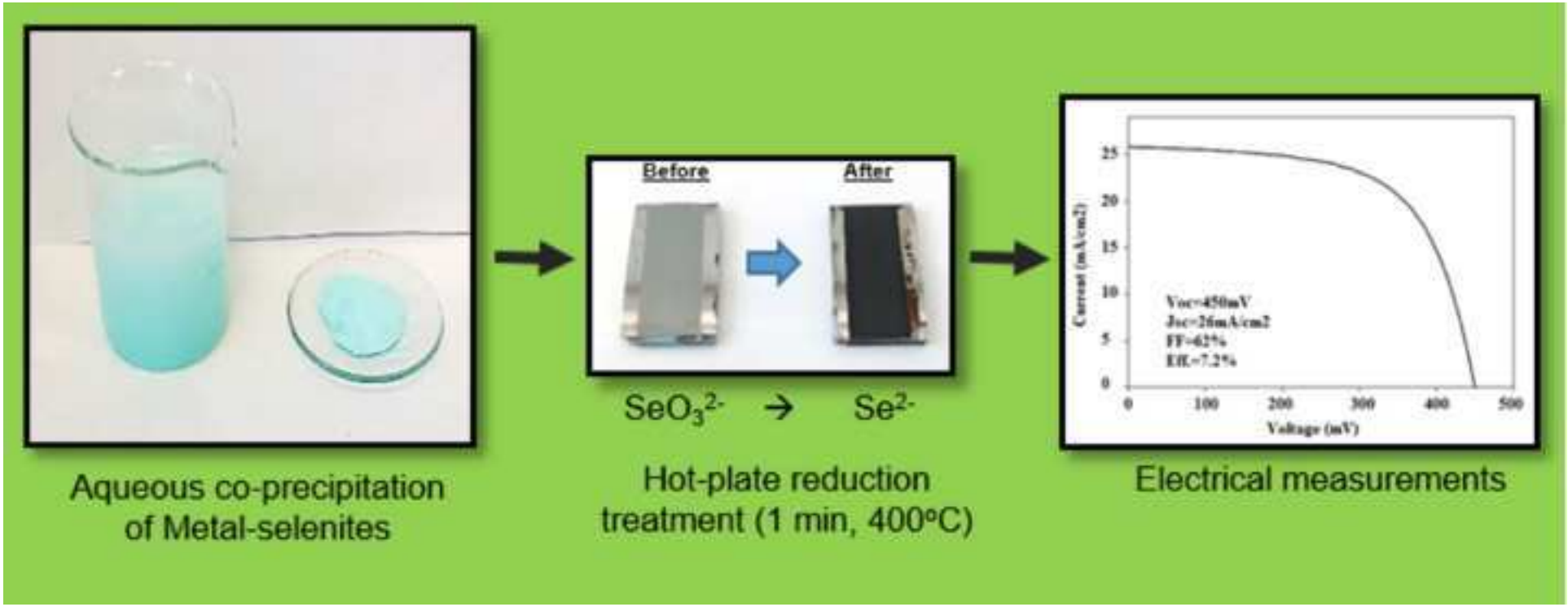
***Graphical Abstract (for review)**



Highlights:

- CIGS photovoltaic solar cell was prepared by aqueous co-precipitation route.
- CIGS layer was obtained depositing paste by doctor blade technique.
- Efficiency of 7.2% and Ga-incorporation in the CIGS crystal lattice was achieved.

Figure 1

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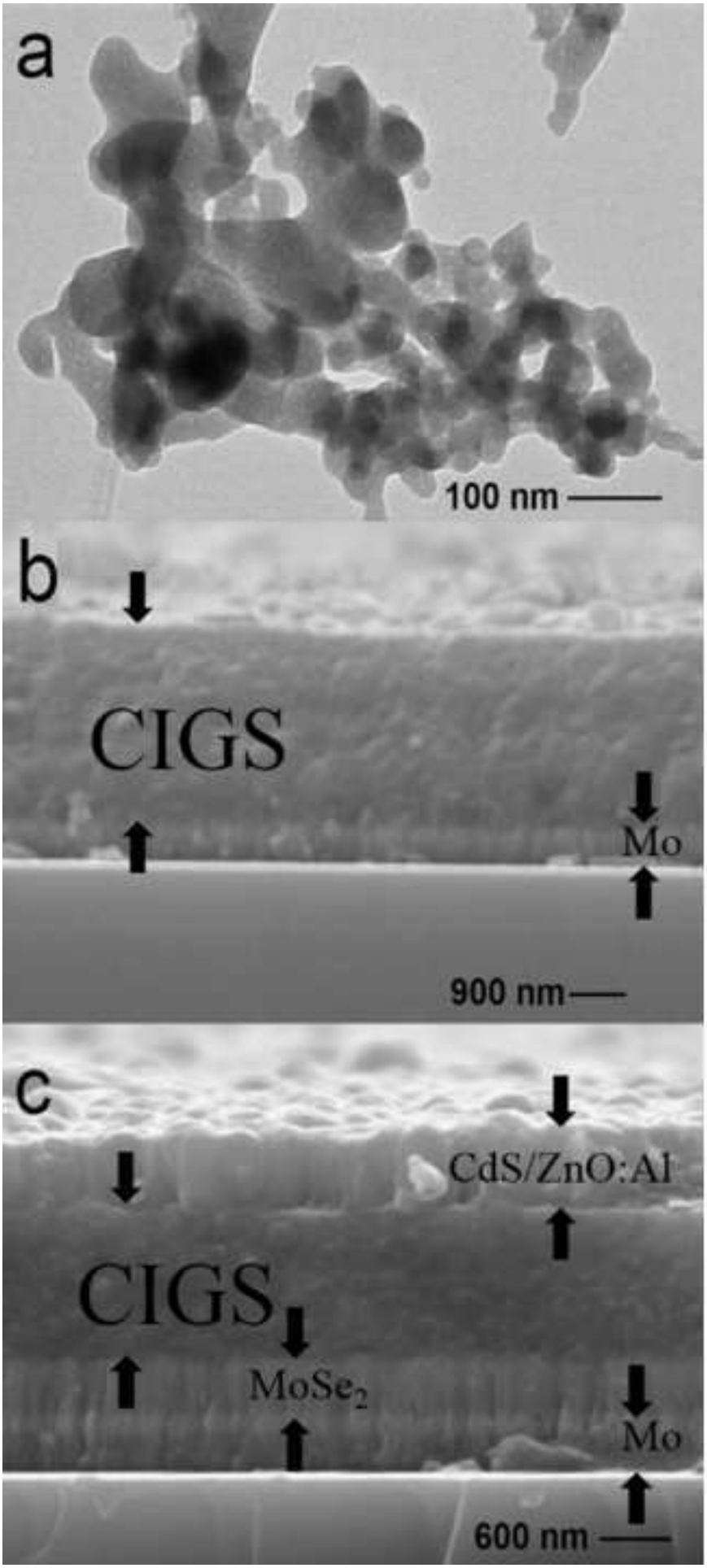

Figure 2

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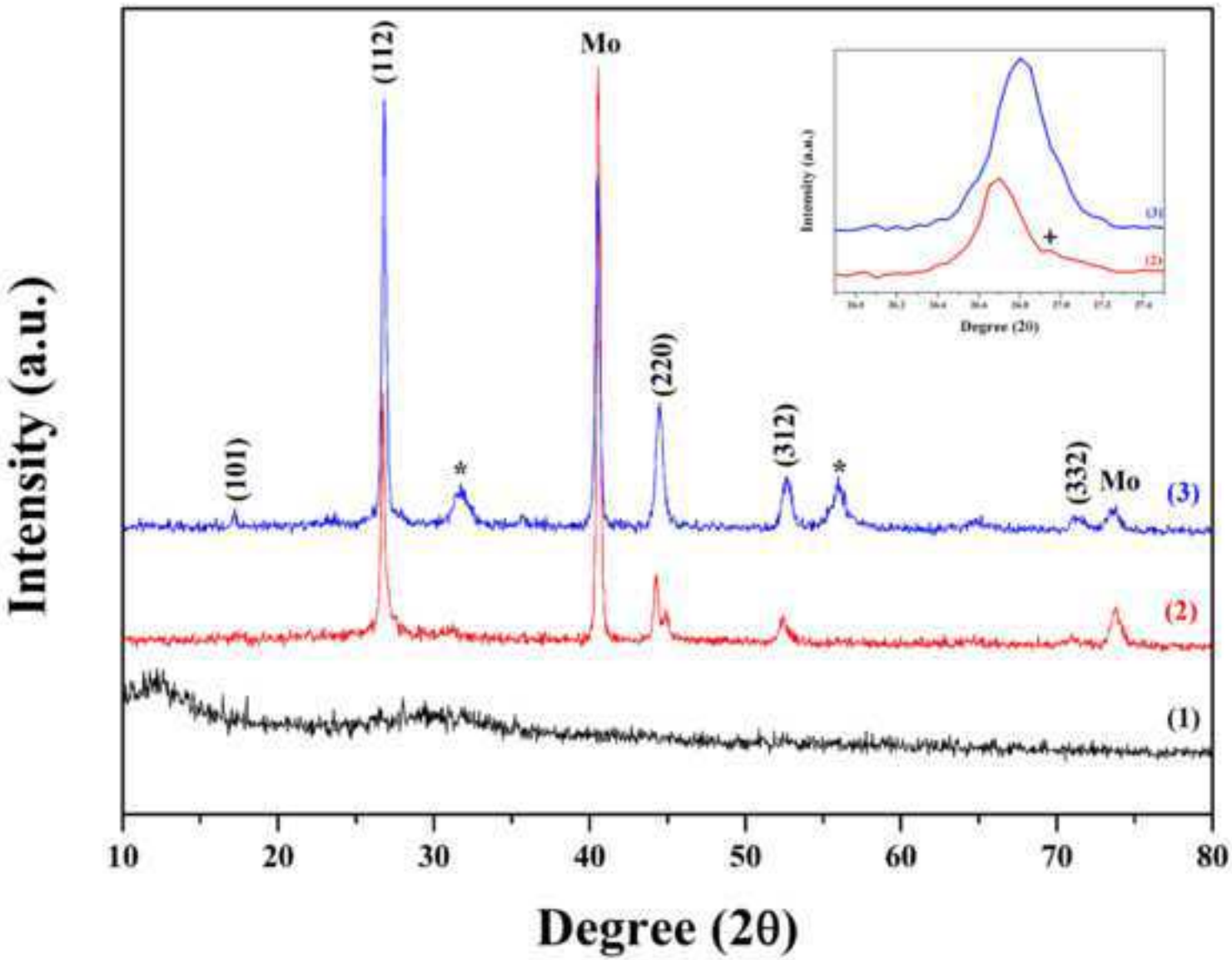

Figure 3

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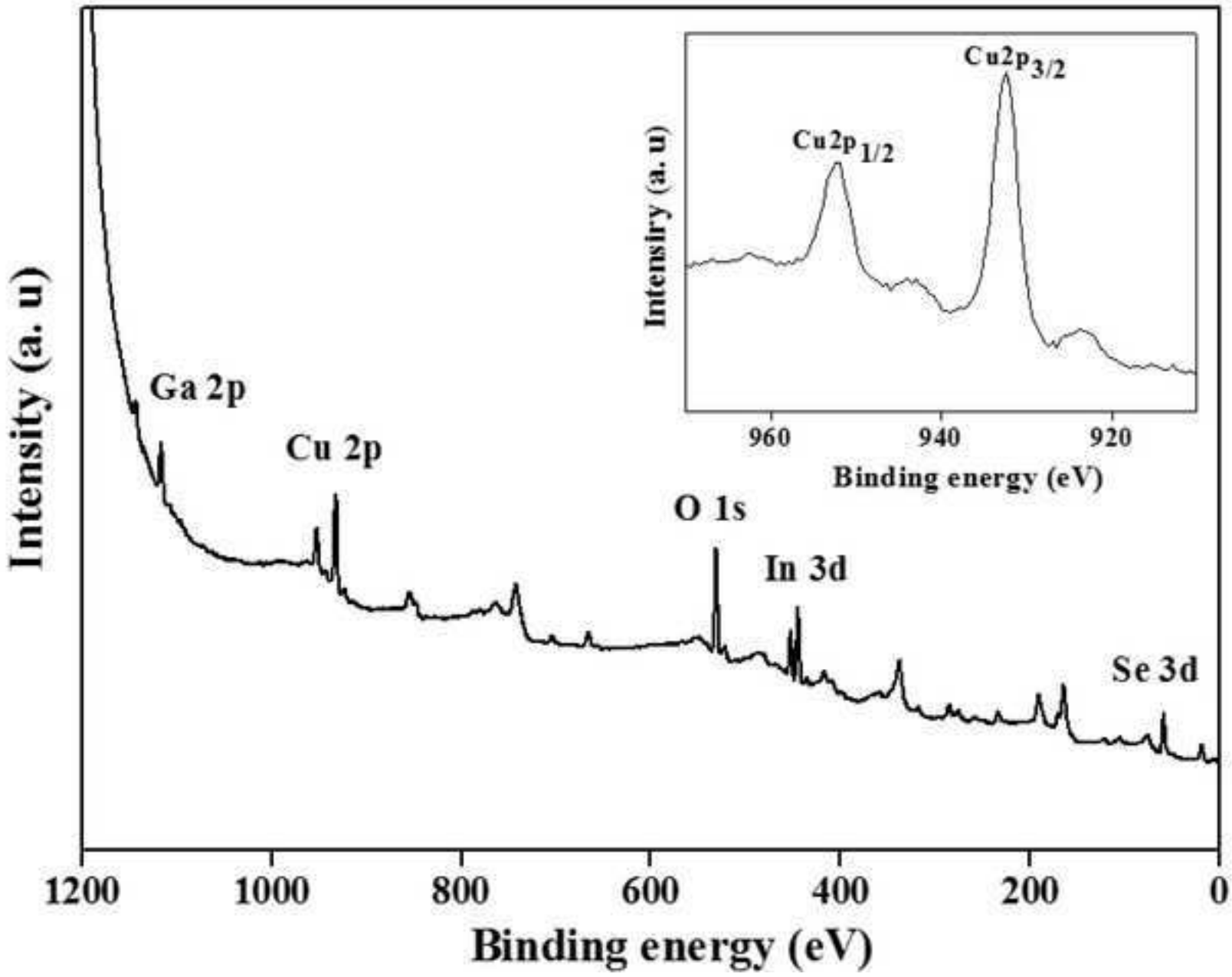

Figure 4

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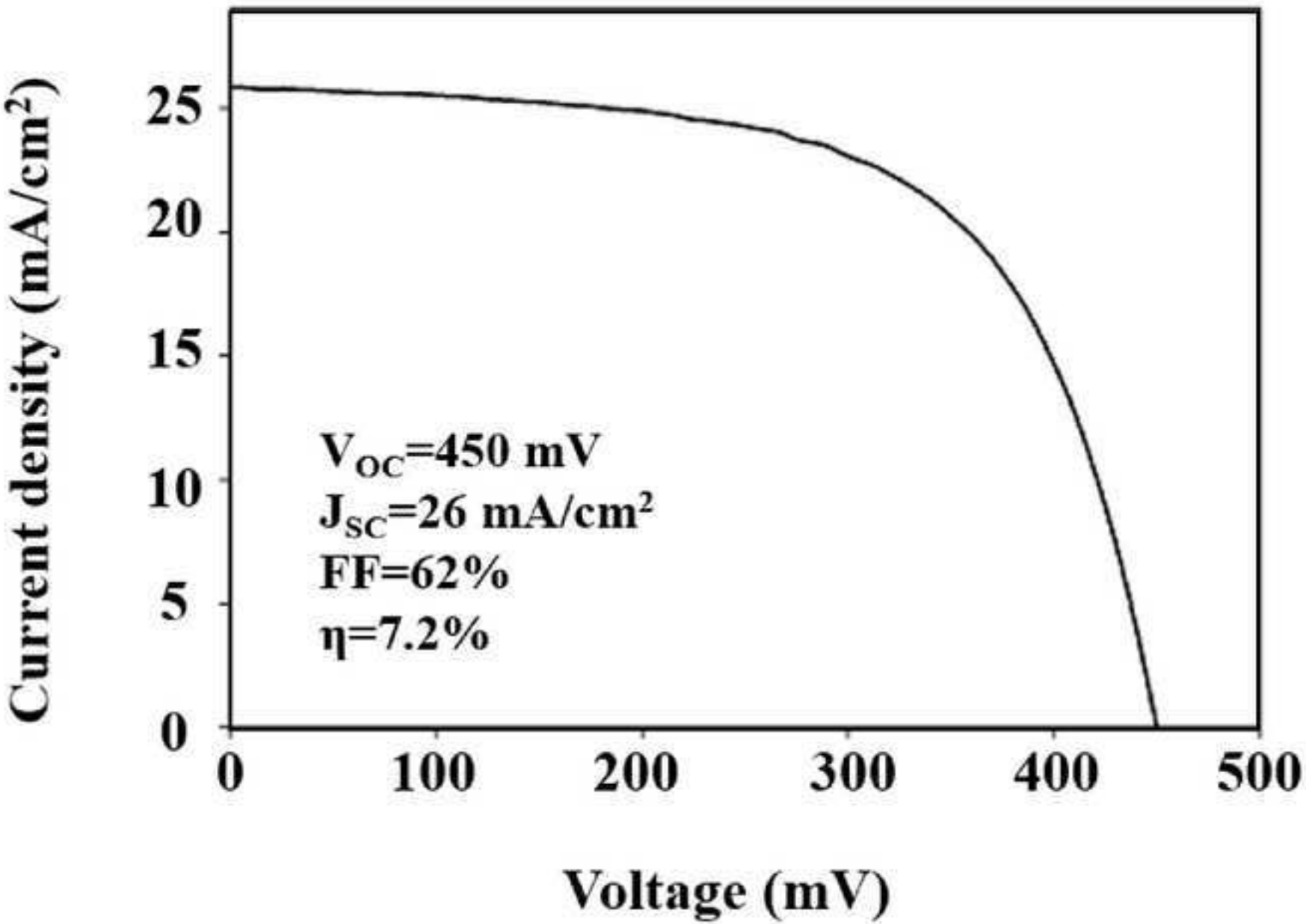

Figure 5

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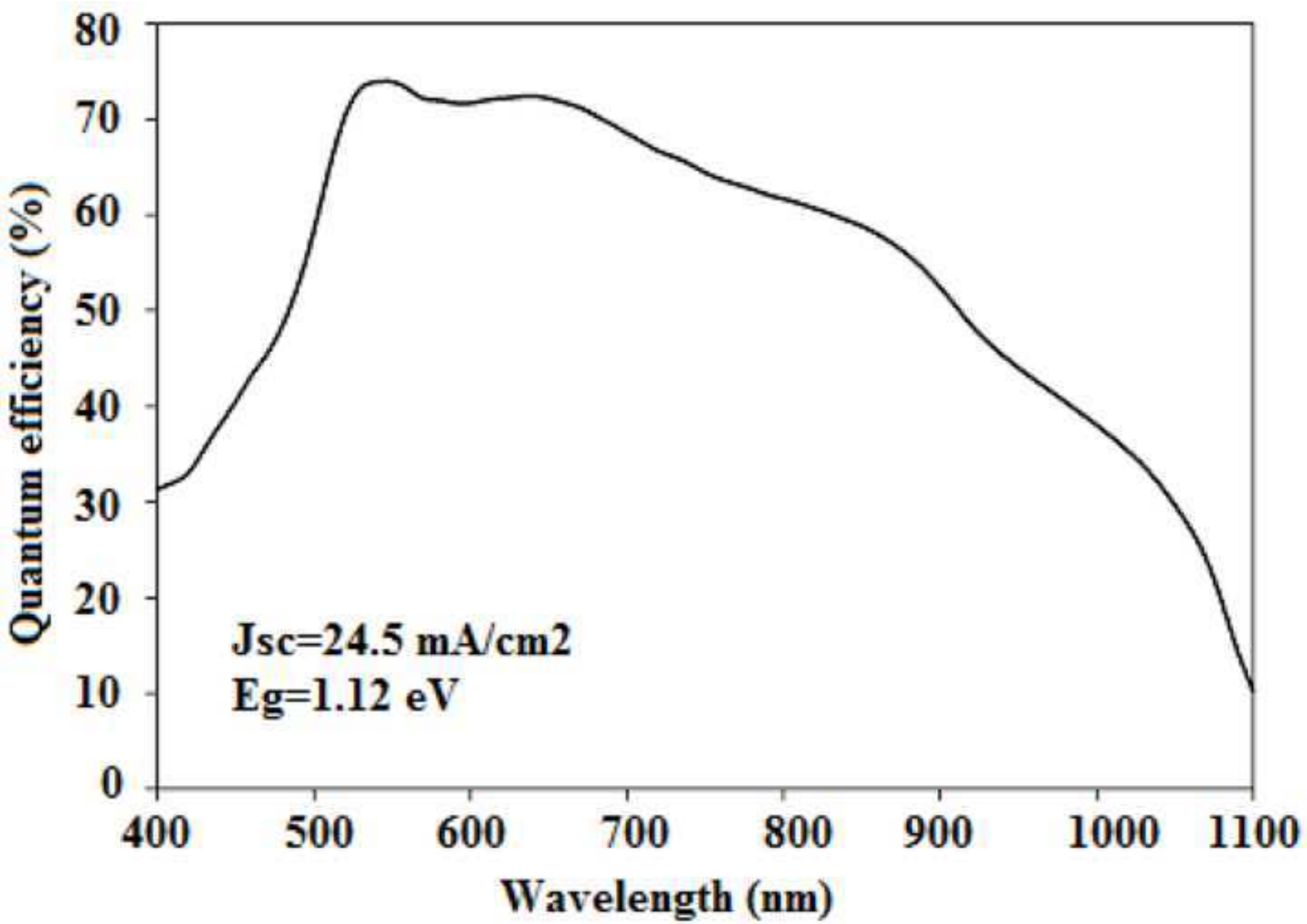

FIGURE CAPTIONS

Figure 1: Micrographs of: (a) TEM image of precursor powder, (b) SEM cross section of a pre-treated at 400ºC film and (c) SEM view of a final solar cell assembly.

Figure 2. XRD patterns of Cu-In-Ga-Se sample: 1-as-prepared precursor precipitate (lower), 2-pre-heated at 400ºC film (intermediate) and 3-thermal treated at 550ºC coating (upper). Reflections indexed by hkl correspond to $Cu(In_{0.7}Ga_{0.3})Se_2$. Peaks labeled as stars (*) are associated to $MoSe_{2.}$

Figure 3. XPS spectrum of Cu-In-Ga-Se as-prepared powder. Inset view: zoomed section of Cu2p peaks

Figure 4 - I-V curve of the best CIGS solar cell under illumination

Figure5. External Quantum efficiency of the best CIGS solar cell.