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Synthesis of n-type and p-type $CuInS_2$ thin films via simple SILAR method

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ABSTRACT

Among various $CuInS_2$-rerlated hetero conjunctions, it is expected that CIS-based p–n junctions are high-performance photo-active electrodes. Herein, both n-type and p-type $CuInS_2$ thin films were synthesized via facile successive ion layer adsorption and reaction (SILAR) method, using aqueous (A-CIS) and mathanolic (M-CIS) SILAR solutions, respectively. Based on UV-visible transmission spectra, M-CIS thin films were more transparent with larger band gap energy (1.6 eV) than A-CIS thin films (1.5 eV). The A1-mode Raman peak of M-CIS thin film was located at 293 cm^{-1} which has a red shift of 5 cm-1 as compared to A-CIS one, indicating that M-CIS has smaller $CuInS_2$ nanoparticles. The Mott-Schottky plots revealed that A-CIS is an n-type semiconductor, while M-CIS thin films have p-type semiconducting behavior, which is due to different Cu/In ratio in these thin films. The obtained results can be very useful to prepared CIS-based p-n junctions toward high performance solar-based devices.

***Keywords**:* $CuInS_2$ thin film; hetero junction; solar- based devices

1. Introduction

$CuInS_2$ (CIS) is a semiconductor with narrow band gap energy of 1.45 eV. It has a high extinction coefficient of α=105 cm^{-1} in the visible region [1, 2]. In addition, CIS is free of toxic elements with satisfactory and stable performance under sun-light irradiation [3]. Therefore, it is an interesting material for solar energy conversion applications.

Among various $CuInS_2$-rerlated hetero junctions, it is expected that CIS-based p─n junctions are high-performance photo-active electrodes [4]. The space charge region (depletion layer), caused by p─n junction, depletes the electrons and an internal electrostatic field is established. Therefore, electrons (e-) and holes (h+) diffuse to opposite directions, leading to reduce e--h+ recombination [2]. It is reported that semiconducting behavior of CIS can be tuned between n-type and p-type by changing the synthesis parameters. For example, CIS exhibits p-type semi conductivity when Cu to in atomic ratio exceeds 1 [2, 5]. It is very important to develop a simple and reliable protocols to synthesis CIS with desired semiconducting behavior.

Herein, we have employed facile successive ion layer adsorption and reaction (SILAR) method, with two different natures of SILAR solutions (aqueous and methanolic solutions) to obtain n-type and p-type $CuInS_2$ thin films. The obtained results can be very useful to prepared CIS-based p-n junctions toward high performance solar-based devices.

2. Experimental

Materials and method

Cupper (II) nitrate trihydrate (KESHI company, China), Sodium sulfide nonahydrate ($Na_2S._9H_2O$, Acros), Indium(III) nitrate hydrate (Sigma), Indium tin oxide (ITO) sheets (30 Ω/□) and absolute methanol (Merck) were used as received without any further purification.

The CIS thin films prepared with aqueous-SILAR solutions (A-CIS) as following: the pre-cleaned ITO substrates were successively immersed in three separated aqueous solutions namely 0.10 M In $(NO_3)_3$ for 60 s, 1.25×10-3 M $Cu(NO_3)2$ for 30 s, and 0.135 M Na_2S for 4 min., to remove unabsorbed ions, the electrode was rinsed with DI water for 1 min after each immersion step. These three immersion steps were considered as one SILAR cycle. 10 SILAR cycles were repeated to obtain the final thin films. After that, the thin films were annealed in Ar environment at 350 °C for 1.5h to prepare crystallized CIS thin films. The M-CIS thin films were synthesized as same as A-CIS layers, except that methanol was used instead of water as solvent and Na_2S was dissolved in methanol/water (7:3, v/v) solvent.

A PGENERAL T6 spectrophotometer was utilized to obtain the UV-Visible absorption spectra of the samples. To identify the samples composition structure, an Invia Renishaw Raman microscope (with exciting laser wavelength of 514.5 nm) was employed. A three-electrode setup (the synthesized thin films as working electrode, saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode) was connected to a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China) to measure all electrochemical analyses. the Mott-Schottky tests were done in 50 mM Na_2S aqueous solution by applying AC voltage varying from - 0.2 to 0.2 V with frequency of 1 kHz and 5mV amplitude.

3. Results and discussion

UV-Visible transmission spectra of synthesized samples have been shown in Fig. 1. As it can be seen, the sample prepared via aqueous solutions (A-CIS) has less transmittance than M-CIS one, meaning that aqueous solutions have resulted in more ion absorption and consequently thicker layer has formed on ITO substrate. The band gap energy (Eg) of the layers were evaluated via Tauc plots [6] (Fig. 1 b). Based on Fig. 1 b results, the Eg of M-CIS and A-CIS was determined to be 1.6 and 1.5 eV respectively. Larger Eg of M-CIS is related to formation of smaller particles and thinner $CuInS_2$ film on ITO substrate.

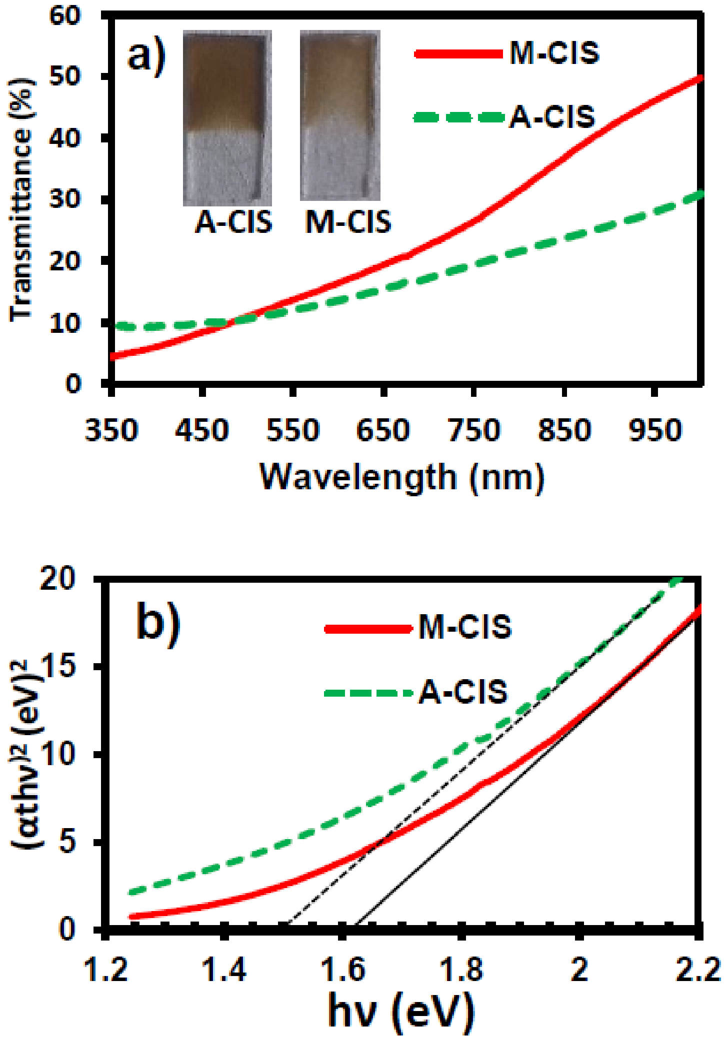

Fig. 1: a) UV-Visible transmission spectra and b) related Tauc plots of A-CIS and M-CIS thin films. The inset of a) is photograph of prepared samples.

The compositions of the synthesized thin films were more characterized via Raman spectroscopy. The obtained Raman spectra have been shown in Fig. 2. There is a dominant peak located at 293 and 298 cm^{-1} for M-CIS and A-CIS, respectively. The observed peak is related to A1-mode of $CuInS_2$ crystal structure [7]. The A1-mode of M-CIS has a shift toward lower frequencies as compared to the A-CIS thin film, which can be attributed to optical phonon confinement and formation of smaller $CuInS_2$ nanoparticles [7]. The Raman results are in good agreement with obtained UV-Visible transmission data.

To determine that the synthesized $CuInS_2$/ITO thin films are n-type or p-type semiconductor, the Mott- Schottky tests were done and the results have been shown in Fig. 3.

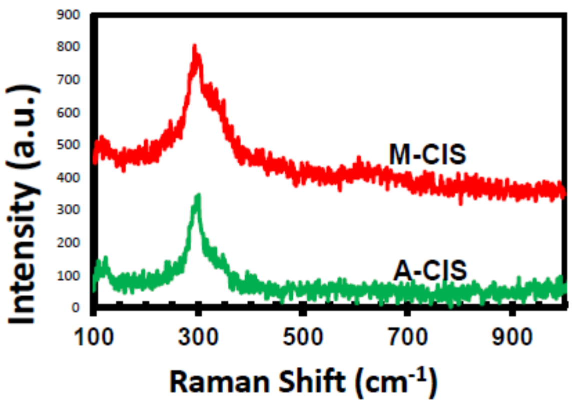

Fig. 2: Raman spectra of M-CIS and A-CIS thin films.

The Mott-Schottky relationship for semiconductors are expressed as following [8]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_o e N_d A^2}\left[(E - E_{FB}) - \frac{kT}{e}\right], \text{ for n type} \quad (1)$$

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_o N_\alpha A^2}\left[(-E + E_{FB}) - \frac{kT}{e}\right], \text{ for p type} \quad (2)$$

Where "ε0" and "ε" are the permittivity of vacuum and semiconductor, respectively. "e" is the electron charge, "k" is Boltzmann's constant, "T" is operation temperature, "Nα" and "Nd" are the acceptor and donor densities, respectively. "E", "EFB" and "C" are the electrode potential, flat-band potential and depletion-layer capacitance, respectively [8]. Based on above equations, the Mott-Schottky plots have positive and negative slopes for n-type semiconductor and a negative slope for p-type one.

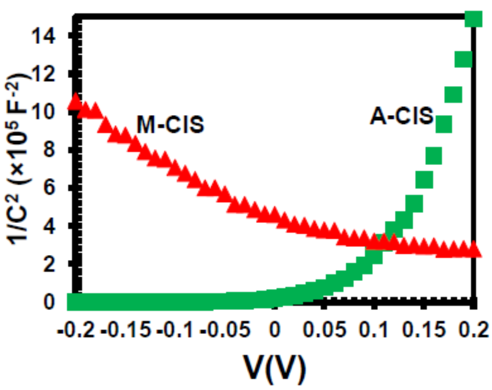

Fig. 3: Mott-Schottky plots of $CuInS_2$/ thin films.

As it can be seen from Fig. 3, the A-CIS has a positive slope and M-CIS has a negative slope. Therefore, the $CuInS_2$ thin films prepared with aqueous SILAR solutions have n-type semiconducting behavior. On the other hand, the CIS thin films prepared with methanolic SILAR solutions are p-type semiconductors. The reason may be related to different Cu/In ratio in A-CIS and M-CIS thin films [2].

4. Conclusions

The $CuInS_2$ thin films were prepared by simple SILAR method using aqueous (A-CIS) and methanolic solutions (M-CIS). The Raman results indicated that the M-CIS thin film has smaller nanoparticles than A-CIS one. The A-CIS thin films were more opaque with smaller band gap energy. The Mott-Schottky plots revealed that A-CIS is an n-type semiconductor, while M-CIS thin films have p-type semiconducting behavior, which is due to different Cu/In ratio in these thin films.

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