Chalcogenide Letters Vol. 15, No. 8, August 2018, p. 429 - 434

OPTICAL AND STRUCTURAL PROPERTIES OF AMMONIA-FREE CdS:Cu THIN FILM GROWN ON FLEXIBLE SUBSTRATE BY CHEMICAL BATH METHOD

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Thin films of ammonia-free copper-doped cadmium sulfide deposited on flexible substrate were obtained by the chemical bath method. The optical and morphological thin films depending on the doping concentration of copper was studied, showing a shift in the band-gap (2.46 to 2.29 eV). The samples are formed of small nanoparticles (5-7 nm) with large agglomerates and have good adhesion.

(Received June 13, 2018; Accepted August 21, 2018)

Keywords: Thin films, Flexible substrate, Ammonia-free, Cadmium sulfide

1. Introduction

Cadmium sulfide (CdS) thin film is one of the most studied due to its numerous optoelectronic applications. Currently one of its important applications is when used as a window layer on solar cells, specifically, CdTe/CdS and CdS-Cu(In,Ga) high efficient solar cells [1, 2]. The CdTe/CdS solar cell is a heterojunction of one p-type (CdTe) and other n-type (CdS) semiconductor, where CdTe thin film semiconductor acts how very well absorber [3] with a 1.45 eV (near infrared wavelength) direct band gap and 2.42 eV (green wavelength) for CdS like windows layer [4]. Even though the commercialization of CdTe solar cells with glass substrate is very high [5], that is precisely the glass substrate one of its major disadvantages, due to transportation and break problems [2, 6].

There are various studies that have been synthesizing copper-doped CdS thin films using different methods of synthesis [7,8,9,10], as well as their effect on the efficiency of solar cells [11,12] using rigid substrates. However, because of the disadvantages mentioned above, it has been investigated to replace the glass substrate with a flexible substrate due to its light weight and unbreakable [13,14].

When the CdS is deposited on a flexible substrate, the substrate is cover with a transparent conductive layer, and it forms a thin layer which acts as a window layer, which it achieves good photo conversion, generated efficient photovoltaic cells [15-18]. Between the methods that have been used to obtain high quality CdS layer on a flexible material, we can mention: pulsed-laser deposition [19], vacuum thermal evaporation [20], Chemical bath deposition [21], electrodeposition [22], spray pyrolysis [19], among others. For a review of deposit methods see [23]. But the most widely used procedure is the chemical bath deposition, because it is cheap, simple and can be obtained a good film uniformity and adequate adhesion to flexible material. All this is achieved in a liquid medium CdS solution to a fairly low temperature [24, 17, 25]. The most commonly used flexible substrates are polyethylene terephthalate (PET), polycarbonate (PC), transparent plastic foil, graphene, viewfoils, cloth and threat [26-30].

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It is known that the Cu ions introduced into the structure of the CdS acts as impurities increasing the dark resistivity. Because the CdS has a high resistivity in the dark, there is some investigation that deal with several ways trying to reduce it [19, 31]. In one investigation [18], two thin films, one of CdS and the other was CdS:Cu (copper doped cadmium sulfide) using the chemical spray pyrolysis technique, the substrate they used was glass. Obtaining as results that the band gap of the films decreases from 2.451 eV, for CdS, to 2.41 eV, for CdS:Cu, and that the electrical measurements indicates that the conductivity of CdS:Cu was dependent on doping concentration. In other work [30], using ultrasonic spray pyrolysis technique and aqueous precursor for the CdS:Cu thin films, use a ITO (indium tin oxide)-coated glass as substrate, the transparent conductive layer. They obtained that if the color of the films became darker was because of the higher doping levels.

In this article, it is studied the dependence of the optical and morphological properties of thin films of CdS on the copper doping concentration, using chemical bath deposition technique on flexible substrate (PET-ITO) presenting good adhesion. The CdS:Cu thin films synthesis eliminates the high ammonia toxicity, a very important characteristic for large scale production.

2. Methods

CdS:Cu thin films of variable doping levels have been grown on flexible substrate coated with ITO by chemical bath deposition technique. The indium tin oxide/polyethelene terephthalate (PET/ITO) substrate properties [from Sigma-Aldrich (ref. 639303)] are: surface resistivity 60 W/□ and the thickness of ITO is 1300 Å. The reactive substances in the solution were: cadmium chloride ($CdCl_2$), cupric chloride ($CuCl_2$), trisodium citrate ($Na3C_6H_5O_7$), potassium hydroxide (KOH), thiourea [$(NH_2)_2CS$], buffer system (NH_4OH/NH_4Cl) and deionized water, contained in a 100 ml beaker. During growth, the bath was maintained at a constant temperature of 40°C for 3 hours. The deposited films were homogeneous, with very good adhesion to the substrate and uniform to the eye, while their colors changed from yellow to brownish yellow with increase of dopant from 0.0M to 0.5M. The Rx spectra of the thin films was obtained with a Rigaku Ultima III-XRD diffractometer for the analysis of its crystalline structure. Optical absorption spectra of the thin films were measured in a Perkin Elmer Lambda 19 spectrophotometer. The morphology was evaluated by Scanning electron microscopy (SEM) using a XL30 ESEM Philips microscope.

3. Results and discussion

The optical properties of CdS thin films were studied with the absorbance pattern and the Tauc´s relation for obtained the bandgap of the samples. The absorption spectra were evaluated from 400 nm to 800 nm, important interval for photovoltaic applications. The Fig. 1 shows the absorption pattern of the CdS:Cu thin films doped with different molarities of Cu grown of PET/ITO flexible substrate by chemical bath deposition technique. It can be observed that the absorption of thin films increases with the increase of Cu doping. On the other hand, the sample doped with 0.5 M of Cu shows an absorption between 10% - 25% in the range of 400 nm - 500 nm, while the other samples its absorption oscillate between 12% - 35%. This feature is important when CdS thin film is used as window in a solar cell. The transmittance's samples (not showed) decrease with the increase of Cu doping. However, the samples with 0.001M and 0M Cu doping have 65% - 90% and 96% (545 nm to 800nm) transmittances, respectively, very important values for solar cells application.

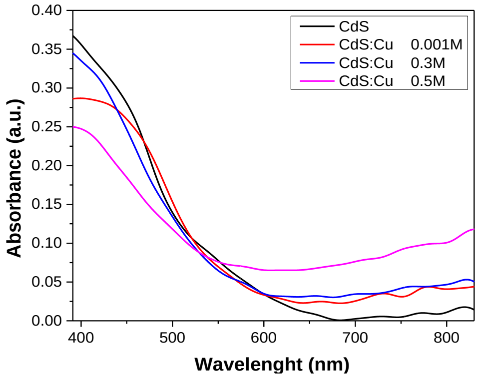

Fig. 1. Optical absorbance spectra of CdS thin films doped with different molarities of Cu on PET/ITO substrate

The Fig. 2, shows the band gap of the samples obtained from the absorption spectra. The bandgap values decrease with increasing amount of Cu dopant (2.46 eV - 2.29 eV).

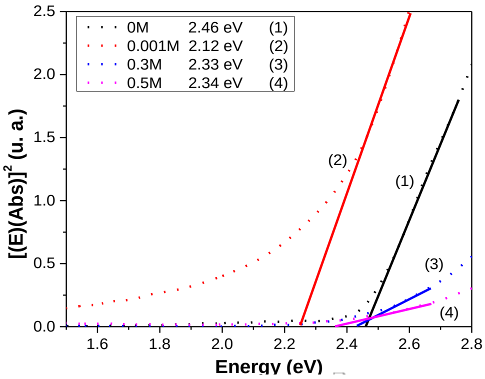

Fig. 2. Band gaps for CdS:Cu thin films with different molarities of Cu on PET/ITO substrate

The morphology of the samples was studied with the Rx patterns and SEM imagens. The Optical Rx patterns of CdS thin film shown in the Fig. 3, with 0.0M, 0.001M, 0.03M and 0.05M of Cu. All the diffract grams shown two peaks: a very intensive and width peak about at 26° and a very small peak at 23°. The peak at 26° is associated with the hexagonal phase in the (002) diffraction plane. It is observed that thin films tend to have an amorphous structure with increased copper doping. On the other hand, the thin films are formed of small particles (see Fig. 4c) that are joined forming agglomerates with different shapes (see Fig. 4).

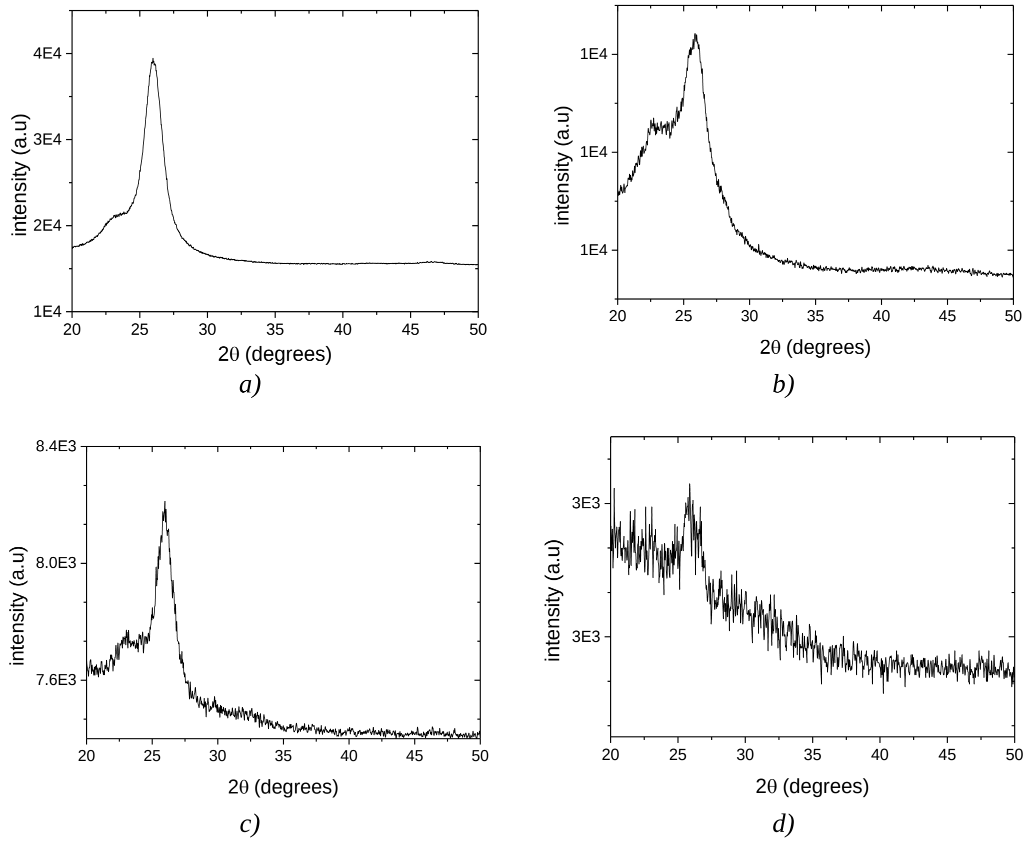

Fig. 3. Optical Rx pattern of CdS of thin films doped with different molarities of Cu on PET/ITO substrate: a) 0M, b) 0.001 M, c) 0.03 M and d) 0.05 M.

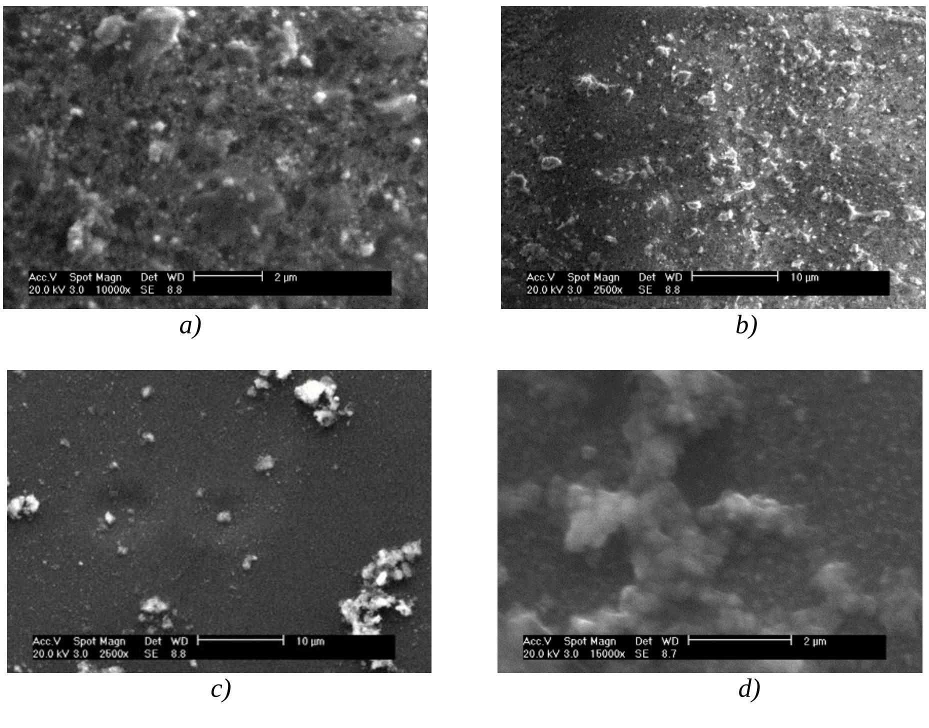

Fig. 4. SEM images of the CdS thin films doped with different molarities of Cu on PET/ITO substrate: a) 0M, b) 0.001 M, c) 0.03 M and d) 0.05 M.

Fig. 4 shows SEM images of the thin films samples. It is know that the average grain size (L_B) is inversely proportional to the width peak (B), which is known as the Scherrer equation:

$$L_B = \frac{0.94\lambda}{B\cos\theta_B}$$

where, λ: x-ray wavelength used, B: full width at half maximum in radians (FWHM) and θ_B: Bragg angle. Using the above equation, were calculated the average grain size of the samples: 5.6 nm (0.0M), 5.64 nm (0.001M), 6.43 nm (0.03M) and 0.55 nm (0.05M).

4. Conclusions

The effect of the doping of Cu on the optical and morphological properties in CdS thin films deposited on flexible substrate using the chemical bath technique was studied. The thin films are more friendly to the environment to be free of ammonia and showed good adhesion.

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