

Preparation and Characterization of CdSnSe Thin Films by DC Plasma Sputtering

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Abstract

In this work, CdSnSe thin films were deposited on glass substrates by dc plasma sputtering technique. The sputtered target was prepared by the thermal casting of Cd, Sn and Se samples at 350°C. The structural characterizations showed that the prepared targets were polycrystalline while the deposited CdSnSe films exhibited amorphous structure due to the growth of nanostructures on the substrates, which was also confirmed by the scanning electron microscopy. These films showed high absorption in the ultraviolet and visible regions while low absorption was observed in the near-infrared region ($>800\text{nm}$). They have two allowed types of energy band gaps; indirect at 1.233eV and direct at 1.655eV. The dispersion relationship showed that these films have approximately constant refractive index in the visible region, which is attributed to the optical homogeneity of the prepared films.

Keywords: CdSnSe; Thin films; Plasma sputtering; Thermal casting

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1. Introduction

Though the domination of certain semiconducting materials in energy conversion devices and applications, the trends to find new materials are intensively continuous. Their main goals are lower production cost and larger area of a single unit used for energy conversion [1]. Recently, materials science and technology assist researchers to approach these goals by presenting compound semiconductors, which in general are on the second rank of production cost after silicon [1-5]. The ternary (II-IV-VI) compound cadmium-tin selenide (CdSnSe) is a p-type semiconductor with graded allowed energy band gaps: direct of 1.6-1.7eV and indirect of 1.23-1.25eV [6-9]. This made this compound semiconductor very good candidate for the photovoltaic applications, especially thin film solar cells [10-12].

The CdSnSe target or source required for some physical vapor deposition techniques, such as plasma sputtering, pulsed-laser deposition and thermal evaporation, is prepared by some casting method [13,14]. This makes it easy to control the partial amounts of each element (Cd, Sn and Se) in the final product to be used as a target or source sample [15]. Research works showed that reasonable variations in the structural, optical and electrical properties of this compound can be resulted from different mixing ratios of Cd, Sn and Se [8-12].

In this work, an attempt to prepare sputtering targets from CdSnSe compound to deposit nanostructured thin films is presented. Some structural and optical properties of these films are introduced.

2. Experiment

Highly pure bulk samples of cadmium (99.99%), tin (99.9%) and selenium (99.999%) were placed in a graphite pot of 8cm diameter and then melted inside digitally-controlled furnace at 350°C with slow increasing rate (5°C/hr). The molten was cooled down to room temperature at the same rate in order to avoid the formation of bubbles and hence cracks in the final sample. The produced sample was characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The partial amounts of Cd and Sn in the produced sample were varied by different weight percentages in the molten, while the partial amount of Se was kept constant.

This sample was cut with dimensions of 5x5cm, grinded and polished to a mirror-like degree to be used as a sputtering target. This target was maintained on the cathode inside discharge plasma chamber. This chamber was initially evacuated down to 10^{-5} mbar using rotary and diffusion pumps before highly-pure argon gas was pumped to the chamber at a pressure of 0.05mbar to generate the discharge plasma. The electrical power required for the breakdown of argon gas was provided by a dc power supply (0-5kV). The quartz substrate on which the thin film is deposited was carefully cleaned then placed on the anode inside the deposition chamber. The cathode was cooled down to 5°C to prevent the secondary electron emission while the anode (and hence the substrate) was kept at room temperature.

The inter-electrode distance could be varied from 1 to 8cm. The deposition parameters, such as inter-electrode distance, gas pressure, discharge current and deposition time, were optimized and more details on the experimental part of this work can be found elsewhere [16-19].

3. Results and Discussion

Figure (1a) shows the x-ray diffraction (XRD) pattern of the polycrystalline CdSnSe sample prepared by thermal casting at 350°C. The crystal planes of (210), (101), (201), (111), (020), (510), (221) and (610) are corresponding to diffraction angles (2θ) of 23.9°, 24.95°, 27.2°, 30.9°, 38.0°, 42.1°, 47.6° and 49.55°, respectively. These values may be all attributed to the formation of CdSnSe, however, some peaks may interfered with others belonging to CdSe or SnSe but for different crystal orientations.

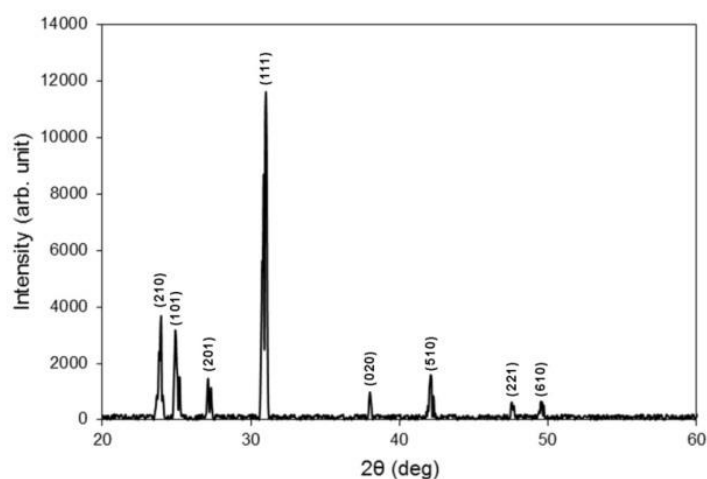
By using the CdSnSe sample as a sputtering target, CdSnSe thin films were deposited on quartz substrates at different deposition times. According to the XRD characterization, all these films showed amorphous structure. The formation of nanocrystalline structure is initially confirmed by the amorphous pattern in Fig. (1b).

Figure (2) shows the scanning electron microscopy (SEM) images of the CdSnSe samples prepared in this work. As shown in Fig. (2a) for the CdSnSe sample to be used as sputtering target, a wide range of grain sizes is observed due to the thermally-induced growth, which is inhomogeneous process in nature. Accordingly, the agglomerated grains are inevitable result of thermal casting at high temperatures. However, such samples can be used as sputtering targets since the sputtering of particles from the target surface is highly-dependent on surface conditions and grain size. Therefore, with precise control on sputtering parameters, especially the energies of bombarding ions, smaller particles are much more likely to be sputtered from the target while the larger particles require ions with higher energies.

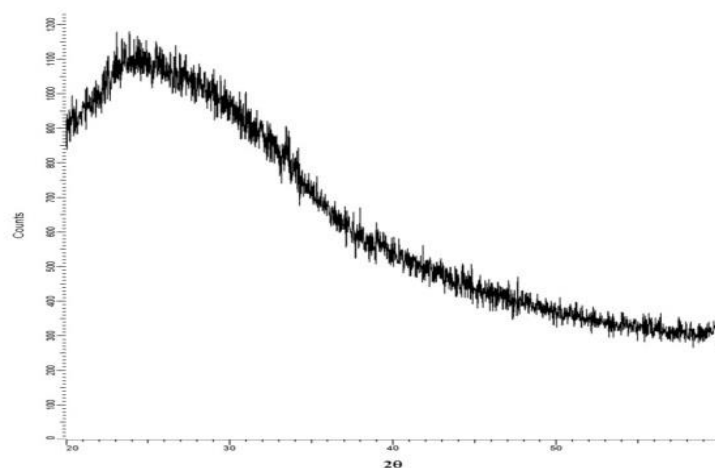
In Fig. (2b), the formation of <100nm CdSnSe nanoparticles is confirmed in thin film sample deposited on quartz substrate by dc plasma sputtering technique at deposition time of 3 hours. This extreme decrease in particle size is a main feature of dc plasma sputtering. However, agglomerations are clearly observed all over the scanned area. Optimization of deposition parameters may work to prevent the growth of large particles and hence result in a homogeneous distribution of particle sizes.

The spectral transmittance of the CdSnSe thin film is shown in Fig. (3) in the spectral range of 200-1000nm. The low transmission behavior of this film in the UV and visible regions is converted into high transmission at 700nm. This behavior put CdSnSe thin films on high rank of energy conversion semiconductors with reasonably high transparency (up to 90%) in the NIR region. The rapid conversion from low transmittance (<10%) at about 600nm to high transmittance (>80%) at about 700nm makes these films very good candidates for optical switching applications in optoelectronics. As well, they can be used as optical filters as such behavior is very sensitive to the partial content of each element in the ternary compound (CdSnSe).

In order to determine the energy band gap of the produced material, the relationship between $(ah\nu)^n$ with photon energy ($h\nu$) is plotted, as shown in Fig. (4), where n denotes to the type of gap and transition of the material. Two types of energy band gap (E_g), direct and indirect, were determined for the CdSnSe thin film samples deposited in this work. The direct allowed energy band gap was determined at 1.655 eV while the indirect allowed energy band gap was determined at 1.233 eV. Consequently, the cutoff wavelengths corresponding to these values of direct and indirect energy band gaps are 749 and 1000nm, respectively.

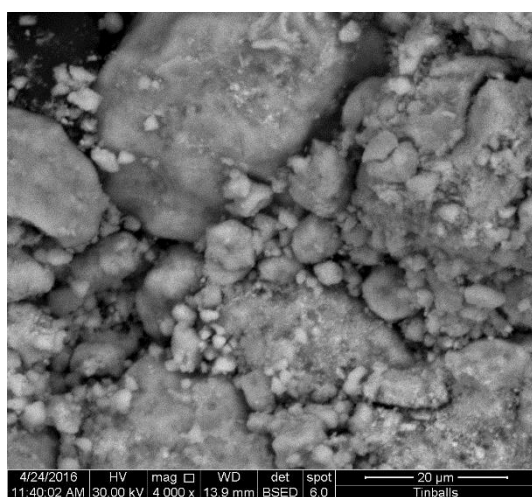


(a)

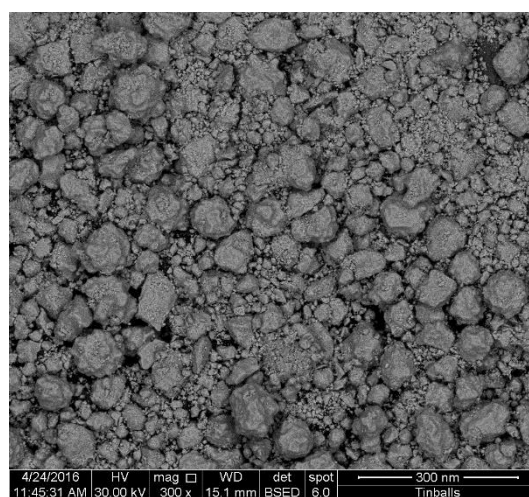


(b)

Fig. (1) The XRD pattern of (a) CdSnSe sample prepared by thermal casting at 350°C and (b) CdSnSe thin film deposited by dc plasma sputtering at deposition time of 3 hours



(a)



(b)

Fig. (2) The SEM images of (a) CdSnSe sample prepared by thermal casting at 350°C and (b) CdSnSe thin film deposited by dc plasma sputtering at deposition time of 3 hours

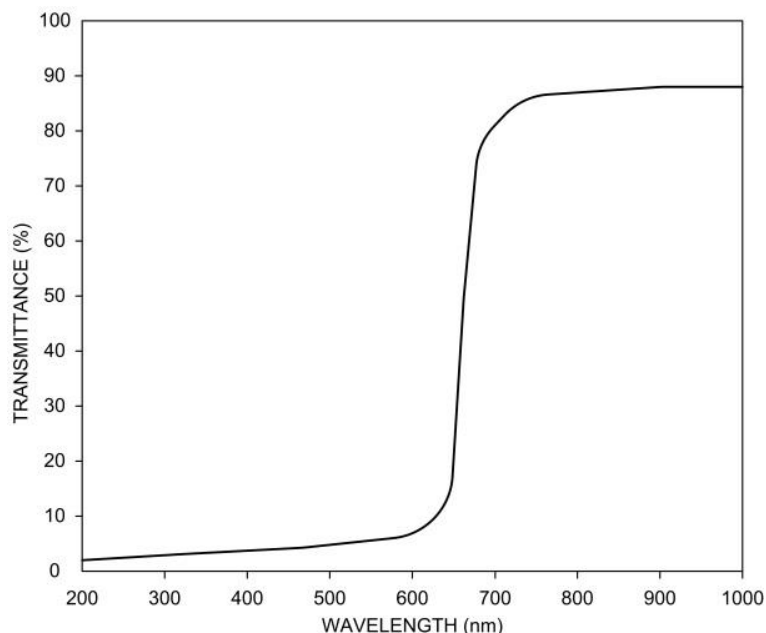
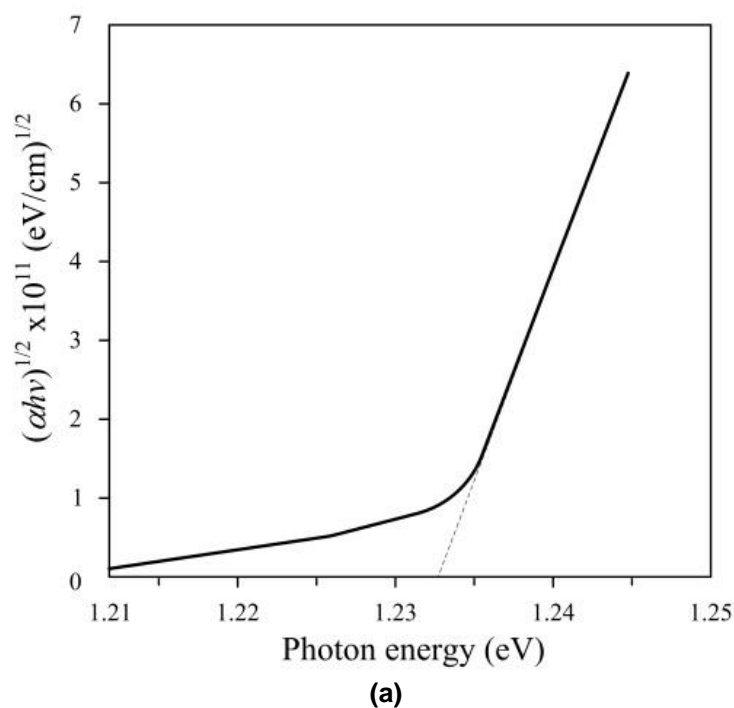


Fig. (3) Spectral transmittance of the CdSnSe thin film deposited by dc plasma sputtering at deposition time of 3 hours

Similar to III-V semiconductors, such as GaAs and InP as well as many of their alloys, such as InGaAs, the photon can be absorbed by the direct energy band gap of CdSnSe without any contribution from the lattice vibration. As well, this ternary compound (CdSnSe) can absorb photons with energies near and above the indirect energy band gap, similar to Si and Ge, which requires the absorption and emission of lattice vibrations (phonons).

A wider range of bandgap energy and lattice constant can be obtained by using compound semiconductor alloys, such as ternary alloy investigated in this work ($\text{Cd}_x\text{Sn}_{1-x}\text{Se}$). Vegard's law says that the lattice constant of an alloy varies linearly with composition. The energy gap of an alloy varies linearly with composition but has some curvature and can also change from direct to indirect.



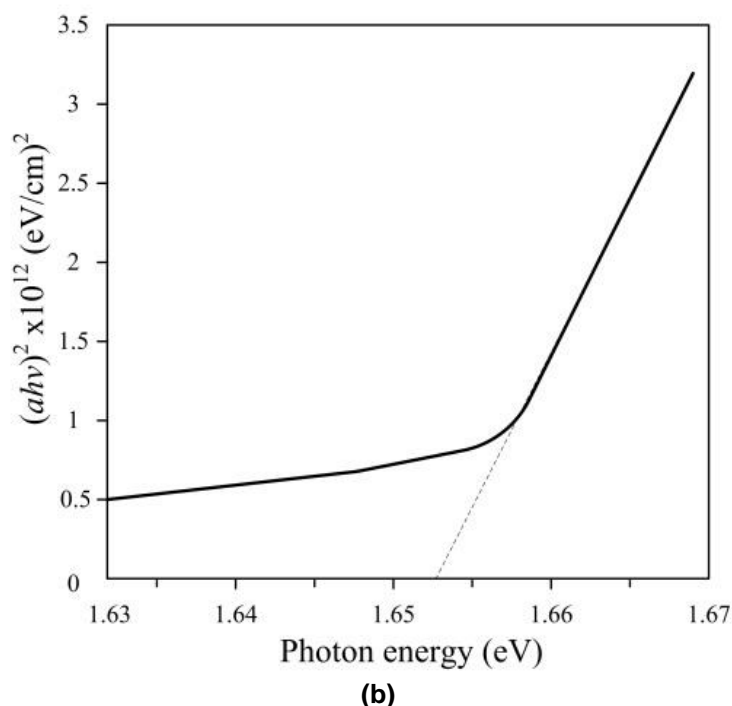


Fig. (4) Determination of energy band gaps of the CdSnSe thin film deposited in this work (a) indirect allowed and (b) direct allowed

In a ternary alloy, such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$, above a composition of $x \approx 0.45$, the alloy changes from direct to indirect. Such materials make up part of the optical waveguide in semiconductor lasers, and thus the refractive index variation with composition is also of interest.

Figure (5) shows the relationship between refractive index of the CdSnSe thin film sample prepared at deposition time of 3 hours and the incident wavelength. The structural homogeneity of the deposited CdSnSe thin films is clearly shown in this figure as the value of refractive index is approximately constant (~ 1.74) within the range 450-750nm. However, this behavior may be controlled by the variation of fractional compositions of Cd and Sn while the fractional composition of Se is kept constant. A form of the Sellmeier equation gives the refractive index of undoped ternary compound.

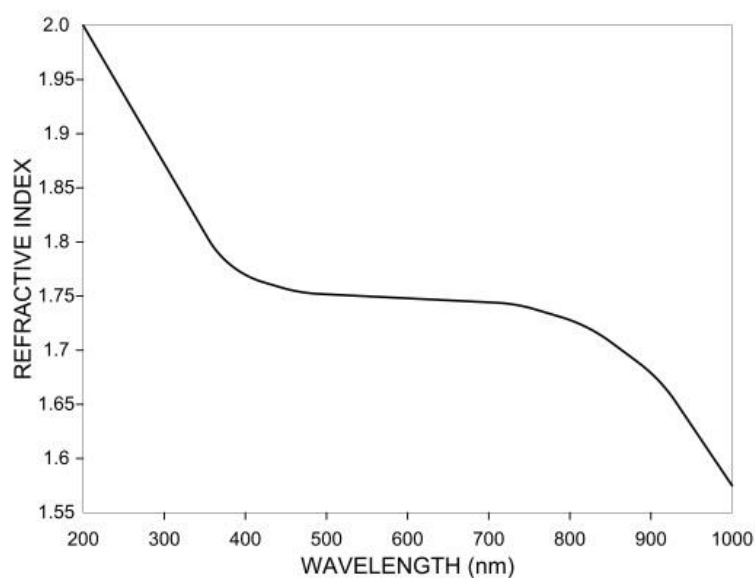


Fig. (5) Dispersion relationship of the CdSnSe thin film deposited in this work

4. Conclusion

In concluding remarks, nanostructured CdSnSe thin films were deposited by dc plasma sputtering of CdSnSe target prepared by thermal casting at 350°C. The optical properties of the deposited films shows low transmission (<10%) in the UV and visible regions, two types of energy band gaps (direct and indirect) and good optical homogeneity (approximately constant value of refractive index) in the visible region. Deposition of homogeneous nanostructured CdSnSe thin films encourages using them for fabrication of low-cost and reliable photovoltaic devices.

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