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RESEARCH ARTICLE

Temperature Dependent Structural and Optical Properties of Doped Cadmium Sulphide Thin Films

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Abstract

Cadmium sulphide thin films were prepared using the SILAR (successive ionic layer and reaction) method. The films were then doped with zinc and annealed at different annealing temperatures. The as-deposited and annealed films were structurally characterised using X-ray Diffractometry (XRD) studies. The optical characterisation was done using the UV spectrophotometer to investigate the transmittance and reflectance versus wavelength measurements. The structural characterisation reveals that the films were polycrystalline, crystallising mostly with the cubic structure. From the optical characterisation, the energy bandgap for the as-grown layers was found to be in the range 2.30 eV to 3.80 eV which is within the range suitable for use as window layers in solar cell devices.

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Introduction

Cadmium Sulphide (CdS) has been successfully utilised as buffer layers in the most advanced thin film solar cells such as CdTe (cadmium telluride) and CIGS (copper indium gallium selenide) based devices. CdS thin films have also been used as window layers in the earth-abundant based solar cell devices such as SnS (tin sulphide) and the kesterites (CuZnSnS). This has been reported by various authors (Susane et al, 2012; Abu Sharma et al, 2004; Nwofe et al, 2013). Cadmium Sulphide belongs to the II-VI group of semiconductor compounds which has been used in making heterojunction thin film solar cells, (Nwofe et al, 2013; Ogah, et al 2011; Vigil-Galan et al 2006; Reddy et al, 2006), mostly because it is a wide band gap semiconductor. It has been reported that CdS exhibits good thermal stability and can be used as light dependent resistors sensitive to visible and near infrared light (Hossain et al, 2012). Cadmium sulphide thin films can be grown using different range of deposition techniques such as thermal evaporation (Kar and Choudri, 2006; Shen et al, 2005), chemical bath deposition technique (Vigil-Galan et al 2007), RF magnetron sputtering (Lee and Lee, 2007), SILAR (Lukaitis et al, 2001; Xie et al, 2005), metal-organic chemical vapour deposition (O'Brien et al, 1996; Halsall et al, 1988), reverse micro emulsion method (Iorgu et al, 2013) and spray pyrolysis (Vijaya, 2014). Some reports in the literature indicate that cadmium sulphide can be doped using different materials such as nickel (Elango et al 2012), lead (Nerle and Rabinal 2014), copper (Tadataka and Jun'ichiro, 1993; Patil, 1972; Tiwari et al, 2013), Zirconium (Thiyagarajan et al, 2009), manganese (Venkatesu and Ravichandran, 2013), cobalt, nickel, magnesium, selenium and zinc (Moore and Klein, 1969), tellurium (Atten and Haanstra, 1964), cerium (Saravana et al, 2012), mercury (Vijaya, 2014), aluminium (Hasnet and Poder, 2012), europium (Saravan et al, 2011), and silver, (Iorgu et al, 2013). Chemical spray pyrolysis method has been widely used recently because its simplicity and inexpensiveness has found to be a better chemical method for the preparation of thin films with larger area compared to other methods. Spray pyrolysis also provides an easy method of doping an element in the required proportion through the solution growth method. Another significant advantage of using spray pyrolysis over other deposition methods is the ease to modify/control the various deposition parameters such as; substrate temperature, rate of deposition, air pressure, source to substrate distance, and cooling

rate after deposition. This is very important since these parameters affect the physical, electrical and optical properties of the thin films. Also the equipments can be easily assembled locally, thus reducing the needs for more sophisticated and expensive equipments. Vijaya (2014) observed that doping of Cadmium sulphide thin films enhanced the use not only as windows in thin film solar cell devices but also on other electronic displays as well as absorber layers in lieu of the doping effect on the energy bandgap. Zinc-doped Cadmium sulphide thin films grown by the closed vapour transport technique has been reported by other research groups (Kim et al, 2007) but report on CdS thin films grown by the SILAR method are relatively rare. In this study, the CdS thin films grown by the SILAR technique and doped with zinc to improve the properties has been reported. The work reported herein is a fundamental step towards improving the properties of cadmium sulphide thin films for applications in different opto-electronic devices.

Material and Methods

Thin films of CdS were deposited on ultrasonically cleaned glass substrates using the SILAR method. The substrate temperature was varied in the range 303 K to 363 K, keeping other deposition variables constant. 169.0 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (cadmium trioxonitrate (V) tetrahydrate) was dissolved in 100 ml of water while 270.6 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (zinc trioxonitrate (V) hexahydrate) was dissolved in 100 ml of water separately. 12 g of $\text{Cs}(\text{NH}_3)_2$ was further dissolved in 100 ml of water in a separate container. Consequently, 20 ml of the prepared 2.7 mol Cd^{2+} solution were poured in a 60 ml beaker to which 20 ml of 0.01M and 0.05M Zn^{2+} were added respectively, and 20ml of 14M ammonia solutions were then added successively. 60 ml of S^{2-} prepared from the 0.4 mol thiourea solution was poured in another beaker. The above procedure was repeated for each of the respective temperatures used.

A PANalytical (XPRT=PRO) D8 advance X-ray diffractometer with a Cu $K\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) was used to determine the phases present and the structural properties of both the as-deposited and doped CdS films. A UV spectrophotometer was used to measure the transmittance (T) and reflectance (R) versus wavelength measurements.

Result and Discussion

The physical observations of the as-deposited and doped CdS films indicates that they are free from pinholes, had no cracks and adhered strongly to the substrate. The films exhibited a yellow colour which increased with an increase in the substrate temperature and the doping concentration. Figure 1 gives the XRD plots for the as-grown cadmium sulphide layers. The structural characterisation reveals that the films were polycrystalline and appeared to be consistent with JCPDS: 03-065-6212 for the as-deposited layers. Also from the XRD analysis, it was observed that

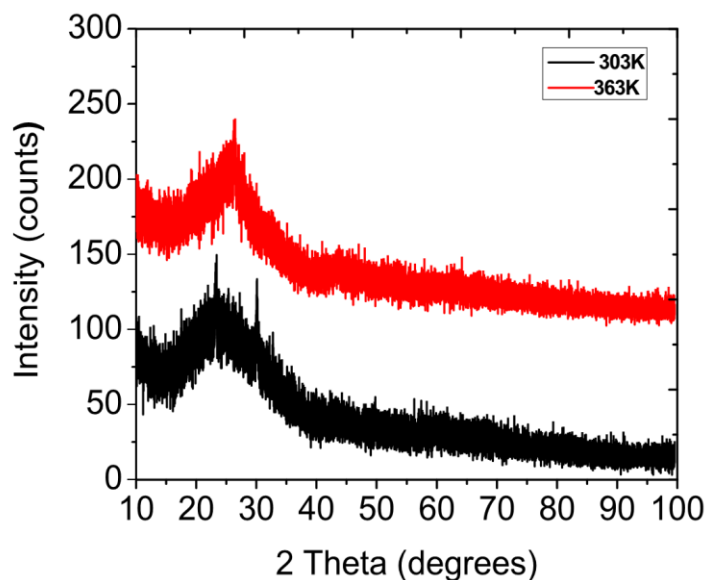


Figure 1. X-ray diffraction profiles of as-deposited CdS thin films grown at different substrate temperatures.

the as-deposited films crystallised in the cubic structure with Bragg peaks corresponding to the (111) and (220) planes (not shown). The doped layers also exhibits the cubic structure with the PDF: 01-075-0018 and the calculated lattice parameter was obtained as; $a = b = c = 5.3900$. Iorgu et al, (2013) has observed similar effects for cadmium sulphide thin films grown by the reverse microemulsion technique while other authors, (Iorgu et al, 2013; Elango et al, 2012; Saravana et al, 2012; Kim et al, 2007) reported a similar observation for doped CdS layers. From the optical transmittance and reflectance versus wavelength measurements, some important optical constants such as the optical absorption coefficient α , and energy bandgap E_g , were deduced. Figure 2 gives a typical $(\alpha h\nu)^2$ versus $h\nu$ plots for the as-grown CdS layers at different substrate temperatures.

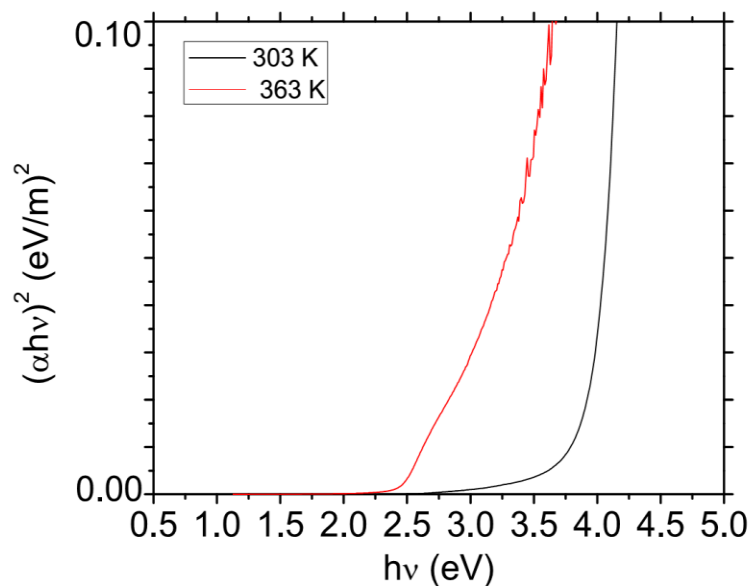


Figure 2. $(\alpha h\nu)^2$ versus $h\nu$ plots of as-deposited CdS thin films grown at different substrate temperatures.

The energy bandgap was deduced using the relation (Nwofe et al, 2012; Pankove, 2012) given as:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

where B is an energy independent constant, α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the energy bandgap and n equals 0.5 for direct allowed transitions.

The plot of $(\alpha h\nu)^2$ versus $h\nu$ is a straight line and its energy axis intercept at $(\alpha h\nu) = 0$ gives the energy band gap E_g of the material. The values of the energy band gap extrapolated from the $(\alpha h\nu)^2$ versus $h\nu$ plots were found to vary between 2.30 eV to 3.80 eV. As indicated in figure 2, the energy bandgap decreased with an increase in substrate temperature. This was attributed to the increase in molarity of the solution due to the addition of Zn^{2+} ions. It is possible that an increase in substrate temperature causes uniformity of the films due to the re-organisation of the atoms arising from the evaporation of the water molecule leading to the observed effects. Increase in substrate temperature could lead to an increase in grain size due to increased surface mobility. Other research groups (Hasnet et al, 2012; Tadataka and Jun'ichiro, 1993) have reported similar observation for doped CdS layers. However it has been argued in the literature for other semiconductor compounds (Devika et al, 2007; Nwofe et al, 2012; 2013), that a decrease/increase in the energy bandgap could also be due to the effect of other deposition parameters such as the source to substrate distance or annealing effects. Agbo (2011) and Agbo (2012) in their investigations on core-

shell thin films observed that the energy bandgap could be altered at different substrate temperatures/and or annealing effects and attributed it to quantum size effects. The energy bandgap of thin films can be modified through different approaches as highlighted in different reports in the literature (Nwofe et al, 2012; Nwofe et al, 2013; Luckert et al, 2011, Potter et al, 1988; Gao et al 2005; Tamborra et al, 2004; Du et al, 2002) irrespective of the deposition techniques. The values of the energy bandgap (2.30 eV to 3.80 eV) obtained in this work is within the range of the energy bandgap reported by other authors (Vigil-Galán et al, 2006; Kar and Chaudhuri, 2006; Patil, 1972) and is suitable for various opto-electronic applications and solar cell devices. Our future work will focus on the use of these layers to make solar cell devices with improved efficiency.

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