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The investigation of Cu doped CdS films produced by ultrasonic spray pyrolysis technique

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Recently, there has been an increasing demand for thin film solar cells due to the decrease of primary energy sources. The materials which are used in these devices need to be produced by low cost production techniques and possess improved characteristics. CdS is a well-known material for thin film solar cell applications. We have tried to investigate the effect of Cu doping (1, 3 and 5 at %) to CdS. Undoped and doped CdS films have been obtained by ultrasonic spray pyrolysis (USP) technique which is economic and simple to process. The structural, surface and optical properties of the films have been investigated. X-ray diffraction has been used to analyze the structural properties. Morphological properties have been investigated by scanning electron microscopy (SEM). Energy dispersive x-ray spectroscopy (EDX) has been used to perform elemental analysis. The optical parameters have been analyzed by a UV spectrometer.

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1. Introduction

Single and polycrystalline semiconductor thin film solar cells can be used to benefit from the solar energy. Polycrystalline thin film solar cells are preferred versus single crystalline ones due to their easy growth and low cost. Especially, undoped and doped CdS semiconductor films are used in solar cells as window material [1-3]. The binary semiconductor compound CdS is a very interesting material for photovoltaic applications. In particular, for CdS/CdTe thin film solar cell efficiencies up to 16.5% [4] have been obtained. CdS is a very desirable window layer for many photovoltaic solar cells because of its outstanding optical and electrical properties [5-8]. CdS films grow usually in the wurtzite structure and without external doping show n-type conductivity [9]. CdS has been the subject of intensive research because of its suitable band gap, high absorption coefficient, reasonable conversion efficiency, stability and low cost [10]. The properties of CdS films depend on the production technique. Amongst all the deposition techniques, spray pyrolysis is simple, economical and a suitable method for large area deposition of many binary, ternary and quaternary semiconducting films [11]. Spray pyrolysis is an effective production method to lead to short production time, homogeneous particle composition and one-step production method [12].

The aim of this work is to obtain CdS and Cu incorporated CdS (CdS:Cu) films at the Cu percentages of 1,3 and 5 using ultrasonic spray pyrolysis (USP) technique and to investigate the effect of Cu incorporation on the optical, structural morphological and elemental properties of CdS films.

2. Experimental

The USP is a versatile method for producing various materials in a wide range of composition, size and morphology. Compared with spray pyrolysis method, the USP method possesses the advantages of high deposition rate, good thickness uniformity over a large area, homogeneous particle composition with controlled particle size [13].

CdS and CdS:Cu films were produced onto glass substrates by USP technique at the substrate temperature of 350±5°C. The films were named as CU0 (CdS), CU1, CU3 and CU5 (Cu incorporated CdS at 1,3 and 5%, respectively). The spraying solution contained 0.1M $CdCl_2.H_2O$ (Cd source), 0.1 M $CS(NH_2)_2$ (sulphur source) and 0.1 M $(CH_3COO)_2.Cu.H_2O$ (copper source). The glass substrates were heated by an electrical heater and the substrate temperature was measured using a chromel-alumel thermocouple. The solution flow rate was kept at 5 $cc.min^{-1}$ by a flow meter. Nitrogen was used as the carrier gas (0.2 $kg.cm^{-2}$). The thicknesses of the films were measured between 1.6 and 5.1 μm by Elcometer 345 Digital Thickness Measuring Gauge. The volumes of the prepared solutions and the thicknesses (w) of the films are listed in Table 1.

Table 1. Volumes of the prepared solutions and thicknesses of the films.

Sample	Cd source (ml)	S source (ml)	Cu source (ml)	w (μm)
CU0	50	50	-	5.1
CU1	49	50	1	1.8
CU3	47	50	3	1.9
CU5	45	50	5	1.6

Optical properties of the films were investigated using the absorption spectra recorded in Perkin Elmer UV/VIS Lambda 2S Spectrometer. The structural properties were studied by x-ray diffraction (XRD) with CuK$_\alpha$ radiation (Rigaku Model, λ =1.5405 Å). The surface morphology were examined using Jeol scanning electron microscope (SEM) 5600 LV and the elemental analysis were made by energy dispersive x-ray spectroscopy (EDS; Noran Voyager EDS 3050).

3. Results

3.1. Optical properties

Fig. 1 shows the absorption coefficient, α, spectra of CdS:Cu films. It was observed that there is an increase in the absorption due to the Cu content. Sample CU1 showed larger absorption especially between 450-500 nm wave length range. Also, there is a little shift of absorption edge as the Cu content increases. The optical band gap values, E_g, and E_0 parameters explained below, were determined using the absorption spectra. For the determination of E_g, the intercept of the straight line portion of the $(\alpha h\upsilon)^2$ against on the $h\upsilon$ axis was used. In real semiconductors, the absorption coefficient for $E<E_g$ does not drop so rapidly to zero, forming the so called Urbach tail of exponentially decaying absorption;

$$\alpha \propto \exp(h\upsilon) / E_0 \qquad (1)$$

where E_0 is the width parameter of the band tail [14]. The determined E_g and E_0 values are given in Table 2. It can be seen that the band gap decreases from 2.37 eV to 2.33 eV and E0 values increases from 0.17 meV to 0.30 meV.

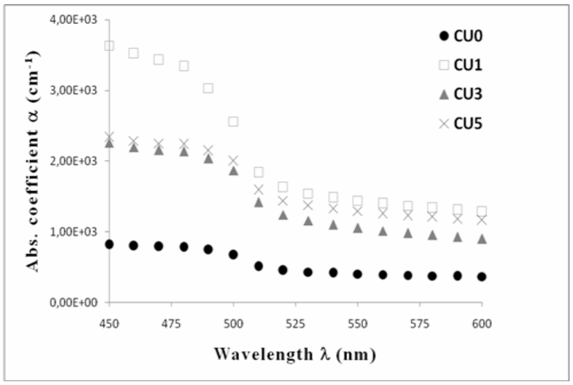

Fig. 1. Absorption spectra of CdS:Cu films.

Table 2. E_g and E_0 values of CdS:Cu films.

Sample	E_g (eV)	E_0 (meV)
CU0	2.37	0.17
CU1	2.37	0.21
CU3	2.35	0.25
CU5	2.33	0.30

3.2. Structural properties

Fig. 2 shows the XRD pattern of CdS:Cu films. The XRD patterns obtained for the films are studied in the 2θ range of 20 to 50°. It was seen that incorporation of Cu into the CdS changed the structural growth of the films. But, Cu and Cu related phases could not be detected. We think that the reasons of this are the little amount of Cu in the films and the sensitivity of the XRD device. The existence of multiple diffraction peaks of (100), (002), (101), (100), (200) and (110) indicate the polycrystalline nature of the CdS samples with hexagonal structure. Only Cu incorporated films exhibit a (200) CdS cubic peak. Cu incorporation caused the reduction of the intensities of some peaks. Especially, for sample CU3, there is only one peak which belong to the (200) CdS cubic reflection. Some structural parameters for CdS:Cu films are given in Table 3. These values are belong to the most intensive peak of the related sample.

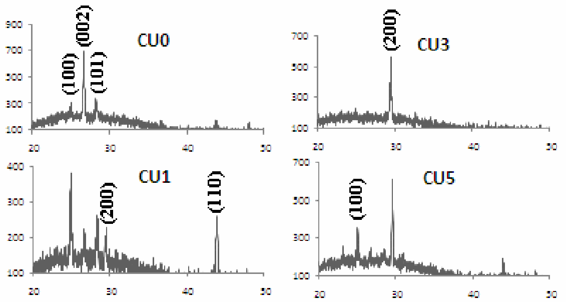

Fig. 2. XRD patterns of CdS:Cu films.

Table 3. Some structural parameters for CdS:Cu films.

Sample	Peak	2θ(°)	d (Å)	Crystal system
CU0	(002)	26.721	3.3334	CdS hex.
CU1	(100)	24.842	3.5813	CdS hex.
CU3	(200)	29.422	3.0333	CdS cub.
CU5	(200)	29.500	3.0255	CdS cub.

3.3. Morphological properties and elemental analysis

Fig. 3 shows the SEM micrographs of CdS:Cu films. The measuring bar indicates 1μm. These micrographs show that sample CuO has relatively smooth morphology than others. Also, sample CU1 has relatively smaller particles and these are better connected to each other when compared to those of other samples.

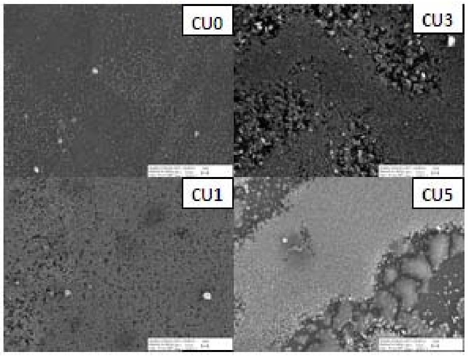

Fig. 3. SEM micrographs of CdS:Cu films.

Table 4 shows the atomic % and Cu/Cd atomic ratio values for the elements in the solid film. There are also the effects of other elements such as Na, Mg, Si, Ca and O, but we will put our interest on the ratio of Cd and Cu and the amount of sulphur. So, this table shows the values only for Cd, S and Cu.

Table 4. Atomic % and weight % and Cu/Cd atomic ratio for CdS:Cu films.

Sample	Element	Atomic %	Cu/Cd atomic ratio
CU0	Cd S Cu	2.27 2.59 -	-
CU1	Cd S Cu	1.29 1.71 -	-
CU3	Cd S Cu	1.39 1.60 0.17	0.122
CU5	Cd S Cu	1.06 1.02 0.10	0.094

4. Discussion

It was determined that Cu incorporation affected the absorption spectra of the films. Cu including samples have greater absorption then CdS film. Sample CU1 has larger absorption coefficient when compared to others. This is probably due to the surface morphology and atomic packing of this sample as can be seen from SEM micrographs. Other samples include cracks on their surfaces. The effect of Cu on the band gap is to reduce it. This variation could probably due to the optical scattering by grain boundaries. Another reason could be the sulphur deficiency as reported by others [15,16]. EDX analysis supports this idea as the sulphur content decreased by Cu incorporation. Incorporation of Cu modified the absorption coefficient near the edge and introduced deep levels into the energy gap. The calculated E_0 values given in Table 2 supports this. Also, lattice strains resulting from the difference between the radii of the Cd^{+2} ion (R_j=0.97Å) and the Cu^{+2} ion (R_j=0.72Å) causes local electric fields that modifies the exponential shape of absorption edge [14,17]. Cu incorporation modified the structural properties of CdS film. We think that this is an other reason for the reduction in the band gap value. Sample CU0 (CdS) has (002) CdS hexagonal peak with max intensity. The intensity of this peak decreased by Cu incorporation. Also, for samples CU3 and CU5 which have larger amounts of Cu, there is no trace of (002) peak. Instead, films tried to grow through (200) plane with a cubic structure. It can be supposed that Cu ions replace either substitutional or interstitial the Cd ions in the CdS lattice and affected the crystalline nature and modified the structure. The increase of E_0 values determined in optical analysis show that there is a structural deformation by Cu incorporation. SEM micrographs of CdS:Cu films can be seen in Fig. 3. There is a homogeneous distribution on the surfaces for samples CU0 and CU1. But, samples CU3 and CU5 have cracks and different sized dense formations like islands. So, we can say that excess amount of Cu incorporation deterioriates the surface morphology of CdS film. The surface morphology of sample CU1 is smother and more compact. The micrograph for sample CU0 reveal the existence of a continuous and thin CdS film on which crystallites (about 0.2μm in diameter) are superimposed, as similar to determined by other reports [18,19].

4. Conclusions

In this study, the effect of Cu incorporation on the optical, structural and morphological properties of CdS films was investigated. CdS films are widely used in photovoltaic applications and these applications need low cost components. With respect to this aim, four samples were produced by USP technique as it is simple to process, economic and a suitable technique for large area depositions. It allows incorporation of different elements and needs no vacuum. It was seen that Cu incorporation decreased the band gap of CdS films. But, increasing Cu content introduced more localized fields (tails) into the band gap. It is known that for low Cu concentrations Cu2+ ions are incorporated mainly in the CdS host lattice sites and create acceptor centers. For rising concentrations of Cu, Cu occupies also interstitial positions and, as a consequence, donors are produced [14]. The local field from the charged defects can also be responsible for the observed increase of the E_0 parameter. Cu incorporation also affected the structural properties. Sample CU0 has various peaks with different intensities. The additional (200) CdS cubic peak appeared for Cu incorporated samples CU1, CU3 and CU5. Cu incorporation forced the films to grow through (200) plane with cubic CdS phase. The surface morphology of CdS:Cu films became homogeneous by Cu incorporation at 1% (sample CU1). But, excess Cu content in CdS diminished the film formation and caused cracks on the surfaces. Sample CU1 has the most homogeneous morphology and has a dense form with better connected particles.

References

[1] J. A. Akintunde, Phys. Stat. Sol. A, **179**:363–371 (2000).

[2] L. C. Moreno, J. W. Sandino, N. Hemandez, G. Gordillo, Phys. Stat. Sol. B, **220,** 289–292 (2000).

[3] S. C. Ray, M. K. Karanjai, D. DasGupta, Thin Solid Films, **322,** 117–122 (1998).

[4] X. Wu, J. C. Keane, R. G. Dhere, C. DeHart, D. S. Albin, A. Duda, T. A. Gessert, S. Asher, D. H. Levi, P. Sheklon, in: Prceedings of the 17th European Photov. Solar Energy Conf, Munich, Germany, vol. **II**, (2001), p.995.

[5] A. G. Valyomana, K. P. Vijayakumar, C. Purushothaman, J. Mater. Sci. Lett. **11,** 616–8 (1992).

[6] H. Chavez., M. Jordan, J. C. McClure, G. Lush, V.P. Singh, J Mater Sci: Electr Mater; **8,** 151–4 (1997).

[7] F. Izci, S. Kose, M. S. Kilickaya, Proc. Suppl. Bpl.; **5**, 1115–9 (1997).

[8] A. G. Valyomana, K. P.Vijayakumar, C. Purushothaman, J Mater Sci Lett. **9,** 1025–7 (1990).

[9] A. Podesta, N. Armani, G. Salviati, N. Romeo, A. Bosio, M. Prato, Thin Solid Films, **511-512**, 448-452 (2006).

[10] S. A. Al Kuhaimi, Vacuum, **51,** 349–55 (1998).

[11] M. Kul, M. Zor, A. S. Aybek, S. Irmak, E. Turan, Solar Energy Materials&Solar Cells **91**, 882-887 (2007).

[12] K.Y. Choi, K. D. Kim, J. W. Yang, J. Mater. Process. Technol., **171**, 118 (2006).

[13] Y. Wang, W. Chen, Q. Luo, S. Xic, C.H. Chen, Appl. Surface Sci. **252** (23), 8096 (2006).

[14] M. Grus, A. Sikorska, Physica B **266**, 139-145 (1999).

[15] X. D. Gao, X. M. Li, W. D. Yu, Thin Solid Films **468**, 43 (2004).

[16] T. Ben Nasr, N. Kamoun, M. Kanzari, R. Bennaceur, Thin Solid Films **500**, 4 (2006).

[17] F. S. Galasso, Structure and Properties of Inorganic Solids, Oxford University Press, Oxford, (1970).

[18] E. Pentia, L. Pintilie, T. Botila, E. Vasile, Rom. J. Phys **40**, 643 (1995).

[19] L. Pintilie, E. Pentia, I. Pintilie, D. Petre, Mater. Sci. Eng. **B44**, 403 (1997).

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