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The Effect of Ag Doping on the Structural, Optical and Electrical Properties of CdSe Thin Films

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ABSTRACT

This work includes a study of the effect of Ag doping in CdSe on optical, structural and Electrical properties, through changing the ratio of the added Ag with (0, 1, 5, 10) % to the final prepared CdSe solution. Measurements of the transmittance, absorption of the prepared samples of CdSe for wave lengths in the band (400nm-750nm) is carried out. It is found that the band gap decreased (Eg=(1.97,1.92,168,152)eV) respectively as Ag concentration increased. X-ray diffraction (XRD) measurements shows that the deposited pure CdSe thin film is polycrystalline with hexagonal structure, whereas doped films with Ag shows cubic structure in the[111] direction. Electrical conductivity measurement of the films showed an increase with increasing the Ag concentration, also an increase in crystal alignment found.

Keywords: Thin Films, CdSe, Optical properties, CBD technique.

تأثير التطعيم بالفضة على الخواص الكهربائية والبصرية التركيبية لأغشيه CdSe

الملخص

يتضمن هذا البحث دراسة تأثير التطعيم بعنصر الفضة Ag لأغشية CdSe الرقيقة على الخواص التركيبية والبصرية والكهربائية وذلك من خلال تغيير نسب الحجوم الخاصة بنترات الفضة وبالنسب 0,1,5,10)%) عند تحضير اغشية CdSe، وتضمن البحث اجراء قياسات النفوذية والامتصاصية للأطوال الموجية nm(400-750) وتم حساب قيمة طاقة الفجوة وقد وجد انها تتغير حسب القيم التالية (Eg=(1.97,1.92,1.68,1.52 (eV)، وهذا يعني ان قيمة فجوة الطاقة تقل مع زيادة تركيز Ag ومن قياسات حيود الاشعة السينية (XRD) لدراسة التركيب البلوري وجد بان التركيب من النوع المتعدد البلورات السداسي للنماذج التي لا تحتوي على عنصر الفضة اما في حالة النماذج المطعمة عنصر الفضة وجد التركيب من النوع المكعبي ويمتلك اتجاهيه مفضلة عند المستوي (111)، أظهرت قياسات التوصيلية الكهربائية زيادة جيدة في التوصيلية مع زيادة التركيز بعنصر الفضة، وكذلك زيادة في الرص البلوري.

الكلمات الدالة: الاغشية الرقيقة، CdSe، الخواص البصرية، تقنيةCBD.

INTRODUCTION

In last two decade much attention has been drawn to II-IV group semiconducting compounds (CdSe, ZnSe, CdS, CdT, etc.) because of their opto-electronic properties and their applications, such as high efficiency, high absorption coefficient in the visible and infrared regions of the solar spectrum (Patel *et al*., 2009), (Sharma *et al*., 2008). Cadmium selenide is a widely used II-IV group semiconductor whose band gap Eg = 1.74 eV lies in the solar energy spectrm (Lade *et al*., 2001) and has been studied in photoelectron-chemical cells (PEC) (Gutierrez and Salvador, 1987), (Gudage *et al.*, 2007) as well as an n-type active layer material in the low-cost high-performance bulk hetero-junction (BHJ) hybrid solar cells (Shaheen *et al.*, 2001), CdSe/p-Si was prepared by depositing CdSe film on the p-type Si substrate (Jamil *et al.*, 2012), thin film transistors (Van Calster *et al.*, 1988) and electro-optic devices (wang *et al.*, 1993). CdSe thin films have been prepared by various film-deposition techniques such as sputtering (Moersch *et al.*, 1989), sol-gel, spray pyrolysis, Vacuum deposition (Hodes *et al.*, 1987), (Golan *et al.*, 1992) and (Mahmoud *et al.*, 1990) Metal Organic Chemical Vapor Deposition (MOCVD) (Chae *et al.*, 2006), electron beam deposition (Murali *et al.*, 2008) and chemical bath deposition (CBD) method which is found to be cheap, and simple way to deposit large area thin film at low deposition temperature (Kale and Lokhande, 2005), (Ezema and Osuji, 2007) and (Elahi and Ghobud, 2008).

Literature survey Shows that there are many investigations to the improved properties of CdSe thin film doped with Al (Poehler and Abraham., 1965). In (Mahalingam *et al.*, 2010), Hg (Bhuse, 2005), Cu (Subba *et al.*, 2001), Sn (Masumadr *et al.*, 2003), and Fe (Thanikaikarasan *et al.*, 2010).

The objective of present work is to study the effect of Ag doping in CdSe on thin films physical properties prepared by the (CBD) technique.

EXPERIMENTAL

Cadmium selenide thin films were deposited on microscopic glass substrates slide of (7.5 cm x 1 cm), in which substrate cleaning plays an important role in the deposition of thin films. Glass microscopic slides were cleaned by soap solution, water and heated in boiled alcohol and was finally rinsed by dia-ionized water before use. Chemical bath deposition technique was adopted for the preparation of the CdSe thin films. Due to the fact that Selenium is not soluble in water, selenium ions were produced in which selenium powder was mixed with a solution of sodium sulphite and the solution was put under reflex condition and heated for a period between (1-2) hours (Eya, 2006).

The resulting Na_2SeSO_3 became the source of (Se^{-2}) which is mixed with ($CdCl_2$) which is the source of (Cd^{+2}) and added (NH_3) as a complex agent in the beaker, After mixing the solution the PH became (11± 1), which was measured by using PH paper agreeing with (Kale *et al.*, 2004), The fundamental chemical reaction in brief can be formulated as follows:

$$Se + Na_2SO_3 \xrightarrow{reflux} NaSeSO_3 \longrightarrow Se^{-2}$$

$$2CdCl_2 + 4NH_3 \longleftrightarrow [Cd\,(NH_4)]^{+2} + CdCl_4$$

$$[Cd\,(NH_4)]^{+2} \longleftrightarrow Cd^{+2} + 4NH_3$$

$$Na_2SeSO_3 + 2OH^- \longleftrightarrow Na_2SO_4 + H_2O + Se^{-2}$$

$$Cd^{+2} + Se^{-2} \longleftrightarrow CdSe \downarrow$$

The glass substrate was inclined vertically around (20°) angle to the walls of beaker immersed in the solution for a deposition time between (20-24) hours. The CdSe thin films were uniform well adherent to the substrate and orange in color. CdSe deposition was carried out at room temperature. As far as Ag NO_3 doping to above solution. $AgNO_3$ then added in varying volume quantities (0, 1, 5, 10) %.

The thin film thickness was measured by gravimetric method: In this method the thickness of the film was determined by weighting the glass substrate before and after deposition on the micro balance and using the equation

$t = m / A \rho$

Where: t is the film thickness

m is the mass of deposited CdSe

ρ is the density of CdSe =5.816g/cm^3

A is the surface area of the films

The optical absorbance and transmittance of the films were studied in the spectral range of (400-750) nm by a spectrophotometer.

Electrical conductivity measurements is done by using four probe technique.

RESULTS AND DISCUSSION

Optical Measurements

Optical measurements of CdSe, as pure and doped with Ag, within the range of (400nm – 750 nm) wave length are shown in Fig.1. For pure thin films transmittance was varied between (80 and 98)% where for the Ag doped thin films the transmittance was obtained (93 -99)% as increasing in the Ag concentration near the UV wavelength range (400nm – 750nm), for the samples doped with 1% silver nitrate, the transmittance exceeded 92% within the UV short wavelengths. Within the visible spectra region, the transmittance increased up to (94 - 98) %, reaching to 99% in the infrared region of the spectra. It was noticed that for the two samples with 5% -10% silver nitrate doping, a very good transmittance (96%) within the UV spectra was obtained, while within the visible region, a transmittance of (96-98) % was achieved, reaching 99% to within the infrared region. The more the silver doping, the more transmittance is obtained, while a reduction in absorption is achieved as a function of wavelength according to Fig. 1.

The effect of Ag doping on optical properties show that the transmittance increased with increase of Ag concentration dopant as shown in Fig.1, as result of that the band gap of doped thin film decreased as increasing of Ag concentration for the 1% doped Eg = 1.92 eV and for the 5% doped Eg = 1.68 eV, while Eg = 1.52 eV for the 10% doped sample.

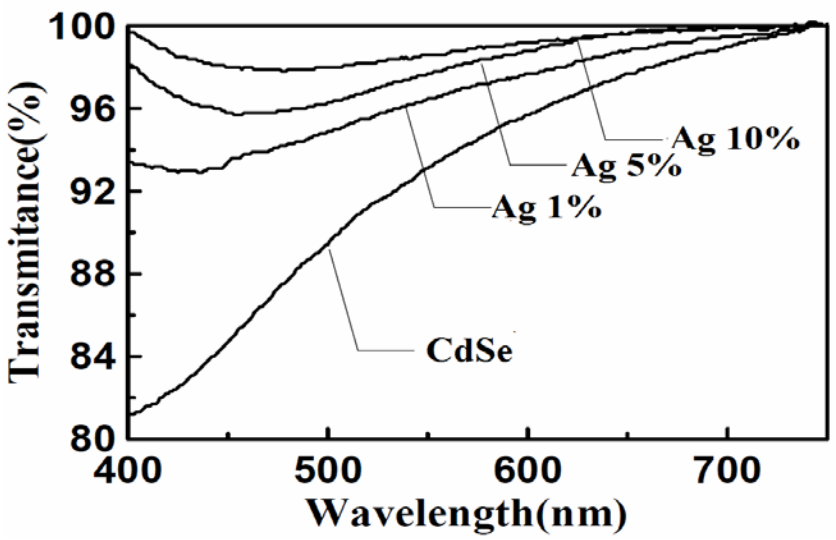

Fig.1: Transmittance spectra of CdSe Thin Films Deposited at different Ratio

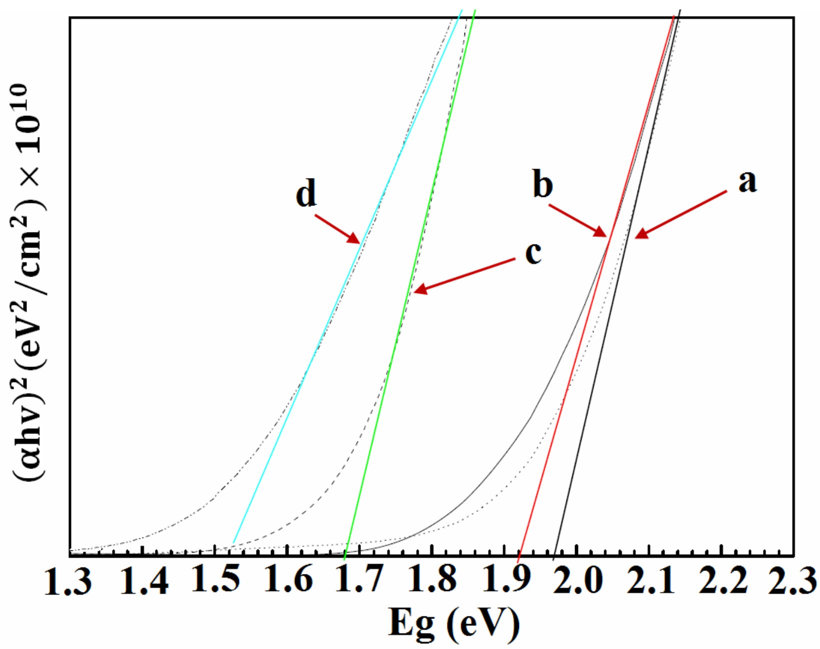

Fig. 2: Plot of $(\alpha h\nu)^2$ versus Eg(eV) of CdSe Thin Film of different ratio

X-Ray Diffraction (XRD)

XRD results show that the deposited pure CdSe thin films are polycrystalline with hexagonal structure, however for doped thin films (b, c, d) results showed cubic structure having (111) plane as a preferred orientation (Fig. 3). The increase in the high of peak intensity it gives improvement in the crystallite of material which agree with (Dhanam *et al.*, 2008) and (Umme, 2010).

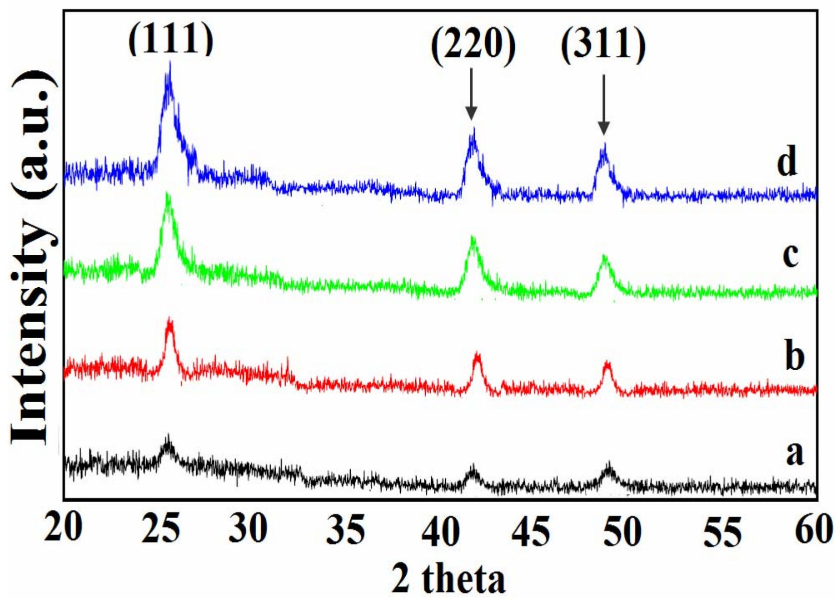

Fig. 3: XRD Patterns of CdSe Thin Films at different ratio

Scanning Electron Microscope

Test results by SEM showed an increase in crystal alignment (with an increase in Ag doping rate) for pure and Ag doped CdSe films with the ratios (0%, 1%, 5%, 10%) as illustrated in Fig. 4 (a, b, c, d) respectively. Comparison shows that pure films suffered from non-homogenous surface to a certain extent with the presence of assembled grains with different patterns and density. In Fig. 4(b) which is doped with 1% ratio, a better homogeneity appears due to smooth surface and the absence of spacing. where in Fig.4(c, d) doped with (5, 10) % respectively, gave a better crystal form with good homogeneity to appear with an increase in crystal grain size. It was noticed that the best diffusion for the doped material grains does happen with the film texture at the 1% rate.

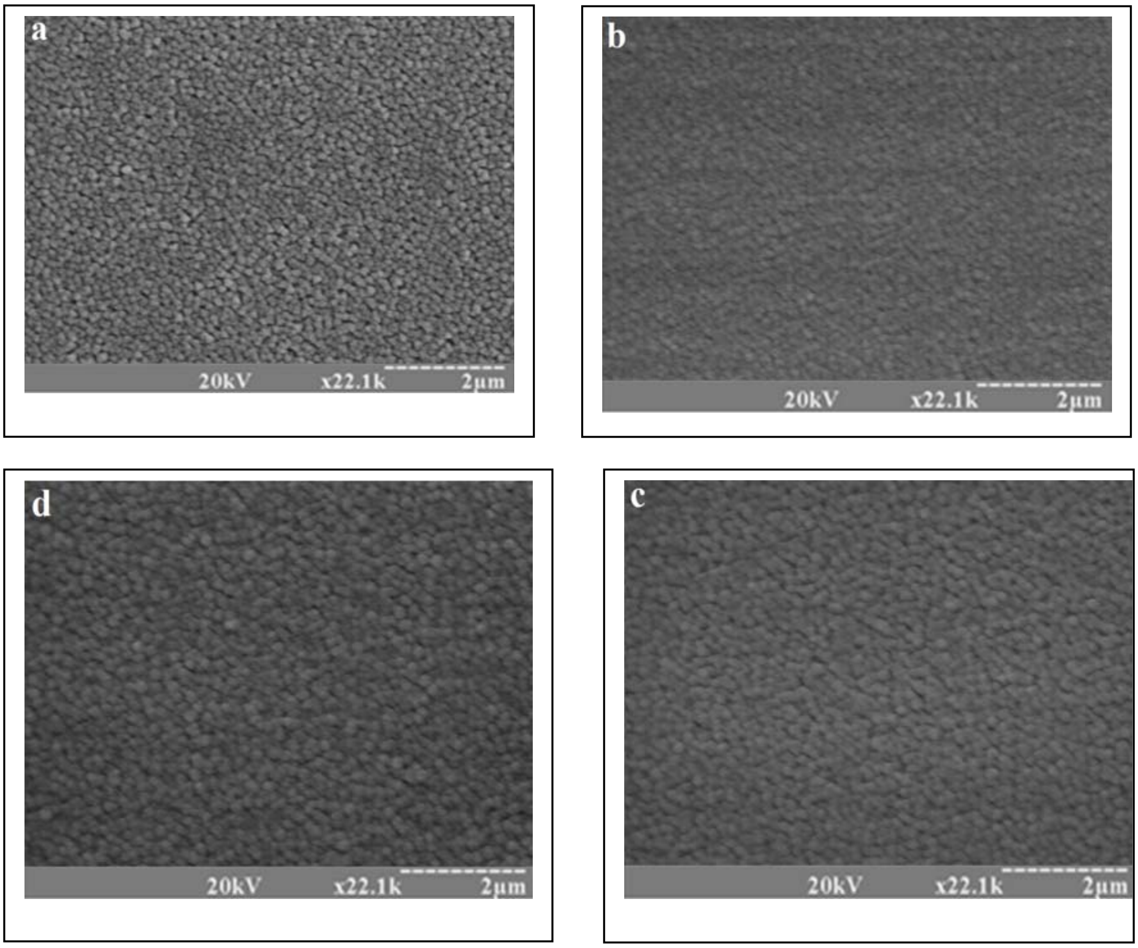

Fig. 4: SEM Image for CdSe Thin Film at different ratio

Electrical measurements

Electrical conductivity measured values of grown films varied between $6.5x10^{-4}$and $9.9\ x10^{-4}$ $(\Omega\text{-cm})^{-1}$, as Ag doped varied from 0% to 10%. Which shows increase in the conductivity with an increase in the Ag concentration. The Hall effect measurements showed that prepared thin films are n-type. This result has been expected since the films are known to be Cd rich. The mobility values were found to vary in between 7.8 and 76.5 cm^2/V^{-s} depending on the Ag concentration.

CONCLUSION

Thin film of CdSe doped with Ag, As the volume ratio of Ag increased (0,1,5,10)% the final prepared CdSe solution optical measurement show that the band gab of doped CdSe decreased as Ag %increased.

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