Iranica Journal of Energy & Environment 5 (1): 87-93, 2014
ISSN 2079-2115
IJEE an Official Peer Reviewed Journal of Babol Noshirvani University of Technology
DOI: 10.5829/idosi.ijee.2014.05.01.13

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Physical Properties of Silver Doped ZnSe Thin Films for Photovoltaic Applications

[1]Nazar Abbas Shah, [2]Mussart Abbas, [2]Waqar Adil Syed and [1]Waqar Mahmood

[1]Thin Films Technology (TFT) Research Laboratory, Department of Physics,
COMSATS Institute of Information Technology, Islamabad 40000 Pakistan
[2]International Islamic University, Islamabad 40000 Pakistan

(Received: December 23, 2013; Accepted in Revised Form: March8, 2014)

Abstract: Closed space sublimation (CSS) technique was used to deposit pure (99.99%) zinc selenide(ZnSe) powder on to glass substrates for fabricating the ZnSe thin films. The temperatures of source, substrate and the deposition time were optimized to deposit thin films of different thicknesses. Silver (Ag) was used as a dopant by ion exchange process in the ZnSe thin films. The structural analysis showed that as-deposited ZnSe thin films were polycrystalline having preferred orientation [111] direction. Micro structural parameters such as crystallite size, lattice parameter were determined using X-rays diffraction (XRD). Grains boundaries, roughness on surface and the grain density of the thin film samples were measured by scanning electron and atomic force microscopy before and after Ag doping.As-deposited, Ag-doped ZnSe samples before and after annealing were optically characterized by spectrophotometer in ultra violet, visible and infrared regions. The energy band gap of as-deposited ZnSe thin films for varying thicknesses were ranging from 2.62-2.67 eV which was reduced after Ag doping.The electrical properties showed that as-deposited thin films were highly resistive of the order of $10^8\Omega$-cm and after Ag immersion, it was reduced to 1Ω-cm. Deposition parameters and Ag doping influenced the structural, surface, optical and electrical properties.

Key words: ZnSe thin films · Vacuum coating · Surface morphology · Electrical properties

INTRODUCTION

Since last few decades zinc selenide (ZnSe) gained a remarkable attention due to its tuneable energy band gap. It belongs to II-VI semiconductor family. It has direct band gap transition type [1]. It is a leading material in the fabrication of solar cells [2]. The energy band gap of ZnSe at room temperature is 2.7 eV, make it suitable candidate for the window layer in the solar cells fabrication [3-5].

ZnSe had been fabricated by different approaches including thermal evaporation [6], sputtering [7], chemical bath deposition [8], pyrolysis [9] two source evaporation [10], pulsed laser deposition [11], Melt-quenching technique [12] and closed space sublimation (CSS) technique [13]. In group I, silver (Ag) increases the electrical conductivity due to acceptor dopant in II-VI materials [14]. Bismuth was used as a dopant to make low resistive P-type ZnSe thin films with complex method of doping [11]. The electrical and the optical properties are important for solar cell applications [1, 8, 10, 13]. Silver and copper (Cu) was doped by ion exchange process in II-VI semiconductor materials [10, 13].

In the present work, ZnSe thin films were sublimated using closed space technique and doped with low concentration solution containing 1 g of $Ag(NO_3)_2$ in 100 ml of distilled water at room temperature by ion exchange process.After immersion, Annealing was carried out for diffusion of Ag into the films. The prepared samples were characterized in various aspects including structural, morphological, elemental composition, optical and electrical parameters. A comparative study was carried out between as-deposited and Ag-doped ZnSe thin film samples.

Corresponding Author: Nazar Abbas Shah, Thin Films Technology (TFT) Research Laboratory,
Department of Physics COMSATS Institute of Information Technology, Islamabad 40000 Pakistan.
E-mail: nazar_abbas@comsats.edu.pk - nabbasqureshi@yahoo.com.

MATERIALS AND METHODS

Zinc selenide powder was used as a source material to deposit polycrystalline thin films on to glass slides (as substrates) under vacuum. The dimension of the glass slide was 75 mm x 25mm. Before deposition, the substrates were cleaned with isopropyl alcohol (IPA) in ultrasonic bath at 65°C for 30 minutes and dried in air. Substrate was loaded in the vacuum chamber with 25 mg source material in the cleaned graphite boat. The vacuum chamber was evacuated up to 10^{-5} mbar with the help of rotary and diffusion pumps.Two Halogen lamps were switched on for direct heating the source and substrate after attaining the desire vacuum. A1000 W lamp was applied to heat the source material and 500 W was used to heat the substrate. The distance between source and substrate was 5 mm for a good quality film. Temperature gradient was created between the source and substrate using mica sheet. A graphite slab was placed on the substrate for uniform heating. K-type thermocouple wires were use to monitor the temperatures of the source and substrate. Halogen lamps were switched on to increase the temperatures of source and substrate up to 575 and 475°C, respectively. Different deposition times were offer ranging from 01 to 05 minutes for varying thickness of films. After attaining the deposition time, the lamps were switched off and left the chamber to cool down to room temperature under vacuum to avoid contamination or oxidization.

Low concentrated (0.1/100ml) solution of Ag $(NO_3)_2$ was prepared in the distilled water. ZnSe as-deposited thin films were dipped in the solution for different times ranging from 5 minute to 40 minutes. After doping, these films were dipped in IPA and dried in a heater. Ag layer was formed on ZnSe thin film surface after immersion which was due to the ion exchange process. The doped thin films were then annealed under vacuum at 400°C for 1 hfor diffusion of Ag in to these films. Different immersed time relates to different composition of Ag into the films. Finally Ag-doped ZnSesamples were characterized by X-rays diffraction (XRD) for structural analysis, scanning electron microscope (SEM) and atomic force microscope (AFM) to analyse the surface, UV-VIS-NIR spectrophotometer to observe the optical properties and four probe method using Hall measurement apparatus for the electrical properties before and after Ag doping for various solar cells applications.

RESULTS AND DISCUSSION

X-Rays Diffraction Analysis: X-rays diffraction was used to estimate the structural properties of thin films. It is a non destructive technique which gives information about phases, crystallite size, lattice parameter, internal stress and dislocation density etc. XRD of the prepared thin film samples were characterized by spectrometer PANalytical X'Pert Pro. The operating parameters of the spectrometer were Cu-Kα line; wavelength was1.5406Å. Diffraction angle varied from 20 to 60 degrees. The XRD traces of as-deposited ZnSe thin filmswith varying thickness are shown in Fig. 1. The crystallite size can be calculated using Scherrer formula:

$$D = (0.89)\lambda / \beta\cos\theta \quad (1)$$

where 0.89 is a constant, λ is the wavelength used, β is full width at half maximum and θ is the diffraction angle. All other parameters including dislocation density, strain etc can be obtained using Eqs. (2) and (3), respectively.

$$\varepsilon = \frac{\beta Cos\theta}{4} \quad (2)$$

$$\delta = \frac{n}{D^2} \quad (3)$$

Fig. 1 relates to the effect of thickness of as-deposited ZnSe thin films. The peak width of (111) and the intensity level increases gradually with the increase in film thickness. This observation may be attributed to the improvement of particle size. The intensity increases due to the orientation in the structure of thin films. Table 1 shows the variation in lattice parameters, the crystallite size, strain and dislocation density. The decrease in dislocation density, strain and the increase in crystallite size are observed as the film thickness increases. These effects are due to the improvement in crystal structure. Fig. 2 represents the XRD traces of A-doped ZnSe samples. The preferred orientation of as deposited ZnSe thin films is (111) with cubic phase as matched with the standard cards. As the thin films were doped in low concentrated silver nitrate solution at room temperature and subsequent annealing, the orientation of the (111) plane was disturbed along with the loss of texture of ZnSe thin films after immersion. The peak intensity of planes (220) and (311) were small as compared to (111) direction of as-deposited ZnSe thin films. After Ag immersion with post annealing, the peak intensity of (220) and (311) were large as the intensity level of (111) was decreased which was evident of loss of texture after Ag immersion. No AgSe compound peak was found which indicated that Ag diffused interstitially [14]. The results are in consistent with the reported literature [10, 13].

Table 1: Table Effect of thickness on micro structural parameters

Thickness (nm)	2θ (Deg.)	Lattice parameters a(A°)	Grain size D (nm)	Strain[a] x 10^{-3} (lin^{-2} m^{-4})	Dislocation Density δ x10^{15} (lin m^{-2})
986	27.1627	5.686	53.8	0.673	0.346
912	27.1982	5.679	51.0	0.709	0.384
895	27.2159	5.675	48.6	0.745	0.423
880	27.3199	5.654	44.8	0.809	0.499

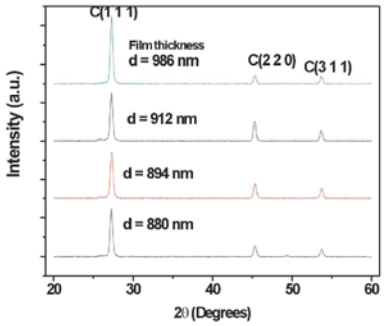

Fig. 1: X-ray diffraction patterns of as-deposited ZnSe thin films with variation in thickness

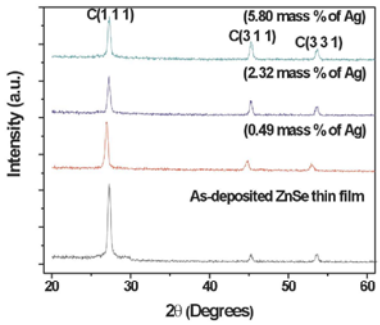

Fig. 2: X-ray diffraction patterns of as-deposited ZnSe thin film and Ag-doped ZnSe samples

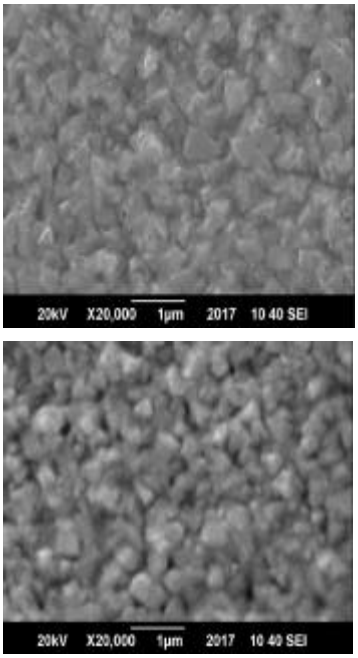

Fig. 3: Scanning electron microscope micrographs of (a) as-deposited ZnSe thin film and (b) Ag-doped ZnSe sample

Surface Morphology: The surface morphological study was carried out using scanning electron microscope. The SEM micrographs of as-deposited and Ag-doped ZnSe thin film samples are shown in Fig. 3. The average grain size of as-deposited ZnSe thin film was 250 nm which was increased up to 400 nm after Ag immersion. The increase in grain size was due to the process of coalescences, a well known phenomenon in II-VI semiconductor material [14]. Annealing temperature is most powerful toolfor Ag diffusion in ZnSe thin films also usefulin the reorientation of the structure [14]. The elemental analysis of un-doped and Ag-doped ZnSe thin film samples are carried out by energy dispersive X-rays (EDX) attached withthe SEM. Theelemental results show the atomic contents of elements, present in the ZnSe thin films. The as-deposited thin films are selenium enriched. After immersion of Ag $(NO_3)_2$ with subsequent annealing at 400°C, the elemental composition are changed. After Ag-doping, the Se composition decreased as the Ag concentration increases.

Atomic Force Microscopy: Atomic force microscopeis an important tool to observe the surface morphology. It provides two and three dimensional images of the sample surface. The average roughness of the sample surface can be measured by using AFM analysis. The images of atomic force microscopy of as-deposited and Ag-doped ZnSe thin film samples are shown in Fig. 4. As the doping contents are increased, the colour of the surface is changed; dark part of the image shows the diffusion of Ag into the ZnSethin filmsamples.As the number of grain decreases, due to the diffusion of Ag impurity in ZnSe films. Thechanges on the AFM images are observed after Ag doping in ZnSethin films. Table 2 shows that the surface roughness of Ag doped ZnSe samples increases due to increase in silver composition.

Optical Analysis: The transmission spectra of as-deposited and Ag-doped ZnSe thin film samples are taken in the ultra violet (UV), visible(VIS) and infrared (IR) regions (300-2000 nm) by using UV-VIS-NIR Perkin Elmer

Table 2: Surface roughness and variation in energy band gap of ZnSe samples

Immersion time (min)	Ag (Mass %)	Roughness on the surface (nm)	Energy band gap (eV)
0	0	15	2.65±0.01
10	0.5	10	2.64±0.01
20	2.3	11	2.63±0.01
30	6	12	2.62±0.01

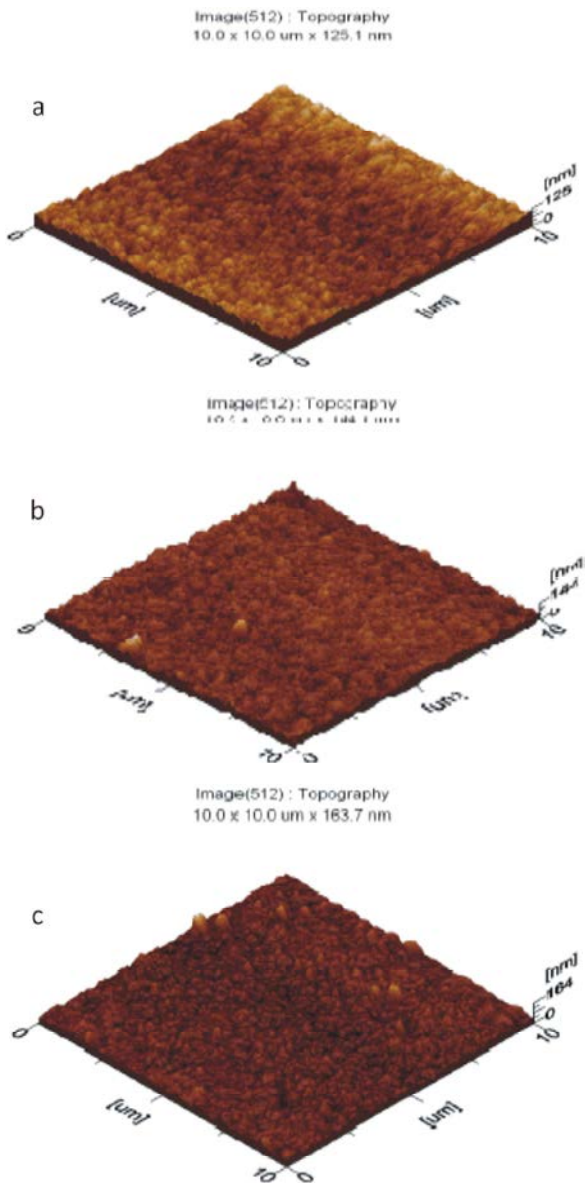

Fig. 4: Atomic force microscopy of (a) as-deposited ZnSe thin film (b) & (c) Ag-doped ZnSe sample

spectrophotometer Lambda 950 with UV Win lab software. The machine directly measures the transmission of the sample. By using the %T data,all other optical parameters can be calculated byswanpoul model [14-16]. The formula for the optical thickness is given by:

$$d = \frac{\lambda_{max}\lambda_{min}}{4n(\lambda_{max} - \lambda_{min})} \quad (4)$$

In Eq. (4)λ_{max} is maximum transmission and λ_{min} is the consecutive minimum transmission respectively. For the calculation of refractive index *n*, the following relation is used:

$$n = \frac{[N + (N^2 - 4s^2)^{\frac{1}{2}}]}{2} \quad (5)$$

and

$$N = 1 + s^2 + 4s\left(\frac{T_{max} - T_{min}}{T_{max} * T_{min}}\right) \quad (6)$$

where T_{max} and T_{min} represents maximum and minimum transmission. '*s*' is the refractive index of glass. The optical energyband gap E_g is determine by thegiven relation

$$\alpha h\nu = A(h\nu - E_g)^{N/2} \quad (7)$$

where '*A*' is the constant and $h\upsilon$ is the photon energy. The absorption coefficientα is measured by the Eq. (8).

(8)

The transmission decreased with the increase of thickness, which is due to trapping of light in the sample. The transmission of light is 70 to 90 % in the visible and IR region, so the ZnSe thin films can be used as window layer material in the solar cells. The energy band gap of ZnSe thin films is 2.7 eV, which is a suitable light absorber in UV region.In Fig. 5 with increasing thickness, there are more possibilities for absorption and scattering of the light while passing through the material, which is one of the reasons of decreasing transmission. The transmission spectra of Ag-doped samples as compared toas-deposited ZnSe thin film are shown in Fig. 6. An increasing the Ag content, the transmission is decreasing due to the fact that Ag is a good reflector. By using Eq. (7) and extrapolating $(\alpha.h\upsilon)^2$ against the photon energy $(h\upsilon)$, the band gap of ZnSe thin films can be calculated. As-deposited ZnSe thin films has 2.66 eV, which was shrink up to 2.62 eV after Ag doping. Although there is a

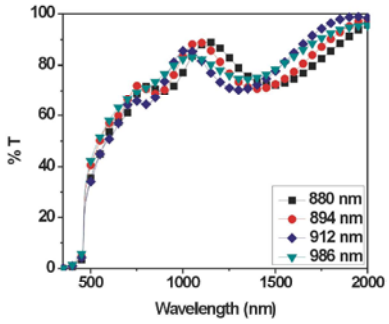

Fig. 5: Optical transmission of as-deposited ZnSe thin films of various thicknesses

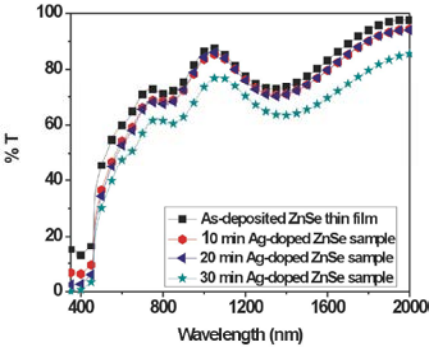

Fig. 6: Optical transmission of as-deposited ZnSe thin film and Ag-doped ZnSe samples

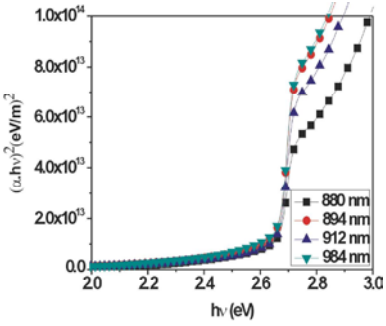

Fig. 7: Optical energy band gap as-deposited ZnSe thin films with varying thicknesses

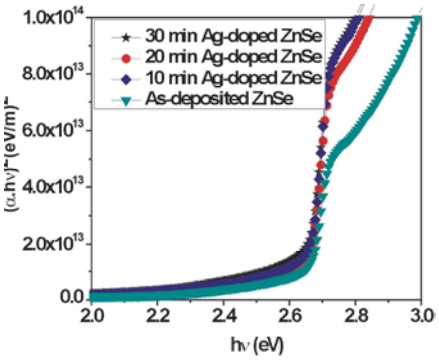

Fig. 8: Energy band gap of Ag-doped ZnSe samples with increasing Ag composition

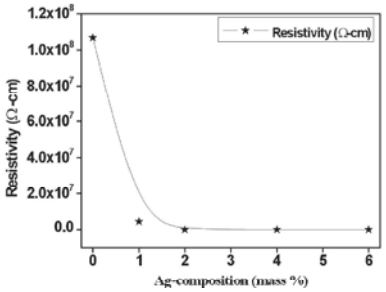

Fig. 9: Change in resistivity with the increase in Ag composition

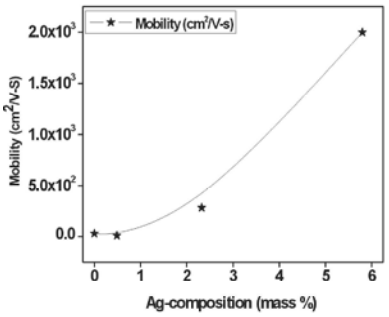

Fig. 10: Mobility variations with the increase in Ag composition

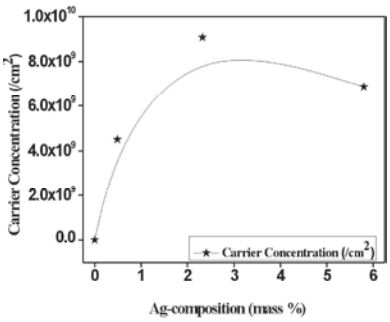

Fig. 11: Variation of carrier's concentration with the increase in Ag composition

small change in energy band gap, the decrease is related to the Ag compositions in ZnSe samples. The energy band gap was reduced due to the overlapping of energy levels which were created due to Ag doping in the ZnSe thin films. Fig. 8 shows the energy band gaps *Eg* of the Ag-doped ZnSe samples with different compositions of Ag. Table 2 shows the variation in energy band gap after Ag doping.

Electrical Measurements: Hall apparatus (Ecopia HMS 5000) was used to measure the electrical properties i.e the resistivity, sheet concentration and mobility. A1 nA current at room temperature with constant magnetic field of 0.5 Twas applied for these measurements.

Ag compositionincreases as the immersion time increased and decrease in resistivity is observed. The lowest value of resistivity 1.4 Ω-cm after Ag doping is observed. The As-deposited ZnSe thin films have the resistivity of 1.069 × 10^8Ω-cm. Decrease in resistivity with the Ag doping isof several orders of magnitude, as shown in Fig. 9. As the Ag composition increases, the value of mobility also increases as illustrated in Fig. 10. The behaviour ofcarrier's concentration with the Ag composition is checked. Carrier's concentration increases to some extent and then decreased sharply as shown in Fig. 11. This behaviour shows that Ag facilitates in ZnSe thin filmsamples due to the larger grains and less grain boundaries. The number of charge carrier increases as the Ag composition increases, confirmed by the change in mobility and resistivity. The results show the change in electrical properties due to the diffusion of Ag in the ZnSe thin film samples.

CONCLUSIONS

ZnSe thin films showed strong adherence with glass substrates. The preferred orientation was (111) with cubic phase as observed in the XRD. The width and intensity of the peaks in the patterns were proportional withthe increase in thickness. The crystallite size increased as thickness increased but a decreased in strain and dislocation density was observed. These effects were attributed to the improvement in the crystal structure. Ag doped ZnSe thin films in low concentrated $Ag(NO_3)_2$ solution and after annealing, the texture was lost. The SEM micrographs showed the average grain size 250 nm for as-deposited which was increased up to 400 nm and grain boundaries were decreased after Ag immersion. The effect might was due to the diffusion of Ag into the ZnSe thin filmsamples. The mass percentage of Ag was about 6 % after Ag immersion. AFM results confirmed the surface roughness decreased from 15 to 12 as the Ag was diffused in ZnSe thin films. Optical parameters including transmission and energy band gap showed the decreasing trend after Ag doping in ZnSe thin films. The resistivity of as-deposited ZnSe thin films was 10^8Ω-cm, which was reduced up to 1 Ω-cm after Ag diffusion. These results confirmed that Ag affects theZnSe and altered the physical properties after immersion. On the basis of these finding, the ZnSe thin films could be used as a window layer/contact in the II-VI thin filmsolar cells.

ACKNOWLEDGEMENTS

The authors are thankful to higher education commission (HEC) Pakistan for the financial supportthrough project No. 20 – 1187 / R & D / 09.We are also thankful to COMSATS Institute of information Technology (CIIT) Islamabad for providing excellent research facilities and funding through project.

REFERENCES

1. Ismail, B. and R. Gould, 1989. Structural and electronic properties of evaporated thin films of cadmium telluride. Physica Status Solidi (A), 115(1): 237-245.
2. Chopra, K.L. and S.R. Das, 1983. Why Thin Film Solar Cells? Springer.
3. Yang, C., Y. Hsieh, M. Kuo, P. Tseng, Z. Yeh, K. Chiu, J. Shen, A. Chu, W. Chou and W. Lan, 2003. Compressive strain induced heavy hole and light hole splitting of $Zn_{1-x}Cd_xSe$ epilayers grown by molecular beam epitaxy. Materials Chemistry and Physics, 78(3): 602-607.
4. Mokili, B., Y. Charreire, R. Cortes and D. Lincot, 1996. Extended X-ray absorption fine structure studies of zinc hydroxo-sulphide thin films chemically deposited from aqueous solution. Thin Solid Films, 288(1): 21-28.
5. Tripathi, L., S. Mishra and R.N. SINGH, 1993. Luminescence in ZnSe doped with Pr and (Sn, Pr) phosphors. Indian journal of Pure & Applied Physics, 31(12): 899-903.
6. Thutupalli, G. and S. Tomlin, 1976. The optical properties of thin films of cadmium and zinc selenides and tellurides. Journal of Physics D: Applied Physics, 9(11): 1639-1646.
7. Kuzel Jr, R., V. Valvoda, M. Chladek, J. Musil and J. Matous, 1995. XRD microstructural study of Zn films deposited by unbalanced magnetron sputtering. Thin Solid Films, 263(2): 150-158.
8. Rizzo, A., M. Tagliente, L. Caneve and S. Scaglione, 2000. The influence of the momentum transfer on the structural and optical properties of ZnSe thin films prepared by rf magnetron sputtering. Thin Solid Films, 368(1): 8-14.
9. Balasubramanian, A., N. Sankar, S. Ramakrishnan and K. Ramachandran, 2004. Thermal conductivity of ZnSe by molecular dynamics simulation. Crystal Research and Technology, 39(6): 558-563.

10. Ali, Z., A.K. Aqili, A. Maqsood and S. J Akhtar, 2005. Properties of Cu-doped low resistive ZnSe films deposited by two-sourced evaporation. Vacuum, 80(4): 302-309.
11. Shen, Y., N. Xu, W. Hu, X. Xu, J. Sun, Z. Ying and J. Wu, 2008. Bismuth doped ZnSe films fabricated on silicon substrates by pulsed laser deposition. Solid-State Electronics, 52(11): 1833-1836.
12. Sharma, J. and S. Tripathi, 2011. Effect of deposition pressure on structural, optical and electrical properties of zinc selenide thin films. Physica B: Condensed Matter, 406(9): 1757-1762.
13. Aqilia, A., Z. Alib and Z. Hussainb, 2012. Optical and structural properties of silver doped ZnSe thin films prepared by CSS and ion exchange process. in Proc. of SPIE Vol. 2012.
14. Shah, N.A. and W. Mahmood, 2013. Physical properties of sublimated zinc telluride thin films for solar cell applications. Thin Solid Films, 544: 307-312.
15. Shah, N., R. Sagar, W. Mahmood and W. Syed, 2012. Cu-doping effects on the physical properties of cadmium sulfide thin films. Journal of Alloys and Compounds, 512(1): 185-189.
16. Shah, N., A. Nazir, W. Mahmood, W. Syed, S. Butt, Z. Ali and A. Maqsood, 2012. Physical properties and characterization of Ag doped CdS thin films. Journal of Alloys and Compounds, 512(1): 27-32.

Persian Abstract

DOI: 10.5829/idosi.ijee.2014.05.01.13

چکیده

روش تصعید فضای بسته (CSS) برای لایه نشانی پودر سلنید روی (ZnSe) خالص (۹۹.۹۹٪) در سوبسترای شیشه ای برای ساخت فیلم های لایه نازک ZnSe استفاده شد. درجه حرارت منبع، بستر و زمان لایه نشانی برای نشاندن فیلم لایه نازک با ضخامت های مختلف بهینه سازی شد. در فیلم های لایه نازک ZnSe، نقره (Ag) در طی فرایند تبادل یونی به عنوان یک دوپه کننده استفاده شد. تجزیه و تحلیل ساختاری نشان داد که فیلم های لایه نازک ZnSe لایه نشانی شده پلی کریستالی با جهت گیری ترجیحی [۱۱۱] بودند. پارامترهای ریز ساختاری مانند اندازه کریستال و پارامتر شبکه با استفاده از پراش اشعه X (XRD) تعیین شد. مرز دانه ها، زبری روی سطح و چگالی دانه از نمونه های فیلم لایه نازک با روبش الکترونی و میکروسکوپ نیروی اتمی قبل و بعد از دوپینگ نقره اندازه گیری شد. نمونه های ZnSe نقره دوپه شده، قبل و بعد از بازپخت نوری با دستگاه اسپکتروفتومتر در ماورا بنفش، ناحیه مرئی و مادون قرمز مشخص شد. گاف انرژی فیلم های لایه نازک ZnSe لایه نشانی شده برای ضخامتهای مختلف در محدوده ۲/۶۷-۲/۶۲ eV بود که بعد از دوپه شدن Ag کاهش یافت. خواص الکتریکی نشان داد که فیلم های لایه نازک نشانده شده بسیار مقاومتی در درجه 10^{8} Ω-cm سانتی متر بودند، و بعد از غوطه ور شدن نقره به Ω-cm ۱کاهش یافت. پارامترهای لایه نشانی و دوپینگ نقره خواص ساختاری ، سطح، نوری و الکتریکی را تحت تاثیر قرار داد.