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OPTICAL AND MORPHOLOGICAL STUDIES OF THERMALLY VACUUM EVAPORATED ZnSe THIN FILMS

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Abstract. Zinc selenide (ZnSe) thin films were deposited on optical glass substrates using thermal vacuum evaporation, by sublimation of zinc selenide powder from a single quartz crucible heated at 600°C. The substrates temperatures were maintained constant during deposition at 220°C. All the samples were subjected to post – deposition thermal treatments in the same deposition chamber, at 250°C for 20 minutes. AFM and SEM studies confirmed that post – deposition annealing improved the grains growth and their distribution over the entire surface of the film. Optical constants (refraction indices and extinction coefficients) of semiconducting ZnSe thin films were measured by spectroscopic ellipsometry in the range of 190 nm to 500 nm. Optical measurements were completed with the spectral dependencies of transmission and absorption using a double beam UV - VIS spectrophotometer. The values for optical bandgaps calculated from the absorption spectra were found to be around 2.7 eV. All these results lead to the conclusion, that ZnSe thin films are good candidates to replace the conventional CdS thin films used as n-type window layers in the thin film heterojunction solar cells.

Key words: zinc selenide, spectroscopic ellipsometry, solar cells.

1. INTRODUCTION

Polycrystalline zinc selenide thin films have been studied for almost 40 years, yet these materials present scientifical interest mainly due to their technologically important applications. Among these applications are optoelectronic devices such as blue light emitting diodes, photodiodes, thin film transistors, piezoelectric devices, electroluminescent devices, etc. [1–5].

Different techniques have been used for zinc selenide thin films deposition, such as chemical vapor deposition (CVD), chemical bath deposition (CBD), vacuum evaporation, radio – frequency assisted magnetron sputtering, molecular beam epitaxy (MBE), etc. [6–10].

Its physical properties – direct wide band gap of about 2.7 eV at room temperature, low electrical resistivity, high optical transmission, good photosensitivity – recommend ZnSe for use as window (buffer) material in chalcogenide based thin film solar cells [11]. This work aims at investigating the possibility of using this material as a substitute for the classical CdS n-type semiconductor window layers, when combined with CdTe in thin film heterojunction solar cells [12–16]. The paper is organized as follows: experimental details on the thin film fabrication procedure and characterization methods we have used are given in the second section. The results are presented and discussed in the third section, the main conclusions being summarized in the last section of the paper.

2. EXPERIMENTAL DETAILS

Zinc selenide thin films were deposited by thermal vacuum evaporation using optical glass as substrates. The substrates temperatures were maintained constant at 220ºC. The ZnSe thin films were prepared by vacuum evaporation of ZnSe powders (from Aldrich, with 99.99% purity) using a single crucible (a quartz container heated at 600ºC) at a pressure inside the deposition chamber of 1.4×10^{-4} Torr. In order to avoid the sputtering of the ZnSe powder during the evaporation (sublimation), the crucible was covered with a special designed quartz-wool plug.

After finishing the deposition of all the samples, the ZnSe thin films were subjected to a thermal treatment consisting in heating the films at 250ºC, in vacuum, for almost 20 minutes. The aim of this post-deposition procedure is to improve the structural, morphological and chemical quality of the films.

The characterization of ZnSe thin films of different thicknesses (by varying the deposition time) were made using spectroscopic ellipsometry (SE), optical spectrophotometry, atomic force microscopy (AFM) and scanning electron microscopy (SEM).

The ellipsometric recording of optical constants for ZnSe thin films were made using an UVISEL^{TM} NIR spectroscopic phase modulated ellipsometer from Horiba - Jobin Yvon. The ellipsometric data were acquired at an incident angle of 70° for the wavelength range of 250 – 500 nm with a 10 nm step. The light source is a non – polarized Xe lamp (75 W power) and after the reflection from ZnSe films surfaces the light beam is analyzed using a photoelastic modulator with a 50 kHz modulation frequency.

The ellipsometric measurements were coupled with optical spectrophotometry measurements using a double beam Lambda^{TM} 35 UV – VIS spectrophotometer from Perkin Elmer. The spectral range is between 190 nm up to 1.1 μm, with 5 nm steps.

Finally the morphological investigations of ZnSe film surfaces were made first using an AFM microscope from TopoMetrix^{TM}, in contact mode in air, at a 320 kHz resonance frequency and for a scanning rate of 1 Hz. SEM investigations were made using a JSM – 6301F scanning microscope from JEOL^{TM}, using a high level of vacuum (10^{-7} mbar), at different magnifications.

3. RESULTS AND DISCUSSION

The optical investigations of thin ZnSe films have been made using the spectroscopic ellipsometry and the optical spectrophotometry techniques. In the ellipsometric investigations of ZnSe vacuum deposited thin films, the fitting of the ellipsometric spectra were made using the Adachi – New Forouhi (ANF) dispersion model [17] with a dedicated software package DeltaPsi2^{TM} that allows the setting for all the fitting parameters, substrate thicknesses, surface layer roughnesses, etc.

The dependencies of the refractive indices on the incident wavelengths are shown in Fig. 1, for two ZnSe films of different thicknesses.

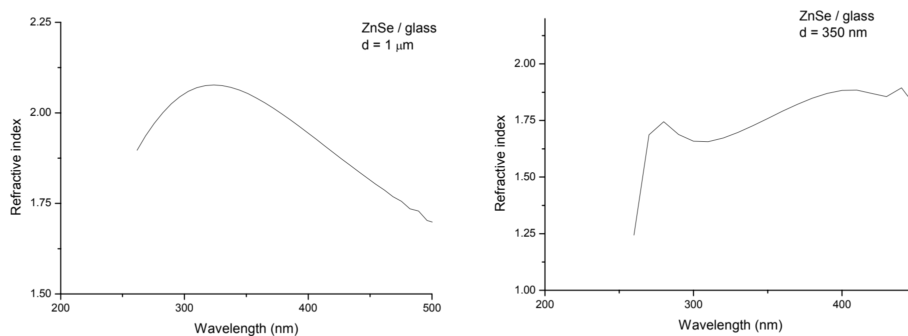

Fig. 1 – Spectral dependencies of the refractive index for ZnSe thin films.

The values for the ZnSe optical constants (refractive indices and extinction coefficients) were obtained indirectly by fitting (psi, del) spectra, until a minimum value for the mean squared error (MSE) were reached. MSE was used as a risk function in order to quantify the fitting procedure. This mathematical procedure has its inconvenients, however the values obtained for ZnSe optical constants are in a good accordance with the literature [18].

The variations of extinction coefficient with photon wavelengths are shown in Fig. 2. It can be observed that regardless of their thickness, ZnSe films have small values for the extinction coefficients confirming the possibility of using these kinds of films as window layers in heterojunction thin film based solar cells.

The spectro-ellipsometric investigations were combined with spectrophotometric characterizations of the same thermally vacuum deposited ZnSe thin films. In Figure 3 the spectral dependence of the optical transmission for ZnSe films is showed, in the wavelength range of interest.

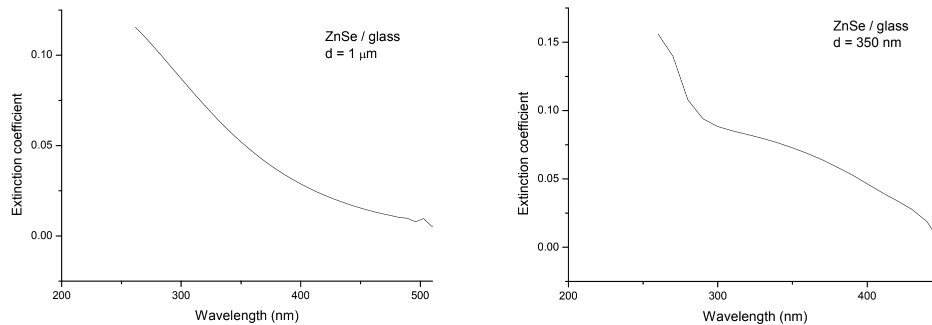

Fig. 2 – Spectral dependencies of the extinction coefficient for ZnSe thin films.

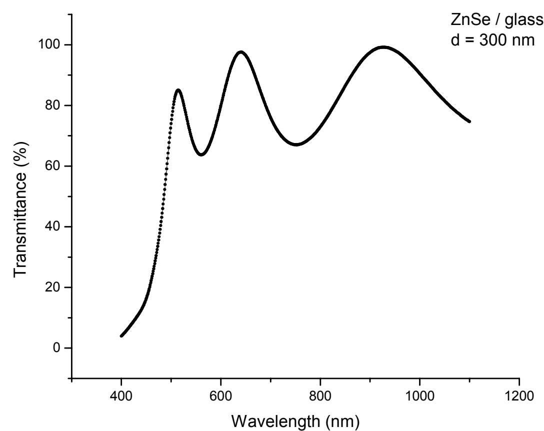

Fig. 3 – The transmission spectrum for thermally vacuum deposited ZnSe thin films.

The sharp fall of the transmittance curve in visible region of the investigated spectrum where the band edge is could indicate that ZnSe films have a good crystallinity. ZnSe thin films have significant great values for the optical transmittance, comparable with the classic CdS semiconductor window layers [13].

In Fig. 4 the plot of $(\alpha h\nu)^2$ *versus* photon energy for ZnSe films is showed (based on the values of α – the light absorption coefficient).

Figure 4 shows that for the studied ZnSe thin films the dependency of the quantity $(\alpha h\nu)^2$ on the photon energy ($h\nu$) indicates the direct nature of band – to – band transitions. The value of 2.7 eV for ZnSe optical band gap has been obtained by extrapolating the linear portion of this dependence when $(\alpha h\nu)^2 \rightarrow 0$.

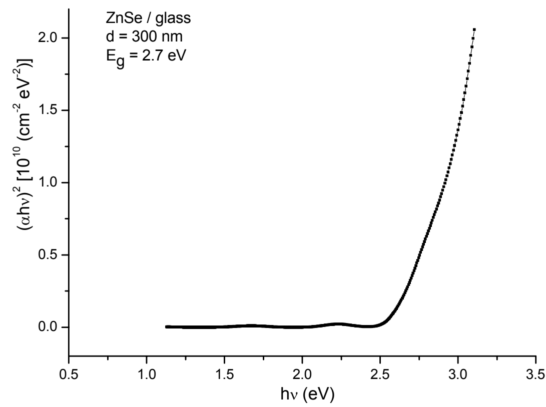

Fig. 4 – Absorption spectra of ZnSe thin films prepared at 600ºC and post – deposition thermally treated at 250º.

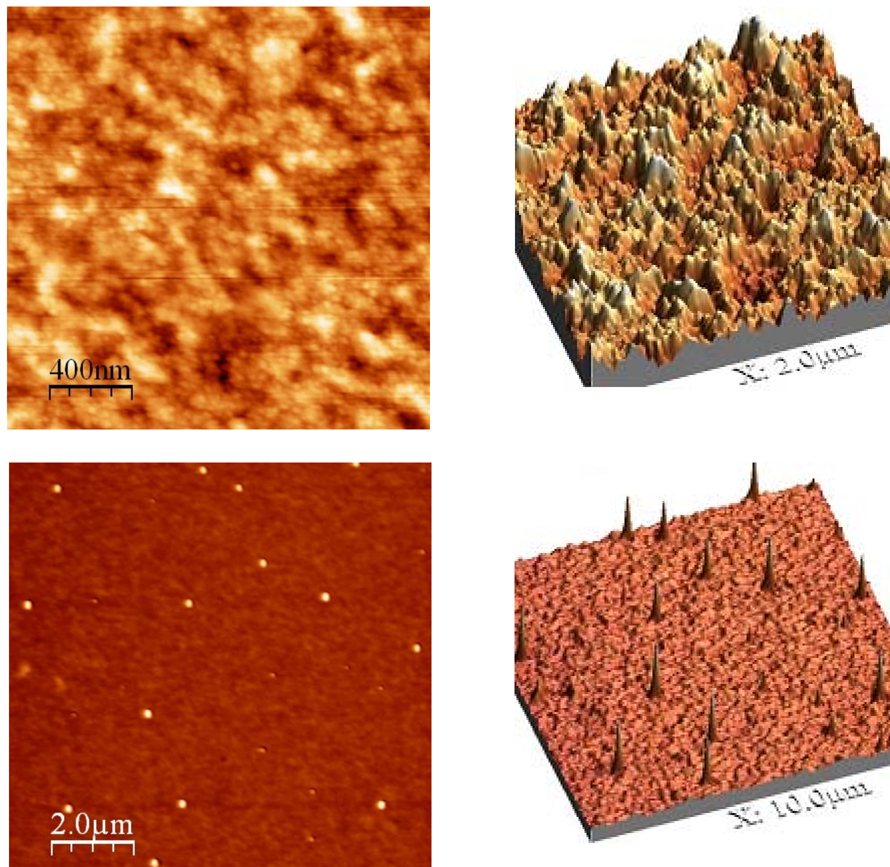

Fig. 5 – AFM images for ZnSe thin films of 350 nm thickness (2D images – left; 3D images – right).

The morphological characterizations were made using both AFM and SEM techniques. In Figure 5 both 2D and 3D images obtained using an AFM microscope for ZnSe films are presented.

The sampling areas used were 2 × 2 [μm x μm] (the upper row) and 10 × 10 [μm x μm] (the lower row). The average roughness values were between 6.5 to 12.7 nm for ZnSe films with the thickness range between 250 nm up to 1μm.

The surface Skewness parameters were between 1.6 to 8.3 which indicates a relatively uniform distribution of peaks on the surface, while the grains have similar shapes and sizes. All these aspects are strongly influenced by the deposition conditions and by the post-deposition thermal treatments.

Figure 6 shows two SEM images for ZnSe thin films deposited at 600º and thermally annealed at 250ºC.

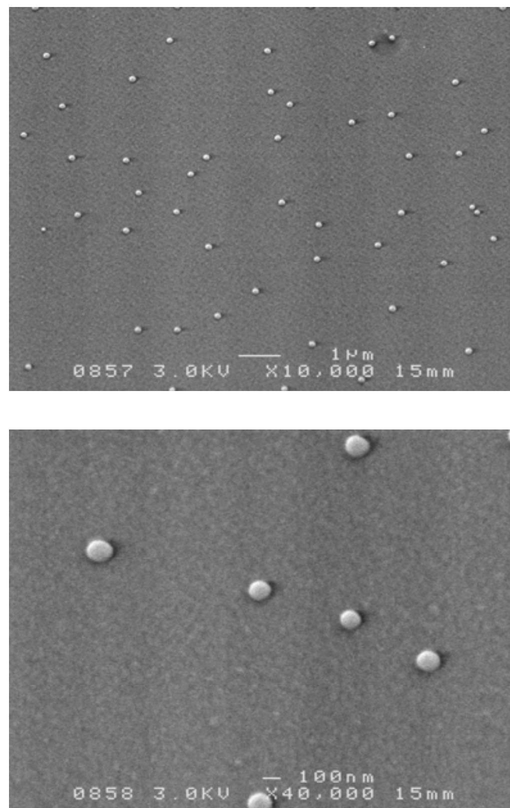

Fig. 6 – SEM images for ZnSe thin films of 350 nm thickness
(× 10000 magnification – up; × 40000 magnification – bottom).

The ZnSe film surfaces are relatively smooth, the thermal treatments applied on all our samples leading to more compact and uniform film surfaces.

4. CONCLUSIONS

Nanocrystalline ZnSe thin films were deposited by thermal vacuum evaporation (TVE) technique on optical glass substrates. Films with different thickness between 250 and 1μm and different particle sizes have been obtained. The optical parameters (refractive indices, extinction coefficients and optical band gaps) of the samples were measured. Both AFM and SEM morphological investigations showed that ZnSe films have well defined nanosized grains. A significant improvement in grain sizes were obtained by performing post-deposition "in – situ" thermal treatments on all samples.

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REFERENCES

1. B. ULLRICH, Mater. Sci. Eng. B, **56**, 69–71 (1998).
2. R.R. Alfano, Q.Z. Wang, T. Jimbo, P.P. Ho, J. Phys. Rev A, **35**, 459–462 (1987).
3. D. Son, D.R. Jung, J. Kim, T. Moon, C. Kim, B. Park, Appl. Phys. Lett., **90**, 101910 (2007).
4. E. Bacaksiz, S. Aksu, I. Polat, S. Yilmaz, M. Altunbas, J. Alloys Comp., **487**, 280–285 (2009).
5. C.D. Lokhande, P.S. Patil, A. Ennaoui, H. Tributsch, Appl. Surf. Sci., **123**, 294–297 (1998).
6. A. Rumberg, C. Sommerhalter, M. Toplak, A. Jager-Waldau, M.C. Lux-Steiner, Thin Sol. Films, **361**, 172–176 (2000).
7. C.A. Estrada, P.K. Nair, M.T.S. Nair, R.A. Zingaro, E.A. Meyers, J. Electrochem. Soc., **141**, 802 (1994).
8. M. Elsherif, F.S. Terra, S.A. Khodier, J. Mater. Sci.: Mater. Electron., **7**, 391–395 (1996).
9. A. Rizzo, M.A. Tagliente, L. Caneve, S. Scaglione, Thin Sol. Films, **368**, 8–14 (2000).
10. H. Goto, T. Ido, A. Takatsuka, J. Cryst. Growth, **214–215**, 529–532 (2000).
11. T.L. Chu, S.S. Chu, G. Chen, J. Britt, C. Ferekides, C.Q. Wu, J. Appl. Phys., **71**, 8 (1992).
12. O. Toma, R. Pascu, M. Dinescu, C. Besleaga, T.L. Mitran, N. Scarisoreanu, S. Antohe, Chalc. Lett., **8**, *9*, 541–548 (2011).
13. O. Toma, S. Iftimie, C. Besleaga, T.L. Mitran, V. Ghenescu, O. Porumb, A. Toderas, M. Radu, L. Ion, S. Antohe, Chalc. Lett., **8**, *12*, 747–756 (2011).
14. S. Antohe, V. Ghenescu, S. Iftimie, A. Radu, O. Toma, L. Ion, Dig. J. Nanomater. Bios., **7**, *3*, 941–946 (2012).
15. M. Ghenescu, L. Ion, I. Enculescu, C. Tazlaoanu, V. A. Antohe, M. Sima, M. Enculescu, E. Matei, R. Neumann, O. Ghenescu, V. Covlea, S. Antohe, Physica E: Low-dimensional systems and Nanostructures, **40**, *7*, 2485–2488, 2008
16. Antohe, S., Iftimie, Sorina, Ghenescu, Veta, Constantineanu, Raluca, Gugiu, M., Ion, M., Stan, I., Radu, A., Ion, L., Romanian Reports in Physics **64**, Supplement, 1153–1162 (2012).
17. H. Yoshikawa, S. Adachi, Jpn. J. Appl. Phys., **36**, 6237 (1997).
18. U. Khairnar, S. Behere, P. Pawar, Mat. Sci. Appl., **3**, 36–40 (2012).