STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CHEMICAL BATH DEPOSITED PBS/CDS FILMS GROWN ON DIFFERENT SUBSTRATES

G. Barikan[1], H. Ertap[1], M. Yüksek[2], H. Mammadov[1], M. Karabulut [1]*

[1]Kafkas University, Faculty of Art and Sciences, 36040-Kars

[2]Kafkas University, Faculty of Engineering and Architecture, 36040-Kars

e-mail: mevlut_karabulut@yahoo.com

Abstract

PbS/CdS bilayer thin films have been grown on glass, GaSe, and InSe substrates by chemical bath deposition. Structural, morphological, optical and electrical properties have been studied by X-ray diffraction (XRD), Atomic Force Microscopy (AFM), optical absorption and I-V measurements. The PbS/CdS layers have been found to grow with cubic and hexagonal structure and showed preferred orientation in (200) and (002) planes, respectively. The particle sizes and energy bang gaps of PbS/CdS films have been shown to be substrate dependent. Particle sizes of PbS/CdS films grown on glass, GaSe and InSe substrates determined from AFM images were in the 81-301 nm range while direct band gap energies calculated from optic absorption spectra were in the 1.22-1.98 eV range. The PbS/CdS bilayers have been shown to be photosensitive through I-V measurements.

Keyword: PbS/CdS thin films, CBD, XRD, optic absorption

Introduction

Cadmium sulfide (CdS) and lead sulfide (PbS) are members of chalcogenide compound semiconductor family with room temperature band gaps of 2.42 eV and 0.41 eV, respectively [1,2]. CdS and PbS semiconducting thin films are being extensively investigated due to their potential applications in electronic and optoelectronic. As a wide direct band gap semiconductor, CdS has appropriate properties to be used as a photovoltaic cell window material with several semiconductors such as $CuInSe_2$, CdTe and Cu_2S [3-5]. PbS thin films have various applications in different fields such as IR detectors [2], display devices [6], solar control coatings [7], LEDs [8], humidity and temperature sensors [9] and in optical switching [10] due to their third-order nonlinear optical properties.

The use of thin film semiconductors are preferred in technology because thin films can be fabricated with various thicknesses and desired properties with low production cost. Thin films can be grown on different substrates of various shapes and sizes as multi-component multi-layer coatings with controlled parameters. A hetero-junction thin film is formed by

successively growing two layers of semiconductors with differing band-gap energies on top of each other.

Several methods have been employed for the growth of CdS and PbS films including electrodeposition [11,12], spray pyrolysis [13,14], vacuum evaporation [15], successive ionic layer adsorption reaction (SILAR) [16,17] and chemical bath deposition (CBD) [18-24]. CBD is a favorable method due to its simplicity, low deposition temperatures and low cost. Large area coatings with good quality can be obtained with this method. It was shown that CBD grown CdS films had better conductivity and surface properties compared to films prepared by other methods [25]. PbS/CdS and CdS/PbS films have been grown by CBD on glass substrate and glass/ITO substrate for solar cell applications [26,27].

Properties of thin films show strong dependence on the substrates and growth conditions/methods. In this study, we have grown PbS/CdS films on glass, GaSe and InSe crystalline substrates by CBD. Structural, morphological, optical and electrical properties have been investigated by X-ray diffraction (XRD), Atomic Force Microscopy (AFM), optical absorption and current-voltage measurements.

Experimental

Film preparation: The CBD method basically consists of 3 steps: Preparation of substrates, preparation of anionic and cationic solutions and finally film growth. Crystalline GaSe and InSe substrates were prepared by cleaving layers from the GaSe and InSe bulk crystals grown by Bridgman method [28] with a razor blade. The thicknesses of the 1cm × 3cm substrates were in the 100 - 500 μm range. No chemical process was applied to these naturally mirror faced GaSe crystals prior to growth process. On the other hand, glass substrates (7.5 cm × 1 cm × 0.2 cm) were chemically cleaned prior to the growth process. PbS films were first deposited on glass, GaSe and InSe substrates. The chemical baths for PbS films were prepared by 5 ml 0.5 M lead acetate ($Pb(CH_3COO)_2.3H_2O$) and 6 ml 1M thiourea ($(NH_2)_2CS$). Sodium hydroxide (NaOH- 5 ml, 2 M)) and triethanolamine ($N(CH_2CH_2OH)_3$ – 2 ml, 1M) were used to adjust the pH of the solution and as the complexing agent, respectively. The chemically cleaned glass, GaSe, and InSe substrates were immersed vertically into chemical solutions. Immersing processes were carried out for 120 min at 27 °C. Afterwards, CdS films were grown on these PbS deposited glass, GaSe and InSe substrates. For the growth of CdS, chemical baths were prepared by 5 ml 0.03 M $3CdSO_4$ $.8H_2O$, 5 ml 0.1 M thiourea ($(NH_2)_2CS$). 1 ml ammonium hydroxide ($NHOH_4$) and triethanolamine

($N(CH_2CH_2OH)_3$ – 2 ml, 1M) were used to adjust the pH of the solution and as the complexing agent, respectively. CdS films were grown at 80 ºC for 1 hr.

Characterization: The structure of the films grown on both substrates was analyzed by x-ray diffraction (XRD) using Cu- Kα radiation (λ = 1.5405 Å). The surface morphologies of the films were probed by using a PSIA XE-100E model atomic force microscopy (AFM). Elemental analysis was carried out by Energy Dispersive Analysis of X-rays (EDAX). The optical absorbance spectra were recorded using a Perkin Elmer UV/VIS Lambda 25 spectrophotometer. Electrical properties were studied with an I-V measurement system.

Results and Discussion

The XRD spectrum of PbS/CdS films grown on glass substrate is given in Figure 1. Analysis of the spectrum reveals that the spectrum consists of peaks belonging to GaSe crystalline substrate and PbS and CdS thin films. Peak assignments are given on Figure 1. Peaks observed at 2θ = 26.7°, 43.6°, and 51.7° are due to the hexagonal CdS films, while the peak observed at 2θ = 30º belong to face centered cubic (fcc) PbS films. The XRD spectrum of PbS/CdS films grown on GaSe crystalline substrate is given in Figure 2. The XRD spectrum of GaSe crystalline substrate is also included for comparison. As can be seen, besides the sharp peaks belonging to GaSe crystal, there are also crystalline peaks belonging to PbS and CdS films. Because of the relatively small intensities of these peaks compared to GaSe peaks, the y axis scale has been adjusted to make these peaks visible. The peak observed at 2θ = 30º belongs to cubic PbS while the peaks observed at 2θ = 26.7°and 51.7° have been identified to be due to the hexagonal CdS films. The XRD spectrum of PbS/CdS films grown on InSe crystalline substrate together with the spectrum of InSe substrate is shown in Figure 3. Similar to the PbS/CdS films grown on GaSe substrate, the peak observed at 2θ = 30º belongs to cubic PbS films while the peak at 2θ = 26.7° is due to the hexagonal CdS films. It is known that CdS may exist in two crystalline forms: hexagonal (wurtzite) and cubic (zincblend).

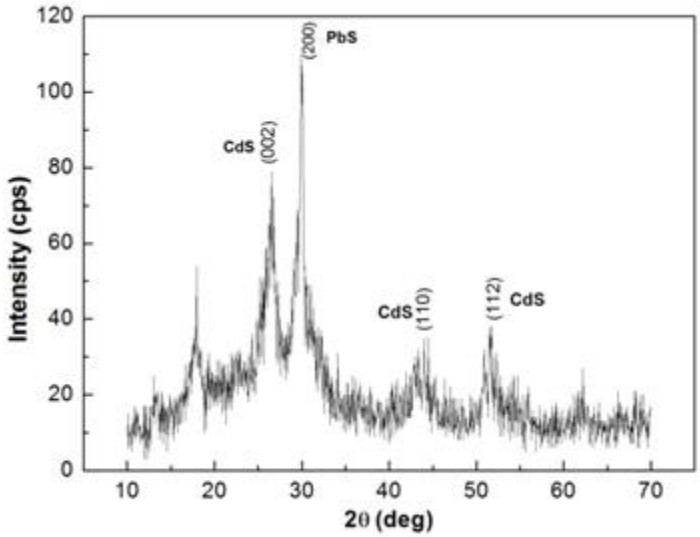

Figure 1. XRD spectrum of PbS/CdS films grown on glass substrate.

Formation of these phases during the film growth depends on deposition techniques and conditions. Both hexagonal and cubic structures or mixtures of these phases have been reported for CBD grown CdS films [4, 19, 26, 27]. It is, however, known that hexagonal structure is preferred for solar applications [29]. Existence of (002), (110) and (112) peaks in the XRD spectrum of CdS films grown on glass substrate and (002) peak on GaSe and InSe crystals indicates that CdS is grown as hexagonal structure. However, there are some reports in the literature that state that the peak observed at 26.7º could be due to hexagonal (002) or cubic (111) [26,29,30]. One other point to note is that both PbS and CdS film show preferred orientation in our samples as the (002) and (200) peaks are the dominant peaks for CdS and PbS films.

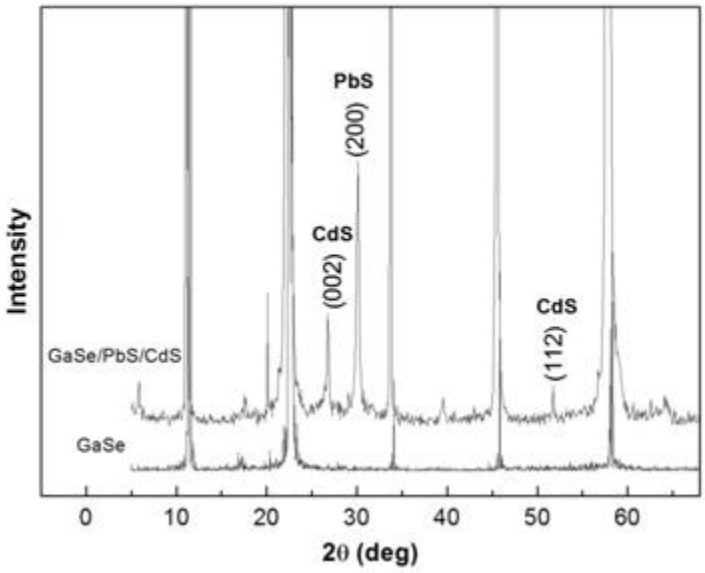

Figure 2. XRD spectrum of PbS/CdS films grown on GaSe substrate. XRD spectrum of crystalline GaSe is also included for comparison.

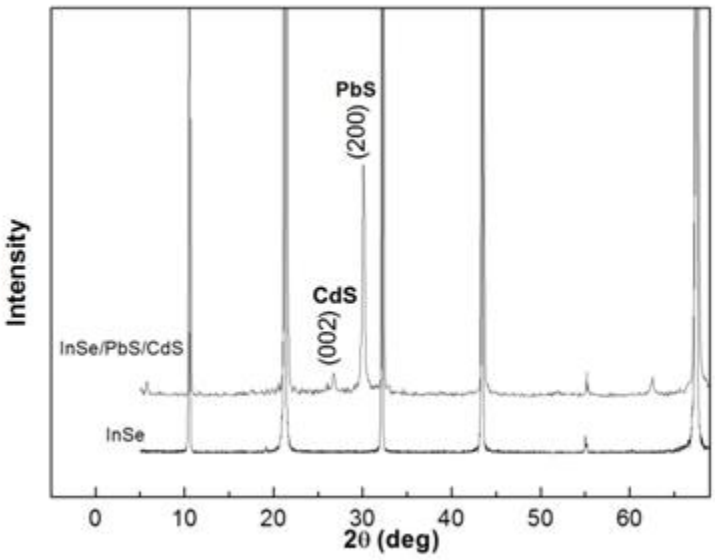

Figure 3. XRD spectrum of PbS/CdS films grown on InSe substrate. XRD spectrum of crystalline InSe is also included for comparison.

It may be expected that the PbS films grown on GaSe and InSe crystalline substrates have different structures than those of films grown on glass substrates as PbS films could

follow the crystalline structures of the substrates. However, it is clearly seen that the PbS films on all substrates grew in cubic structure which is different from any of the polytypes of GaSe and InSe crystals [31]. Similar observations were made in our previous study of PbS films grown on GaSe crystal [32] where the reason for not observing the GaSe/PbS van der Waals hetero-junction was given as the possibility of the formation of sulfur pre-layer on which cubic PbS grew as in GaAs. Similar discussion seems to be valid for the PbS films grown on InSe crystalline substrate as the PbS films do not follow the structure of the substrate but grew with cubic structure. On the other hand, when CdS is grown on both crystalline GaSe and InSe substrates as a monolayer, it has only the (002) peak of hexagonal structure.

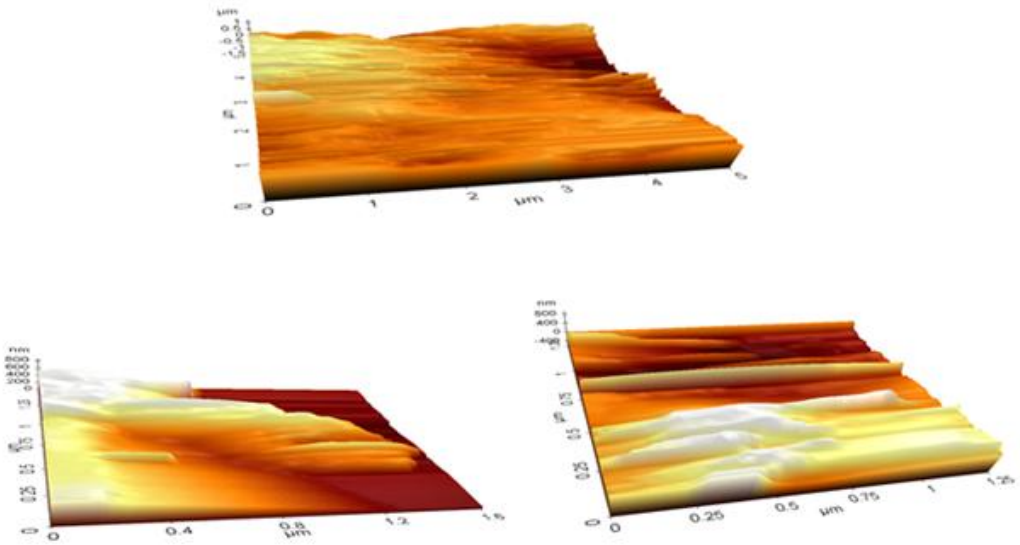

Figure 4. AFM images of PbS/CdS films grown on glass (top), GaSe (bottom-left) and InSe (bottom-right) substrates.

AFM images were taken on PbS/CdS films grown on glass, GaSe and InSe substrates which are shown in Figure 4. From the analysis of these images, the crystallite sizes of nanoparticles grown on glass/PbS/CdS, GaSe/PbS/CdS and InSe/PbS/CdS were determined as 81 nm, 301 nm, and 292 nm, respectively.

The optical absorption spectra of PbS/CdS films grown on glass, GaSe, and InSe substrates are given in Figures 5. The band gaps of films were calculated using the following standard equation $(\alpha h\vartheta) = A\left(h\vartheta - E_g\right)^n$, where α is the absorption coefficient, hν is the incident photon energy, A is a constant, E_g is the band gap energy and n is a number that determines the nature of transition which is ½ for direct transitions. The direct band gaps of

films were obtained from the linear portions of the $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ plots which are given as insets in Figure 5. From these plots, the energy band gaps of PbS/CdS films grown on glass, GaSe and InSe substrates are calculated to be 1.47 eV, 1.98 eV, and 1.22 eV, respectively. The band gaps of PbS/CdS films grown on GaSe and InSe substrates are close to the energy band gaps of respective substrates.

The electrical properties of PbS/CdS films were investigated through current-voltage measurements. Measurements were performed in dark and illuminated environments. The I-V characteristics of PbS/CdS/Ag films grown on glass, GaSe and InSe substrates with parallel contacts are given in Figure 6. The contacts were made using silver paste. As can be seen, the I-V characteristics of the PbS/CdS thin films vary with the substrates used. The current values obtained for the same voltage from PbS/CdS films grown on glass substrate is lower than the current values obtained from the films grown on GaSe and InSe substrates. All of the films show some degree of photosensitivity, which is evidenced in the I-V characteristics obtained under illumination. The photosensitivity has been shown to increase when the measurements were conducted with sandwich contacts for the films grown on crystalline substrates.

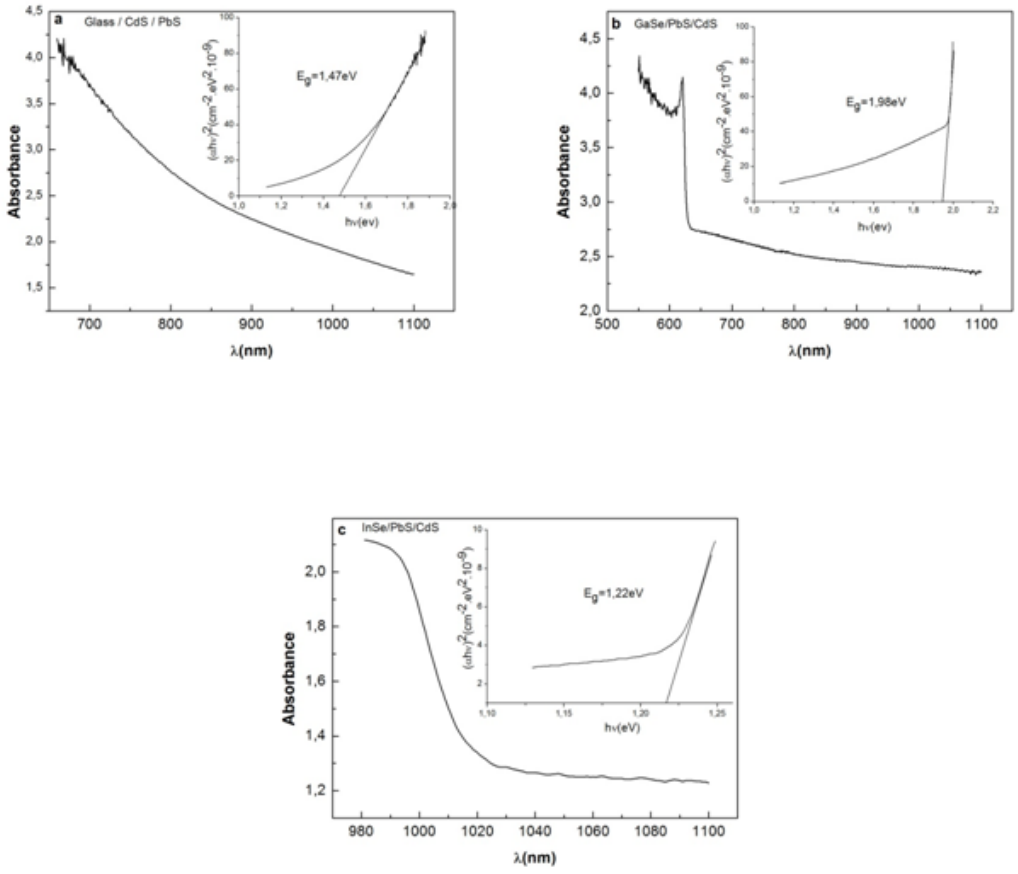

Figure 5. Absorption spectra of PbS/CdS films grown on **a)** glass, **b)** GaSe, and **c)** InSe substrates. Plots of $(\alpha hv)^2$ vs energy are given as insets.

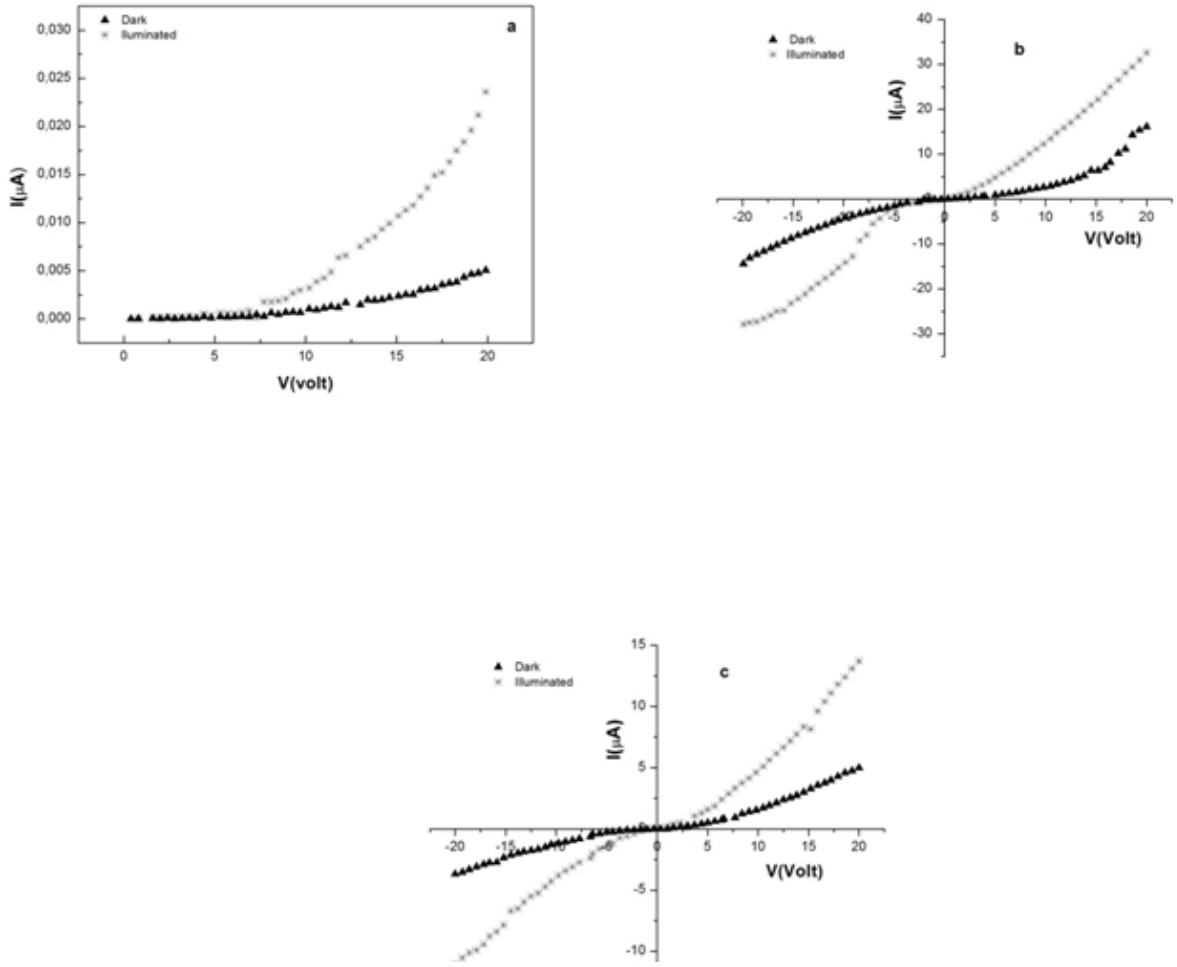

Figure 6. I-V characteristics of PbS/CdS films grown on **a)** glass, **b)** GaSe, and **c)** InSe substrates.

Conclusions

PbS/CdS bilayers have been deposited on glass, GaSe and InSe substrates by CBD. XRD spectra of all films contained peaks corresponding to PbS and CdS. The structure of PbS and CdS films were identifies as cubic and hexagonal, respectively. The particle sizes of CdS films grown on glass, GaSe and InSe substrates have been found to be 81 nm, 301 nm, and 292 nm, respectively. Band gaps of PbS/CdS films have been found to be substrate dependent as they were calculated as 1.47 eV, 1.98 eV, and 1.22 eV for films deposited on glass, GaSe, and InSe substrates. The PbS/CdS films have been shown to be photosensitive through I-V measurements.

Acknowledgments

This work was supported by the Kafkas University Scientific Research Projects Coordination by project no: 2012-FEF-06

References

1. Rajeshwar, K., de Tacconi, N., R. Chenthamarakshan, C. R., *Chem.Mater*. 13 (2001) 2765.

2. Bube, R. H., *Photoelectronic Properties of Semiconductors*, Cambridge University Press, 1992.

3. Wu, X., *Solar Energy* 77 (2004) 803.

4. Liu, F., Lai, Y., Liu, J., Wang, Bo., Kuang, S., Zhang, Z., Li, J., Liu, Y., *J. Alloy and Comp.* 493 (2010) 305.

5. Pillai, P. K. V., Vijayakumar, K.P., Sol. Energ. Mat. Sol. C. 51 (1998) 47.

6. Yang, P., Song, C. F., Lü, M. K., Yin, X., Zhou, G. J., Xu, D., Yuan, D. R., *Chem. Phys. Lett.* 345 (2001) 429.

7. Nair, P. K., Nair, M. T. S., *J. Phys.D: Appl. Phys.* 23 (1990) 50.

8. Sun, L., Choi, J J., Stachnik, D., Bartnik, A. C., Hyun, B.-R., Malliaras, G. G., Hanrath, T., Wise., W., *Nature Nanotechnology*, 7 (2012) 369.

9. Kane, R. S., Cohen, R. E., Silbey, R., *J. Phys. Chem.* 100 (1996) 7928.

10. Li, D., Liang, C., Liu, Y., Qian, S., *J. Lumin.* 122-123 (2007) 549.

11. Choy, K. L., Su, B., *Thin Solid Films* 388 (2001) 9.

12. Saloniemi, H., Kemell, M., Ritala, M., Leskela, M., *Thin Solid Films* 386 (2001) 32.

13. Ramaiah, K. S., Raja, V. S., *Sol. Energ. Mat. Sol. C.* 32 (1994) 1.

14. Thangaraju, B., Kaliannan, P., *Semicond. Sci. Technol*. 15 (2000) 849.

15. Chu, T. L., Chu, S. S., *Solid State Electron*. 38 (1995) 533.

16. Pathan, H. M., Lokhande, C. D., *Bull. Mater. Sci*. 24 (2004) 85.

17. Poisso, J., Lindroos, S., Tamulevicius, S., Leskela, M., Snitka, V., *Thin Solid Films* 428 (2003) 223.

18. Metin, H., Esen, R., *J. Cryst. Growth*, 258 (2003) 141.

19. Prabahar, S., Dhanam, M., *J. Cryst. Growth*, 285 (2005) 41.

20. Wenyia, L., Xun, C., Qiulong, C., Zhibin, Z., *Mater. Lett.* 59 (2005) 1.

21. Ximello-Quiebras, J. N., Contreras-Puente, G., Aguilar-Hernandez, J., Santana-Rodriguez, G., Arias-Carbajal Readigos, A., *Sol. Energ. Mat. Sol. C.* 82 (2004) 263.

22. Joshi, R. K., Kanjilal, A., Seghal, H. K., *Appl. Sur. Sci.*, 221 (2004) 43.

23. Seghaier, S., Kamoun, N., Brini, R., Amara, A. B., *Mater. Chem. Phys*. 97 (2006) 71.

24. Garcia-Valenzuela, A., Baez-Gaxiola, M. R., Sotelo-Lerma, M., *Thin Solid Films*, 534 (2013) 126.

25. Mendoza-Perez, R., Santana-Rodrıguez, G., Sastre-Hernandez, J., Morales-Acevedo, A., Arias-Carbajal, A., Vigil-Galan, O., Alonso, J. C., Contreras-Puente, G., *Thin Solid Films*, 480-481 (2005) 173.

26. Orozco-Teran, R. A., Sotelo-Lerma, M., Ramirez-Bon, R., Quevedo-Lopez, M. A., Mendoza-Gonzales, O., Zelava-Angel, O., *Thin Solid Films*, 343-344 (1999) 587.

27. Hernandez-Borja, J., Vorobiev, Y.V., Ramirez-Bon, R., *Sol. Energ. Mat. Sol. C.* 95 (2011) 1882.

28. Karabulut, M., Bilir, G., Mamedov, G. M., Seyhan, A., Turan, R., Lumin. J., 128 (2008) 1551.

29. Ramaiah, K. S., Pilkington, R. D., Hill, A. E., Tomlinson, R. D., Bhatnagar, A. K., *Mater. Chem. Phys.* 68 (2001) 22.

30. J.P. Enriquez, X. Mathew, Sol. Energ. Mat. Sol. C.76 (2003) 313.

31. Guskov, A., Camassel, J., Guskov, L., *Pro g. Cryst. Growth and Charact.* 5 (1982) 323.

32. Karabulut, M., Ertap, H., Mammadov, H., Ugurlu, G., Ozturk, M. K., *Turkish J. Phys.* 38 (2014) 104.