Chalcogenide Letters Vol. 19, No. 1, January 2022, p. 1 - 7

Studies on the effects of annealing on the structural and optical properties of nanocrystalline ZnCdS thin films

S. Kumar[a], R. Bhushan[b], S. R. Kumar[c], S. Rajpal[c,*]
[a]*Department of Physics, Chaibasa Engineering College, Chaibasa, Jharkhand-833215, India*
[b]*Department of Physics, Amity University , Ranchi, Jharkhand-834002, India*
[c]*Department of Applied Sciences & Humanities, National Institute of Foundry & Forge Technology, Ranchi-834003, India*

Zinc Cadmium Sulphide (ZnCdS) is a ternary direct band gap semiconducting material having potential applications in different opto-electronic devices. The deposition temperature can be effectively used to enhance the structure and optical properties of the films. In this paper, we have investigated the effect of air annealing on the various properties of ZnCdS films. A nanocrystalline ZnCdS thin film was successfully deposited on molybdenum substrate and the effect of annealing on structural, morphological, and optical properties were studied. The main impact was found to be slightly increase in crystallite size which effectively reduced the defects. It is observed that deposited film annealed at higher temperature provide a smooth and flat texture suited for optoelectronic applications. SEM photographs reveals the deposited grains are well connected and uniformly distributed over the surface. The experimental results show that the energy gap of the films is not much affected by the annealing temperature and varies from 2.6 eV to 2.7 eV. However, the oxygen annealing improves crystalline structure.

(Received September 12, 2021; Accepted January 4, 2022)

Keywords: Annealing, Thin Films, ZnCdS, XRD, Optical Properties

1. Introduction

Group II-VI compound semiconductors are known to be as suitable materials for thin film photovoltaic device applications due to their high absorption coefficients. II-VI compound for ternary alloys with a direct bandgap attributed over the entire alloys composition range and lattice parameters can be varied [1]. Recently, there is an increasing interest in chalcogenide-based semiconducting materials which were widely used for photodetectors, photovoltaic devices, etc. Chalcogenide ZnCdS films have much interest due to the possibility of using these films in solar cells [2]. It is useful as window material for the fabrication of p-n junction without lattice mismatch in the devices based on quaternary materials like $CuIn_xGa_{1-x}Se_2$ [3] or $CuIn_xGa_{1-x}S$ [4]. It has variable energy bandgap of nearly 2.4 eV – 3.7 eV, in heterojunction solar cells, low-voltage cathode luminescence, high density optical recording, blue and ultraviolet laser diodes [5,6].

Many techniques have been reported for the ZnCdS thin film deposition which includes vacuum evaporation [7], spray pyrolysis [8], ion beam deposition [9], Molecular beam epitaxial growth [10,11], chemical bath deposition [12], etc. Among these deposition techniques, CBD is simple, cheap and easy coating technique for large surface area deposition of material. ZnCdS thin film can be prepared by CBD techniques in non aqueous medium. Non aqueous bath offer greater flexibility in choosing deposition sources, higher working temperature ranges and also free from the ubiquitous hydrogen evolution reaction which is offer a nuisance in producing stress and pinhole free deposits [13]. The as deposited ZnCdS films were annealed with varying temperature (350^0C, 400^0C and 450^0C). In this paper, we have reported that the effect of annealing with varying temperatures on the prepared ZnCdS films deposited on molybdenum substrate by CBD in

---

[*] Corresponding author: sraj1162@gmail.com

https://doi.org/10.15251/CL.2022.191.1

non-aqueous medium. The annealed ZnCdS films are characterized to study the crystal structure, surface morphology, elemental analysis, optical bandgap and emission spectra of the films.

2. Experimental procedure

The electrolyte was prepared by using AR grade of 0.2M $CdCl_2$, 0.12M $ZnCl_2$ dissolved in 40ml of ethylene glycol. The temperature of electrolyte was maintained at 160^{0}C and aged for two hours under continuous stirring. The molybdenum substrate of dimension 1.5cmx1cmx0.1cm was dipped inside the electrolyte with the help of rigid support. At time t=0, 0.4M thiourea was introduced into the electrolyte under moderate stirring and film was deposited for 15 minutes. The prepared as deposited ZnCdS films were annealed at 350^{0}C, 400^{0}C and 450^{0}C in air.

The crystallographic structure of the annealed films were analyzed by Bruker AXS Diffractometer model D8 with CuK_α radian (λ= 1.54Å). Surface morphology with elemental analysis of the annealed films were characterized by using FESEM model Quanta 200F, FEI Netherland. The optical properties were measured by UV-VIS spectrophotometer model Lambda-25 Perkin-Elmer with wavelength range 300 nm- 900 nm. PL studies were carried out by spectrophotometer model- RF 5301 PC, Shimadzu with wavelength range 300 nm-800 nm.

3. Results and discussions

3.1. Structural characterization

X-ray diffraction measurements were carried out to study the crystal structure and crystalline quality of varying temperatures (350^{0}C, 400^{0}C and 450^{0}C) annealed ZnCdS films deposited over molybdenum substrate. XRD pattern of varying temperature annealed ZnCdS films are presented in figure 1 which shows the diffractive peaks have same characteristics and show same preferential orientation. XRD spectra gives information that varying temperature annealed ZnCdS films exhibited peaks corresponds to (100), (002), (101), (102) and (103) respectively. The entire duration of varying temperature, the (002) diffraction peak is present indicating that the films have hexagonal structure. Spectra indicates that the intensity of (002) diffraction peak increases with increasing temperature upto 400^{0}C. With further increasing temperature to 450^{0}C, the decreasing tendency of (002) diffraction peak was identify. Reflections due to molybdenum substrate, the subsequent peaks attributed to the scattering from (110), (200) and (211) planes of ZnCdS.

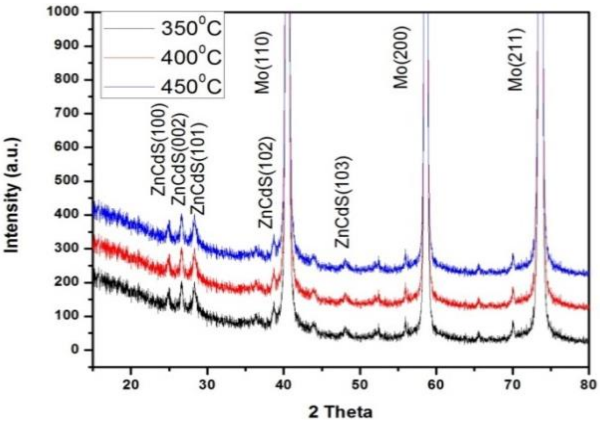


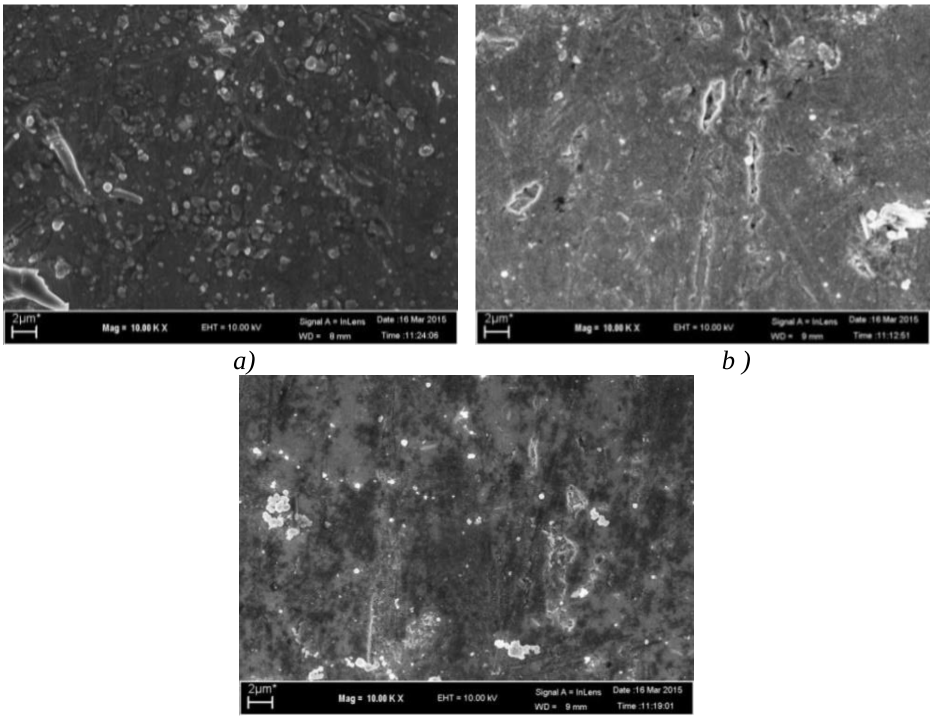
Fig. 1. XRD spectra of varying temperature annealed ZnCdS films.

The average grain size (D) of varying temperatures ZnCdS films were calculated using Scherrer's relation [14-16] $D= k\lambda/\beta Cos\theta$ Where, K = Constant equal to 0.94, λ = Wavelength of incident X-ray (=1.54Å), β = Full width at half maxima of (002) peak in radian and θ = Diffracted angle.

The calculated grain size value (D) of varying temperatures annealed ZnCdS films are 23 nm, 25 nm and 26 nm respectively. It concludes that increase in average grain size with increment of annealing temperature [17].

3.2. Surface morphology studies

The surface morphology using FESEM of annealed ZnCdS films with varying temperature are shown in figure 2(a,b,c). The magnification was fixed at 10,000X in all varying temperature for FESEM photograph. The microstructure of annealed ZnCdS films at 350^0C indicates that grains are uniformly distributed and heavily densed throughout the entire film surface area. However annealed at 400^0C, film surface appears smooth, covers equal sized spherical shaped grains in single state and no cloudy surface is observed. On further increasing annealing temperature to 450^0C, film surface is homogenous, grains are distinct with vacant spaces in single state as well as cluster form over the film analyzed area.



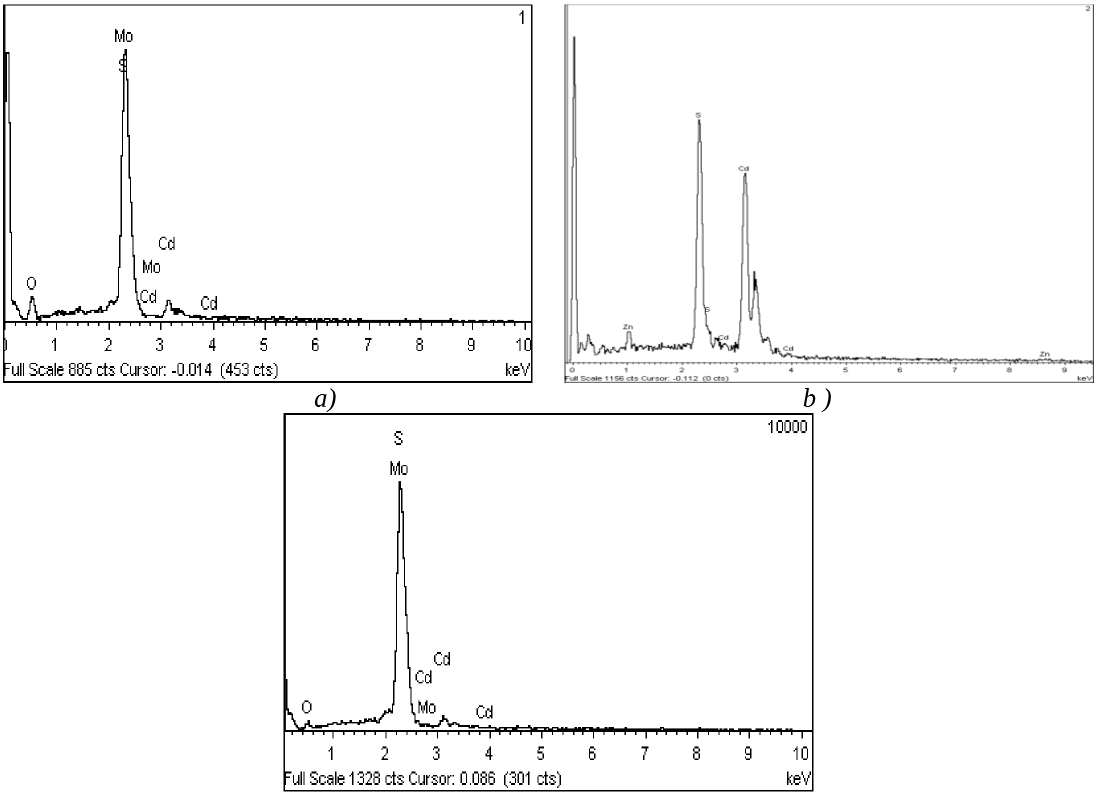
a) *b)*

c)

Fig. 2. (a-c). FESEM photographs of varying temperature annealed ZnCdS films.
a = 350^0C, (b = 400^0C, c) = 450^0C

3.3. Compositional analysis

The chemical composition of varying temperatures annealed ZnCdS films are confirmed by EDS analysis and shown in figure 3(a,b,c). Varying temperature annealed ZnCdS films deposited on the molybdenum substrate. The peak of molybdenum arise on the spectra is due to the substrate. It clearly shows that the sulphur peak overlaps with the molybdenum substrate. EDS spectra of annealed ZnCdS films at 350^0C indicates that the film have no traces of Zn was found and the spectra of cadmium (Cd), sulphur (S) in addition to oxygen elements are observed. The presence of oxygen is due to surface contamination. Further temperature increases to 400^0C, it is observed that the presence of Zn spectra. However a temperature increase up to 450^0C, it reveals that the films have again traces of Zn is absent. EDS patterns of varying annealing temperature of ZnCdS films with the parameters shown in Table 1. From the Table it is noticed that the elemental ratio of annealed films at 400^0C have the ratio of Zn is very much less than the Cd ratio.



a) *b)*

c)

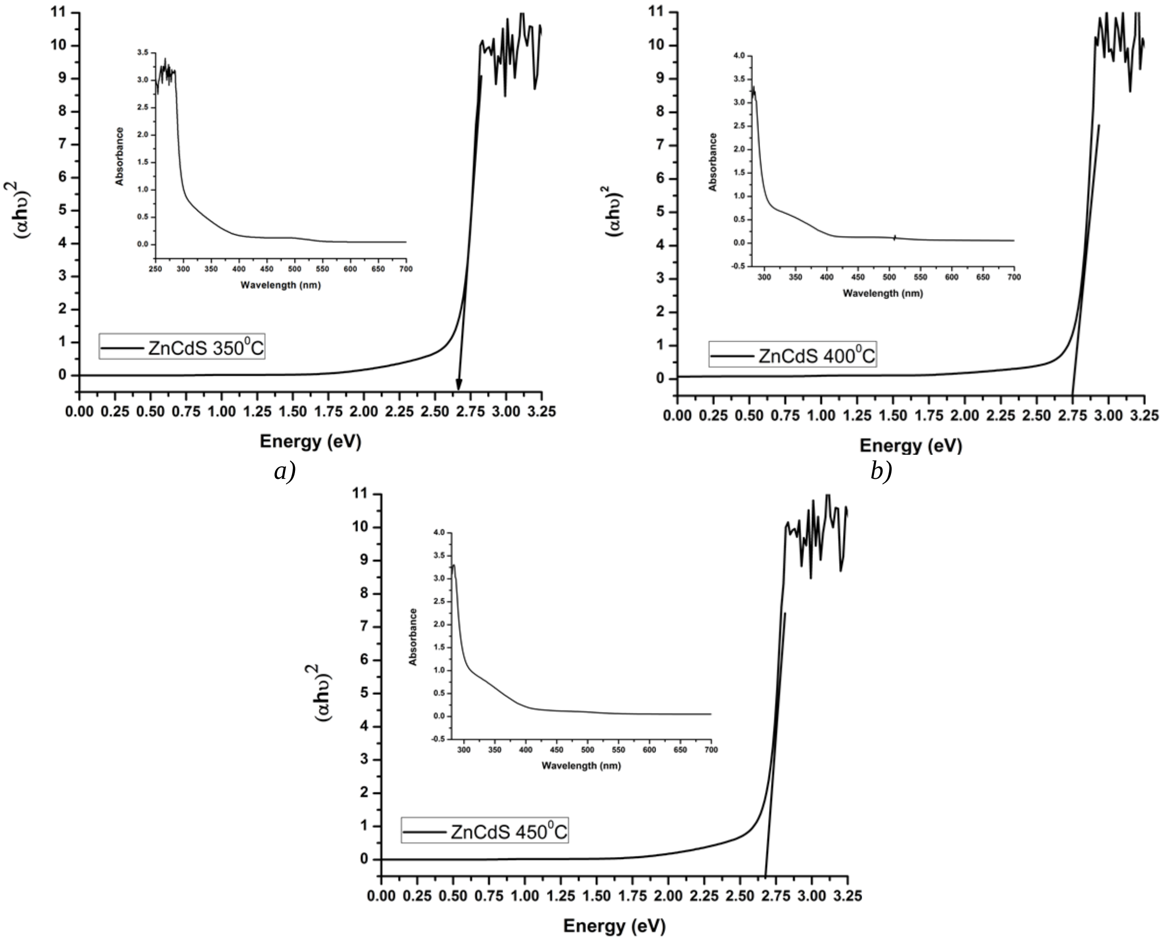
Fig. 3. (a-c). EDS spectra of varying temperature annealed ZnCdS films.
a = 350^{0}C, (b = 400^{0}C, c) = 450^{0}C

Table 1. Atomic percentage and weight percentage of varying temperature annealed ZnCdS thin films.

Elements	Atomic percentage			Weight percentage		
	350^{0}C	400^{0}C	450^{0}C	350^{0}C	400^{0}C	450^{0}C
Cd	3.49	42.72	4.37	7.97	64.25	6.74
S	5.77	41.22	1.49	3.76	17.48	0.66
Zn	-	5.4	-	-	4.82	-
Mo	36.25	10.49	65.49	70.58	13.45	86.30
O	54.49	-	28.65	17.69	-	6.30

3.4. Optical study

ZnCdS is considered as direct bandgap semiconductor thin film. For optical studies film were developed on glass substrate. Figure 4(a,b,c) shows the change in absorption spectra due to change in wavelength of 250 nm-700 nm. Rseults of the absorption spectra shows higher annealing temperature exhibits lower absorption in visible region. Figure shows the energy bandgap was estimated from the absorbance data by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ where the interception of linear portion on the energy axis gives the energy bandgap of material. The relation between absorption coefficients (α) and photon energy ($h\nu$) is expressed to measure the energy bandgap (E_g) by the relation $\alpha h\nu = A\ (h\nu - E_g)^{1/2}$ [18].



a) b)

c)

Fig. 4. (a-c). Plot of (αhν)^2 versus energy of varying temperature annealed ZnCdS films.

It is evident from the graph that bandgap of annealed films increases as the annealing temperature increases upto 400^{0}C and at 450^{0}C, the bandgap decreases but is more than 350^{0}C. The bandgap decreases at 450^{0}C increases the average grain size. The decrease in bandgap by low annealing temperature (<350^{0}C) may be due to increase in crystalline nature of the film [19]. The observed bandgap of annealed films at 350^{0}C, 400^{0}C and 450^{0}C are 2.66 eV, 2.75 eV and 2.70 eV respectively.

Table 2. Shows the average grain size and bandgap of annealed ZnCdS films (350^{0}C, 400^{0}C and 450^{0}C).

S.No.	Annealed Temperature range (^{0}C)	Average crystalline size (nm)	Bandgap (E_g) (eV)
1.	350	23	2.66
2.	400	25	2.75
3.	450	26	2.70

3.5. Photoluminescence studies

The photoluminescence study is carried out to know the optical behavior of varying temperatures annealed ZnCdS films grown on molybdenum substrate as shown in Figure 5(a,b,c). As evident from the the spectra that visible emission peak is observed at 565 nm corresponds to ZnCdS crystalline thin film. Bandgap peak is appeared at annealing can eliminate defects and stresses inside the crystal lattice. The removal of defects decrease in deep-trap- emission [20] and enhances the crystallinity of annealed films.

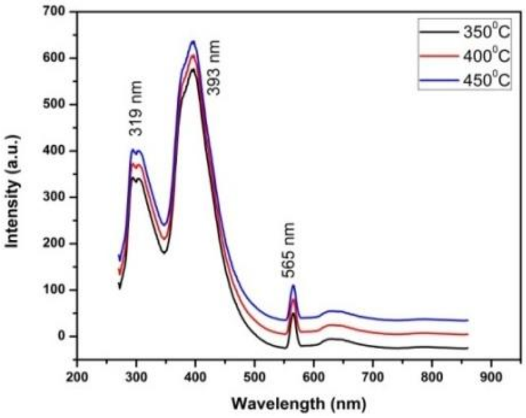


Fig. 5. PL spectra of varying temperature annealed ZnCdS films.

4. Conclusion

ZnCdS nanocrystalline films can be prepared by chemical method using non-aqueous medium. CBD allows for the preparation of films of zinc cadmium sulfide on a molybdenum plate more uniformly using non aqueous medium as compared to aqueous medium. The success of the method depends upon the manner of preparation of a molybdenum substrate coating method which remains stable during the deposition process. The XRD shows the different phases of ZnCdS. The average crystallite size of ZnCdS particle was around 25 nm which increases on annealing. The films prepared with the optimized deposition parameters show preferential orientation along (101) plane. The SEM images show uniform, smooth, compact and void-free surfaces at annealing temperatures. The excitation peak of ZnCdS is observed by PL at 556 nm. ZnCdS film presented have good characteristics to be used as for solar cells, photovoltaic and sensor application.

Acknowledgements

The authors are thankful for the fund provided by Ministry of HRD, Govt. of India, Central Instrumentation Facility Lab., Birla Institute of Technology Mesra, Ranchi and Indian Institute of Technology, Dhanbad for various Characterizations.

References

[1] W. E. Devaney, W. S. Chen, J. M. Stewart, R. A. Mickelsen, IEEE Transactions on Electron Devices 37, 428 (1990); https://doi.org/10.1109/16.46378

[2] Shashikant Rajpal, S.R. Kumar, Solid State Sciences 108, 106424 (2020); https://doi.org/10.1016/j.solidstatesciences.2020.106424

[3] Toshiyuki Yamaguchi, Jiro Matsufusa, Akira Yoshida, Japanese Journal of Applied Physics

31, 703 (1992); https://doi.org/10.1143/JJAP.31.L703

[4] T. Walter, M. Ruckh, K. O. Velthaus, H. W. Schock, Proceedings of the 11th EC photovoltaic solar energy conference, 124 (1992)

[5] S. Y. Kim, D. S. Kim, B. T. Ahn, H. B. Im, Journal of Materials Science: Materials in Electronics 4(2), 178 (1993); https://doi.org/10.1007/BF00180470

[6] S. Rajpal, V. Bandyopadhyay, Journal of Nano- and Electronic Physics 5(3), 03021 (2013)

[7] C. Tian, R. Tang, S. Hu, W. Li, L. Feng, J. Zhang, L. Wu, Adv. Mat. Research 784(8), 225 (2011); https://doi.org/10.4028/www.scientific.net/AMR.225-226.784

[8] Y. Raviprakash, Kasturi V. Bangera, G. K. Shivakumar, Current Applied Physics 10(1), 193 (2010); https://doi.org/10.1016/j.cap.2009.05.020

[9] Akio Kuroyanagi, Thin Solid Films 249, 91 (1994); https://doi.org/10.1016/0040-6090(94)90091-4

[10] Takeshi Karasawa, Kazuhiro Ohkawa, Tsuneo Mitsuyu, Journal of Applied Physics 69, 3226 (1991); https://doi.org/10.1063/1.348541

[11] S. A. Telfer, C. Morhain, B. Urbaszek, C. O'Donnell, P. Tomasini, A. Balocchi, K. A. Prior, B. C. Cavenett, Journal of Crystal Growth 214(1), 197 (2000); https://doi.org/10.1016/S0022-0248(00)00080-4

[12] V. B. Sanap, B. H. Pawar 3(2), 39 (2011).

[13] S. Kumar, S. Rajpal, S. K. Sharma, D. Roy, S. R. Kumar, Digest Journal of Nanomaterials and Biostructures 12(2), 339 (2017).

[14] V. B. Sanap, B. H. Pawar, Chalcogenide Letters 6(8), 415 (2009).

[15] Jiyon Song, Sheng S. Li, S. Yoon, W. K. Kim, Jihyun Kim, J. Chen, V. Craciun, T. J. Anderson, O. D. Crisalle, Fan Ren, 31st IEEE Photovoltaic Specialists Conference, 449 (2005).

[16] V. B. Sanap, B. H. Pawar, Chalcogenide Letters 7(3), 227 (2010).

[17] M. Kamruzzaman, Kamal Uddin Azad, Jiban Podder, Asian Journal of Applied Sciences 7(7), 607 (2014); https://doi.org/10.3923/ajaps.2014.607.620

[18] S. Rajpal, S. R. Kumar, Physica B: Condensed Matter 534, 145 (2018); https://doi.org/10.1016/j.physb.2018.01.046

[19] M. A. Hossain, M. A. Islam, M. M. Aliyu, P. Chelvanathan, T. Razykov, K. Sopian, N. Amin, Energy procedia 33, 214 (2013); https://doi.org/10.1016/j.egypro.2013.05.060

[20] Changqing Jin, Wei Zhong, Xin Zhang, Yu Deng, Chaktong Au, Youwei Du, Crystal Growth and Design 9(11), 4602 (2009); https://doi.org/10.1021/cg9009724