Journal of New Technology and Materials(JNTM)
J. New Technol. Mater.
Vol. 07, N°02 (2017)93-99

OEB Univ. Publish. Co.

Effect of dye extracts on the optical properties of chemically deposited ZnS thin films

P. A. Nwofe

Department of Industrial Physics, Ebonyi State University, Abakaliki, P.M.B 053, Nigeria

Corresponding author: patricknwofe@gmail.com

Received date: August 03, 2017; accepted date: Dec 16, 2017

Abstract

The study reports on the influence of dye extracts of Naulcea latifolia (*Uvuru*-ilu) leaves *on the optical properties of Zinc Sulphide (ZnS) thin films grown by the chemical bath deposition method. The concentration of the ZnS thin films were varied in the range 0.1 M to 0.7 M and other deposition variables (pH, and bath temperature) were kept constant. The films were characterised using optical spectroscopy (transmittance versus wavelength, reflectance versus wavelength, absorbance versus wavelength) to investigate the optical constants (optical absorption coefficient, energy bandgap, extinction coefficient and the optical density). The results show that the transmittances of the dye –sensitized films were higher compared to the as-deposited layers. The transmittance exhibited a concentration dependent behaviour for films grown without addition of the dye extracts. The transmittance were typically < 50 % for the non dye-sensitized ZnS thin films grown at concentrations ≤ 0.3 M and > 50 % for films grown at concentrations ≥ 0.5 M. However the presence of the dye extracts increased the transmittances significantly, independent of the different concentrations used. The energy bandgap was direct, with values ≤ 3.60 eV for films grown at concentrations ≥ 0.5 M and 3.80 eV for films grown at lower concentrations. These values strongly suggest the use of these films in optoelectronic applications and related device designs.*

Keywords: Transmittance; dye extracts; Naulcea latifolia (*Uvuru*-ilu); *concentrations; optical constants;*

1. Introduction

Zinc Sulphide is a wide bandgap semiconductor material that has been under investigation for use in various device designs over the years. The applications in optoelectronic devices, medicinal use, luminescence materials, and in various industrial uses have been widely reported in the literature [1-6]. For instance, in photovoltaic applications, ZnS has been used as window layers to partner the p-type absorber layers in heterojunction solar cell devices [7]. In the literature, reports by different research groups indicate that ZnS thin films can grown using variety of different thin film technology including; chemical bath deposition [8-9], spray pyrolysis [10], physical vapour deposition [11-12], pulsed laser deposition [13], glancing angle deposition technique [14], pulsed ion beam deposition technique [15], successive ionic layer and reaction (SILAR) technique [16], RF sputtering [17-18], photo-electro chemical methods [19], thermal evaporation [20], dip coating [21], electrodeposition [22], pulsed electrodeposition [23], and screen printing techniques [24] among others.

Among these different deposition techniques, chemical bath deposition method is a more commonly used technique because it offers high quality thin films at low temperature, suitable for depositing large area semiconductor thin films, and has proved to be the simplest and the most economical since the equipment used for deposition are very common and easily affordable. According to the literature [25], it is generally understood that thin film deposition on a substrate can be achieved by either or all of the two steps of nucleation and particle growth. For thin films grown by the chemical bath deposition technique, the process of nucleation and film growth are chiefly due to an inter-play of other processes which includes; simple-ion cluster mechanism, simple hydroxide cluster mechanism, complex ion-by-ion decomposition mechanism, and the complex-cluster decomposition mechanism. The simple ion process could diffuse to the substrate to initiate nucleation and the nucleated layers then grow by adsorption of ions in the solution and or nucleation of new crystals. The films formed by the crystals are generally held together by weak forces (Van der Waals forces). Thus, the chemical bath deposition process mostly employs a controlled chemical reaction to achieve thin film deposition by precipitation of the desired compound.

In the literature [26-29], the intrinsic properties of ZnS thin films has been modified by introducing different dopants in order increase its versatility in device applications. The use of dye extracts of Naulcea latifolia (*Uvuru*-ilu) to optimise the properties of ZnS thin films has not been reported elsewhere to the best of our knowledge hence this report is novel in engineering the

properties of ZnS for enhanced device applications. In the present investigation, the aim of the study is to grow thin films of ZnS, dope the layers with a given volume of Naulcea latifolia (*Uvuru*-ilu) dye extracts, and to characterise the layers using optical spectroscopy to investigate the optical constants. The influence of the dye extracts on the optical properties are reported. This report is a fundamental step toward exploring new pathways for utilization of ZnS-based thin films in different device designs.

2. Materials and Methods

2.1 Substrate cleaning and reagents

Substrate cleaning plays a fundamental role in thin film deposition. The glass slides of dimensions 75 mm by 25 mm by 1mm, were purchased from local suppliers. Prior to the deposition, the glass substrates were cleaned first by a mild detergent solution, then degreased with acetone, and further etched with 5% of hydrochloric acid (HCl) for 60 minutes. Finally, the glass slides were cleaned ultrasonically by double distilled water and then dried in air. All the source chemicals used for the deposition of ZnS thin films were analytical grade, and were obtained from Sigma Aldrich UK through local suppliers and employed directly without further purification.

The source of the zinc ions and sulphide ions were Zinc sulphate ($ZnSO_4.7H_2O$) and Thiorea $(SC(NH_2))_2$ respectively. The complexing agent used was hydrazine (N_2H_4). A 25% liquor ammonia (NH_4OH) was used for pH adjustment.

2.2. Extraction of the Naulcea latifolia (*Uvuru*-ilu dye extracts

The aqueous extraction method according to the literature [30] was used in the investigation. A 20 gm of fresh leaves of Naulcea latifolia (*Uvuru*-ilu) were boiled in 200 ml distilled water at 358 K for 60 minutes. The decolorized leaves were carefully taken out from the extraction solvent. The dye extracts were filtered into an already clean and dry container and sealed with the cap and stored at room temperature.

2.3. Deposition of the dye-sensitised ZnS thin films

The different concentrations (0.1 M to 0.7 M) of the Zn^* source were prepared and kept in separate containers and labelled accordingly. A 0.3 M of Thiorea and 0.2 M of the complexing agent were also prepared, labelled and kept in separate containers. The temperature of the reaction bath was maintained at 333 K and the rotational speed of the stirrer was fixed at 50 revolutions per minute. The ZnS thin films were grown by mixing 30 ml of the source of zinc ions with 30 ml of the source of sulphide ions, 10 ml of the complexing agent for the as –grown samples. In the dye-sensitised ZnS thin films, a 10 ml of the dye extract was also included before stirring for 15 minutes. The pH were all maintained at 9.6 in both the as-gown and the dye-sensitised films by drop-wise addition of the ammonia solution. The glass substrates were held vertically using a synthetic foam and deposition was allowed to take place for 2 hours. The films were then removed carefully at the end of the deposition time, and washed with distilled water, and then dried.

2.4. Characterisation

The film thickness was measured using standard procedure in the current literature as contained in Rika and Hardhienata [31] and by other research groups [32-33], hence the film thickness was measured using the gravimetric method or double weight method. The film thickness were in the range 90 nm to 101 nm for the as-deposited layers and between 120 nm to 140 nm for the dye-sensitised layers The transmittance and reflectance versus wavelength measurements were done using a Unico –UV-2102 PC spectrophotometer operated at normal incident of light in the wavelength range of 300 nm to 1000 nm. All the transmittance and reflectance versus wavelength measurements were done at room temperature of 298 K with a blank glass substrate in the reference beam path before inserting the films for actual measurements.

3. Results

Fig. 1 show the transmittance versus wavelength plots for the as-grown layers at the different concentrations investigated in the study. The transmittance exhibited a concentration dependent behaviour in that the transmittances were higher for films grown at concentrations ≤ 0.3 M and decreased by almost 50% for films grown at concentrations ≥ 0.5 M. This behaviour was attributed to the increase in the film thicknesses at the higher concentrations. Such increase can induce increased crystallites sizes in the films grown at the higher concentrations. The increased crystallites size as they tend to approach the bulk crystalline ZnS could lead to larger unfilled inter-granular volume so that the absorption per unit thickness is reduced in the films, hence causing the observed effects.

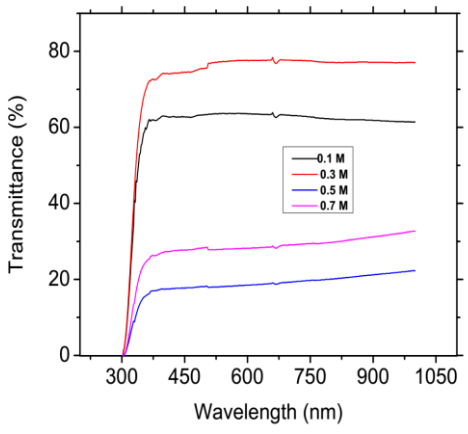


Fig. 1. Transmittance vs wavelength plots for as-grown ZnS films

In the literature, reports by other research groups indicate the ZnS thin films generally exhibit high transmittances independent of the deposition technique [34-35].

Fig. 2 show the variation of the absorbance against wavelength for the as-deposited layers. The result indicate that the absorbance decreased in the region of higher photon energies (lower wavelengths) up to the region of the fundamental absorption, and then decreased gradually to minima at the longer wavelength region. Such behaviour are commonly observed in the absorbance versus wavelength plots for various chalcogenides thin films [34, 36-38]. As expected, the absorbance were typically lower for the films grown at the higher concentrations and increased otherwise. The reason for this behaviour was attributed to that adduced earlier since the thicker films (higher concentrations) will show more absorbance as observed in the study.

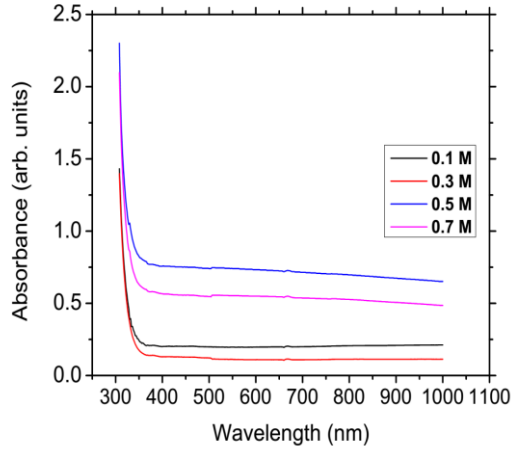
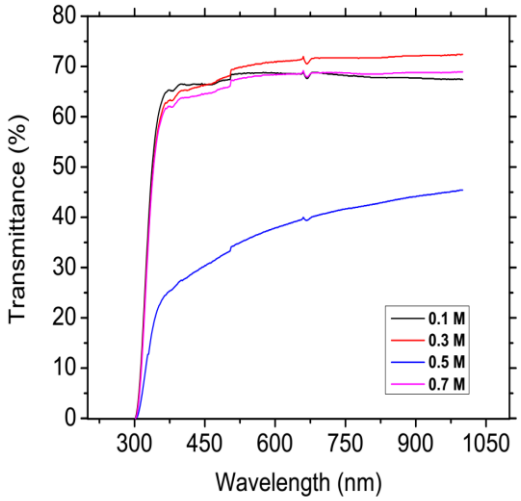


Fig. 2. Absorbance vs wavelength plots for as-grown ZnS films

Fig. 3 gives the plots for the transmittance against wavelength for the dye-sensitized ZnS thin films. The results show that the presence of the Naulcea latifolia (*Uvuru*-ilu) dye extracts increased the transmittances significantly independent of the concentrations. In particular, all the films exhibited transmittances > 50%. Variation of the transmittances of ZnS thin films caused by introduction of different dopants or deposition variables have been widely reported in the literature [39-40].

Fig. 4 show the variation of the absorbance vs wavelength spectra for the dye-sensitised ZnS thin films. Genearally the trend of sharp decrease down the fundamental absorption before flattening is also observed as shown on Fig. 4. However the absorbance values were higher for the former compared to the latter. The results indicate that the influence of the Naulcea latifolia (*Uvuru*-ilu) dye extracts decreased the absorbance significantly independent of the concentrations. In particular, all the films exhibited transmittances > 50%. Varition of optical properties induced by the introduction of different impurities to modify the properties of ZnS thin films have been widely reported by different research groups [26-29, 41-42] independent of the deposition techniques.



F.ig. 3. Transmittance vs wavelength plots for dye-sensitized ZnS thin films

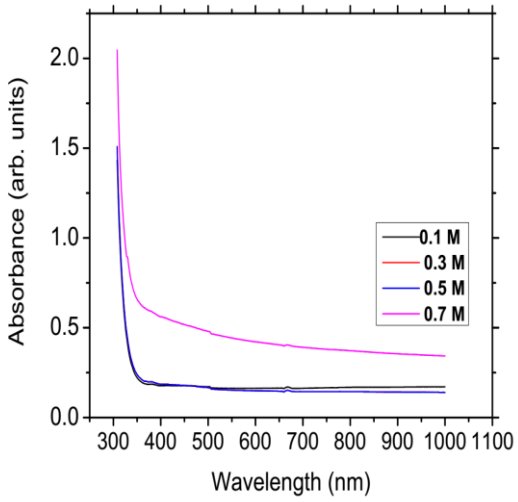


Fig. 4. Absorbance vs wavelength plots for dye-sensitised ZnS thin films

Fig. 5 show the plots of $(\alpha h\nu)^2$ vs $h\nu$ for the as-deposited layers. The optical absorption coefficient α, was calculated using the relation [43];

$$\alpha = \frac{1}{d}\ln\left(\frac{100}{T\,\%}\right) \quad (1)$$

In equation (1), α retains its meaning, d is the film thickness, and T is the transmittance in percentage. The values of the optical absorption coefficients were used to evaluate the energy bandgap using the formula according to the literature [44];

$$(\alpha h\nu) = B(h\nu - E_g)^n \quad (2)$$

As contained in equation (2), α retains its meaning, h is the Planck's constant, ν is the frequency of the electromagnetic radiation, B is an energy independent constant, but generally depend on the refractive index and the effective masses of the hole and electron respectively as contained in the literature [43-44], Eg is the energy bandgap, and n is an index that determines the nature of the transition exhibited by the materials under investigation. In direct transition, it is universally accepted that n = 1/2. As shown on Fig.5, the transition are all direct with values in the range 3.6 eV to 3.8 eV. The values are within the range reported by other authors [26, 34-35]. These values also indicates that the films could be utilized in different optoelectronic applications including lasers, light emitting diodes (LED), and in solar cell devices.

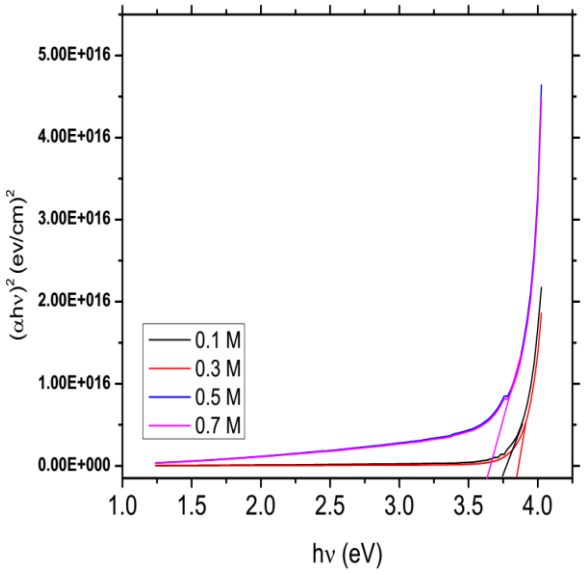


Fig.5. Plots of $(\alpha h\nu)^2$ *vs* $h\nu$ for as-grown ZnS films

Fig. 6. indicates the influence of the dye extracts on the plots of $(\alpha h\nu)^2$ vs $h\nu$. A close look on Fig. 6, clearly show that the energy bandgap were slightly reduced compared to the values of the as-deposited layers. This behaviour was attributed to better crystal ordering, leading to quantum confinement in the dye-sensitized layers.

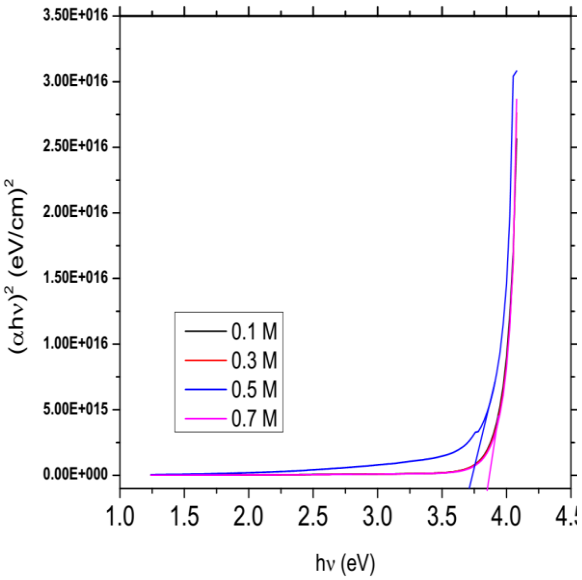


Fig. 6. Plots of $(\alpha h\nu)^2$ *vs* $h\nu$ for the dye-sensitised ZnS films

Fig. 7 shows the variation of the extinction coefficient with photon energy in the as-grown films. The extinction coefficient was calculated using the relation contained in the literature[44-45];

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

In equation (3), α retains its meaning, λ is the wavelength (300 nm to 1000 nm), and π is a constant. The extinction coefficients increased gradually down to the region of the fundamental absorption and then increased. Such behaviour is typical of most thin films including the chalcogenides family. This behaviour observed in Fig. (6) is in agreement with the reports of other research groups [43, 45-47]. As shown in Fig. 6, it was also observed that the films grown at concentrations ≥ 0.5 M exhibited lower values of the extinction coefficient with the minima occuring in the range 0.018 to 0.020.

However for films grown at concentrations ≤ 0.3 M, the values of the extinction coefficient were typically higher, exhibiting a minima at 0.05.

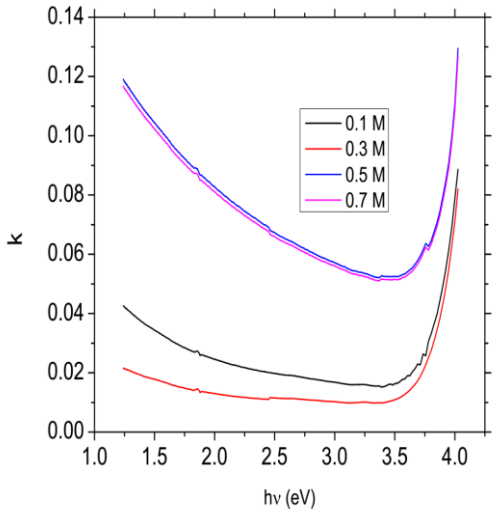


Fig. 7. Plots of extinction coefficient k, vs photon energy for as-grown ZnS films

Fig. 8. show the change imposed on the variation of the extinction coefficient with photon energy by the dye extracts. The values the extinction coefficient obtained from normal-incidence transmittance spectra were generally lower for the dye sensitized films compared to the as-deposited ZnS layers. In particular, the dye-sensitised ZnS layers exhibited a minima in the range 0.015 to 0.03 as indicated in Fig. 8. However the graphs also portrayed similar trend of parabolic shape as obtained in the as-grown ZnS layers (Fig. 7).

Figi. 9 show the variation of the optical density with the photon energy for the as-deposited ZnS thin films at the various concentrations investigated in the study. The optical density was calculated using the relation [43];

$$Optical \quad density \quad = \quad \alpha d \qquad (4)$$

In equation (4), α retains its meaning and d is the film thickness. The optical density exhibited similar shapes with the $(\alpha h\nu)^2$ vs $h\nu$ graphs possibly due to the relationship in the formula. The optical density were typically in the range 0.2 to 5.4.

Fig.10 indicate the influence of the dye extracts on the graphs of the optical density against photon energy on the dye-sensitized layers. The values of the optical density was between 0.3 to 5.7. It could be recalled that the transmittances of the dye-sensitised ZnS layers (Fig.3) were generally higher than that of the as-grown ZnS layers hence the cause of the observed effect.

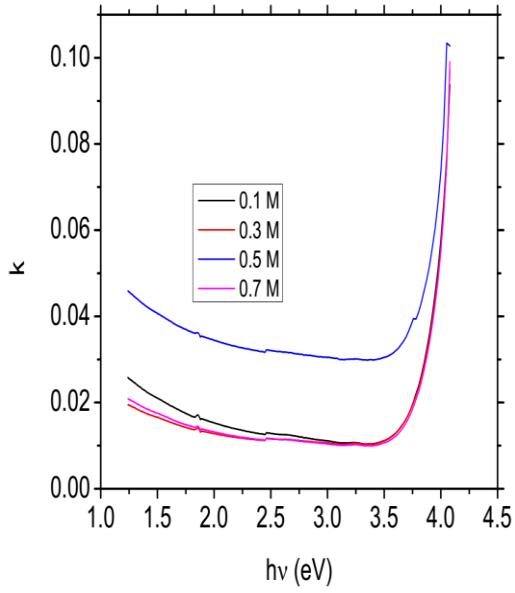


Fig. 8. Plots of extinction coefficient k, vs photon energy for dye-sensitized ZnS layers

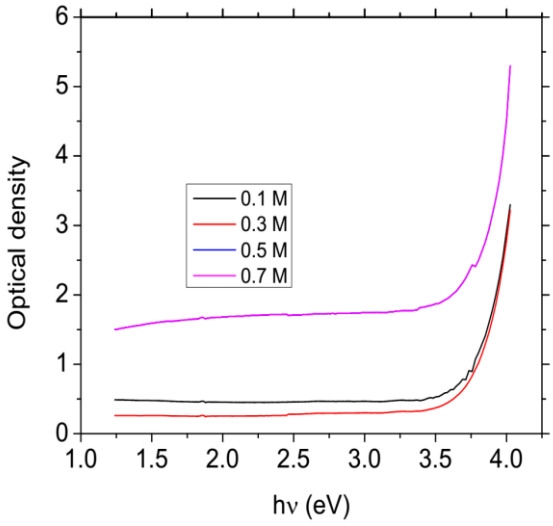


Fig. 9. Plots of optical density vs photon energy for as-grown ZnS layers

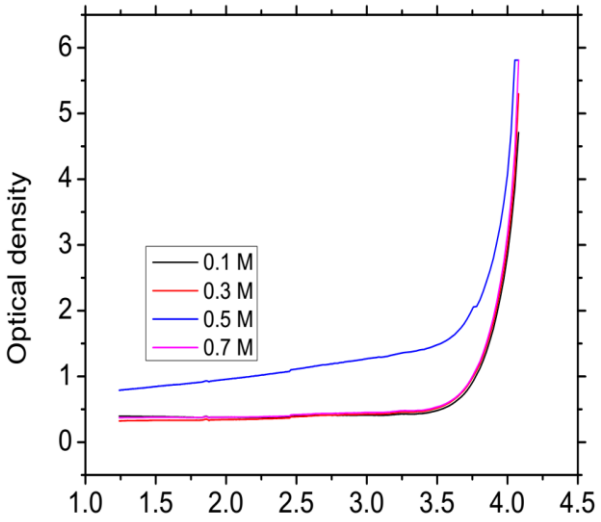


Fig. 10. Plots of optical density vs photon energy for the dye-sensitised ZnS layers

4. Conclusions

The influence of Naulcea latifolia (*Uvuru*-ilu) dye extracts on the optical properties of ZnS thin films is reported. The results show that the dye extracts modified the optical properties significantly. In particular, the transmittances of the dye-sensitized layers were higher compared to the transmittances of the as-deposited ZnS layers. The energy bandgap were found to be direct in both cases, with values in the range 3.6 eV to 3.8 eV. The extinction coefficient were typically lower for the dye-sensitised ZnS layers. The values of the energy bandgap strongly indicate that the films could be used in different device designs including optoelectronic applications.

References

[1] K. Nabesaka, Y. Ishikawa, Y. Hosokawa, Y. Uraoka, *Applied Physics Express*, *10* (2017) 021201.
[2] A. Q. Meng, X. Xiong, K. Qiu, Y. Lin, *Nanotechnology*, *28* (2017) 105502.
[3] M.C. Divyasree, N.K. Siji Narendran, K. Chandrasekharan, in: J. Ebenezar, (Ed.), *Recent Trends in Materials Science and Applications: Nanomaterials, Crystal Growth, Thin films, Quantum Dots, & Spectroscopy (Proceedings ICRTMSA 2016)* Vol. 189, Springer, (2017).
[4] M. Khalkhali, H. Zeng, Q. Liu, H. Zhang, *The Journal of Physical Chemistry C*, *120* (2016) 7870.
[5] Y.K. Liao, Y. T. Liu, D.H. Hsieh, T.L. Shen, M.Y. Hsieh, A.J. Tzou, Y.P. Shen, *Nanomaterials*, *7* (2017) 78.
[6] J. Gan M.G. Kang, M. A. Meeker, G. A. Khodaparast, R.J. Bodnar, J.E. Mahaney, S. Priya, (2017). *Journal of Materials Chemistry C*, *5* (2017) 5387.
[7] K. Qiu, D. Qiu, L. Cai, S. Li, W. Wu, Z. Liang, H. Shen, *Materials Letters*, *198* (2017) 23.
[8] G. Wary, M. P. Sarma, *Indian Journal of Pure & Applied Physics (IJPAP)*, 54 (2016) 385.
[9] B. Pejjai, V.R.M. Reddy, K. Seku, K., T.R.R.VKotte, C. Park, *Optik-International Journal for Light and Electron Optics*, 130 (2017) 618.
[10] K. Alnama, B. Abdallah, S. Kanaan, *Composite Interfaces*, *24* (2017) 513.
[11] K. Mohammadrezza, N.A. Kobra, H. Arefe, *Journal of Research on Many Body Systems*, *6* (2016) 15.
[12] H.Howari, I. Uddin, *J. Modern. Mater.,* 2 (2016) 25.
[13] P. Patel, P. Shiv, J. C. Pivin, Ramesh Chandra, D. Kanjilal, L. Kumar. *Journal of Materials Science: Materials in Electronics,* 27 (2016) 5640.
[14] S. Wang, X. Fu, G. Xia, J. Wang, J. Shao, Z. Fan, *Applied surface science*, *252* (2006) 8734.
[15] Y. Shimotori, M. Yokoyama, H. Isobe, S. Harada, K. Masugata, K. Yatsui, *Journal of applied physics*, *63* (1988) 968.
[16] K. Priya, V.K. Ashith, G.K. Rao, G. Sanjeev, *Ceramic International*, 43 (2017) 10487.
[17] P. Chelvanathan, Y. Yusoff, F. Haque, Md. Akhtaruzzaman, M. M. Alam, Z. A. Alothman, M. J. Rashid, K. Sopian, N. Amin, *Applied Surface Science* 334 (2015) 138.
[18] L. Kong, J. Deng, L. Chen, *Chalcogenides Letts.,* 14 (2017) 87.
[19] F. Kurnia, Y.H. Ng, Y. Tang, R. Amal, N. Valanoor, J.N Hart, *Crystal Growth & Design*, *16*, (2016) 2461.
[20] Rashmitha, M.G. Mahesha, International Conference on Materials Science and Technology, St Thomas College Pala, 5-6 June, 2016;
[21] S.G. Pandya, *International Journal of Recent Scientific Research,* 2 (2016) 14700.
[22] M.L. Madugu, O.I.O. Olusola, O. K. Echendu, B. Kadem, I.M. Dharmadasa, *Journal of Electronic Materials*, 45 (2016) 2710.
[23] M.B. Dergacheva, K. A. Urazov, G. M. Khussurova, K. A. Leontyeva, *Coatings* , 6 (2016) 14.
[24] J.G. Christobel, *International Education and Research Journal*, *2* (2016) 2228.
[25] L.I. Maissel, R. Glang, Handbook of thin film technology, McGraw Hill Inc, USA, 1970.
[26] K.S. Wanjala, W. K. Njoroge, J. M. Ngaruiya, *International Journal of Energy Engineering*, 6 (2016) 1.
[27] M. Sreedhar, I. Neelakanta Reddy, P. Bera, T. S. Shyju, C. Anandan, *Surface and Interface Analysis* 49, (2017) 284.
[28] M.J. Rivera-Medina, J. Hernández-Torres, J. L. Boldú-Olaizola, J. Barreto-Rentería, J. M. Hernández-Alcántara, V. Jancik, J. C. Alonso-Huitrón, *RSC Advances* , 6 (2016) 107613.

[29] E.A. Karhu, N. Tolstik, E. Sorokin, S. Polyakov, R. Zamiri, V. Furtula, U.J. Gibson, IEEE *Lasers and Electro-Optics, (2016) 1.*
[30] D.B. Patil, K. N. Patil, P. V. Gaikwad, P. J. Patil, U. L. Shewale, S. B. Bhamburdekar, International *Journal of innovative research in multidisciplinary field*, 2 (2016) 135.
[31] W. Rika, H. Hardhienata, *IOP Conference Series: Earth and Environmental Science,* 54 (2017) 012094.
[32] T.H. Abood, A.T. Mohi, M.S. Karim, *World Scientific News*, *67* (2017) 149.
[33] K.S. Aneja, H.L. Mallika Bohm, A.S. Khanna, S. Bohm, *FlatChem,* 1 (2017) 11.
[34] R.W. You, Y.P. Fu, *Adv., Tech., Innovation,* 2 (2016) 95.
[35] D.C. Harish Kumar, H.M. Mahesh, I*nternational Journal of Advance Research, Ideas and Innovations in Technology*, 3 (2017) 97.
[36] P.E. Agbo, P.A. Nwofe, C.N. Ukwu, F.U. Nweke, *International Journal of Nanomaterials and Chemistry,* 2 (2016) 1.
[37] P.E. Agbo, P.A. Nwofe, C.A. Elekwa, M.N. Nnabuchi, *J. Ovonic Res.,* 12 (2016) 163.
[38] A.M. AL-Diabat, N. M. Ahmed, M. R. Hashim, K. M. Chahrour, M. Bououdina, *Procedia Chemistry* 19 (2016) 485.
[39] K.S. Wanjala, W.K. Njoroge, J.M. Ngaruiya, International Journal of Energy Engineering, 6 (2016) 1.
[40] E. Shahriari, Z.M. Farsani, M.G. Varnamkhasti, R. Zamiri, *Optical and Quantum Electronics*, *49* (2017) 151.
[41] D. Hwang, C.S Son, *Journal of Nanoscience and Nanotechnology*, *17* (2017) 5042.
[42] U. Jabeen, T. Adhikari, S.M. Shah, J.M. Nunzi, A. Badshah, I. Ahmad, *The European Physical Journal Applied Physics*, *78* (2017) 34810.
[43] P.A. Nwofe, P.E. Agbo, *J. Non-Oxide Glasses,* 9 (2017) 9.
[44] J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood Cliffs, New Jersey, 1971.
[45] R. Vishwakarma, A. Sahoo, *Journal of Advanced Physics*, *6* (2017) 274.
[46] M. Cheikh , M. Chaik , H. El aakib, M.Elyaagoubi, M. Aggour, A. Outzourhit, *Journal of Chemical, Biological and Physical Sciences*, 7 (2017) 247.
[47] D.R. Kim, D. Hwang, C.S. Son, Y.G. Son, *Journal of Nanoscience and Nanotechnology*, *17* (2017) 5046.
[48] G. Salman, M. Medhat, A. Muhammed, *Aust. J. Basic & Appl. Sci.,* 11 (2017) 29.