CHARACTERIZATION, MORPHOLOGY AND ELECTRICAL PROPERTIES OF CHEMICALLY DEPOSITED NANOCRYSTALLINE PbS/Si HETEROJUNCTION THIN FILMS

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A nanocrystalline thin films of PbS with different thickness (400, 600)nm have been prepared successfully by chemical bath deposition technique on glass and Si substrates. The structure and morphology of these films were studied by X-ray diffraction and atomic force microscope. It shows that the structure is polycrystalline and the average crystallite size has been measured. The electrical properties of these films have been studied, it was observed that D.C conductivity at room temperature increases with the increase of thickness, From Hall measurements the conductivity for all samples of PbS films is p-type. Carrier's concentration, mobility and drift velocity increases with increasing of thickness. Also p-PbS/n-Si heterojunction has been fabricated at different thickness. The reverse bias capacitance was measured as a function of bias voltage, and it is indicated that these HJs are abrupt. The capacitance decreases with increasing the reverse bias, and fixed at high value of reverse bias voltage. The capacitance increases with increasing thickness. The width of depletion layers decreases with increases thickness. The value of highest built in potential has been measured. The current-voltage characteristic show that the forward current at dark condition varies exponentially with applied voltage and the junction was coinciding with recombination-tunneling model. The difference between forward and reverse current with applied voltage indicates that the junction has a high rectification characteristic. The value of ideality factor was varies between (1.821-1.715), From the I-V measurements under illumination, the photocurrent increased with increasing thickness.

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1. Introduction

Lead sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate energy band gap of 0.4 eV at 300K and a relatively large excitation Bohr radius of 18 nm. These properties make PbS very suitable for infrared detection application. This material has also been used in many fields such as photography, Pb^{2+} ionselective sensors and solar absorption. In addition, PbS has been utilized as photoresistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings.[1,2] These properties have been correlated with the growth conditions and the nature of substrates. Their attractiveness arises from their low synthetic cost, their solution processing ability and the dependence of their optoelectronic properties as a function of size, shape, doping and surface chemistry. Therefore, many studies on shape controlled synthesis of semiconductor nanocrystals with different nanostructures have been reported.[3,4]. For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition, spray pyrolysis, photoaccelerated chemical deposition, microwave heating and chemical bath deposition (CBD).[5]

It is well known that the chemical bath deposition technique (CBD) is the most convenient and frequently used deposition technique to grow PbS thin films. It has been found that the properties of chemically deposited PbS thin films depend strongly on the growth conditions. Typically, this typeof PbS films are deposited at room temperature and have a well-defined grainy

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with somewhat loose compact structure, which has a marked influence on their photosensitivity properties.[6,7]

The morphological structure characteristic of chemically deposited PbS films evidenced in surface images measured by scanning electron microscopy is also manifested on their electrical and optical properties. On one hand, the features of the electrical transport in PbS films are those characteristics of polycrystalline materials constituted by grains and grain boundaries. On the other hand, the surface roughness and voids in the films strongly affects their reflection and transmission spectra. In the latter case, it would be expected that the differences between the optical properties of polycrystalline films and bulk PbS would arise mainly from their different morphological structure.[2,3].

We have selected the CBD method owing to its many advantages such as low cost, large area production and simplicity in instrumental operation. In this present study, we demonstrated simple CBD for making different PbS nanostructures. Of particular interest of the study is the dependence of the optical properties of PbS on morphology and shape, with the hope that such knowledge will enable us to construct efficient nanomaterials for electroluminescent devices PbS band gap can be changed by changing the grain size of the nanocrystalline structure with lattice constant of 5.936A.[8]. Thus many researchers have reported CBD to synthesize PbS thin films in literature. The aim of this paper is to preparation of nanocrystalline PbS/Si heterojunction and investigates the effect of thickness on the structure, morphology and electrical properties of PbS nanoparticles prepared by the CBD method.

2. Experimental

The lead sulfide films were deposited by the chemical bath deposition. Before the deposition, the glass substrate were very carefully cleaned using oxidant mixing ($K_2Cr_2O_7$:H_2SO_4), HNO_3, 1% EDTA, and successive rinsing with bi-distilled water. The cleaning state of the substrate surface is very important for the quality of the film formation. The deposition of PbS films was done in a solution prepared in a 100 ml beaker by the sequential addition of 5ml of 0.5M lead acetate, 5ml of 2M sodium hydroxide, 6ml of 1M thiourea and 2ml of 1M triethanolamine. The solution was diluted with deionized water to complete a total volume of 100ml. To obtain the films, the glass substrates were immersed into the solution, supported on the wall of the beaker and the beaker was put on the stirrer. The temperatures of the solution for growth were 20º C and kept constant for all deposition time. For this, the beaker with the reactive solution was immersed in water heating bath circulator, the PH was measured by PH meter and kept at 10, and here we analyze the samples obtained after 180min of deposition.

Microstructure surface topography was estimated using AFM by AA3000 Angstrom advanced lmtd. The resultant films were uniform, homogeneous, well adhered to the substrates and brown black in color, and the XRD phase patterns of the PbS deposited film of several thicknesses (0.4, 0.6μm) are established using Shimadzo x-ray difractometre model 6-2006. The electrical resistance has been measured as a function of the temperature (T). The measurements have been done with used sensitive electrometer type of Keithly Digital Electrometer (616) and vacuum electric oven. The resistivity and conductivity as a function of thickness can be calculated from these measurements.

I-V characteristics with dark for PV (at forward and reverse bias) and C-V characteristics have been measured with different thickness. The C-V measurement is useful to determine the type of the heterojunction (abrupt or graded), built-in potential (V_{bi}), concentration and the width of junction by using LRC meters model HP-R2CC4274A and 4275A, from measuring the capacitance of PbS/ Si heterojunction films as a function of reverse bias(0-5)V, the value of V_{bi} can be found from plots the relation between $1/C^2$ and reverse bias, then the interception of the straight line with voltage axis is represents the built-in voltage. The concentration of carrier can be determined from the relation:

$$1/C^2=[2(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})/ q N_{D2} N_{A1} \varepsilon_1 \varepsilon_2] (V_{bi}-V_a) \quad (1)$$

Where $[2(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})/ q N_{D2} N_{A1} \varepsilon_1 \varepsilon_2]$ is represent the slope. The current-voltage measurements in the dark have been measured by using Keithly Digital Electrometer 616 and D.C power supply. The CBD is based on sequential reaction at the substrate surface.

3. Results and discussions

The structure properties of the PbS thin films of thickness (400, 600) nm have been studied by X-ray diffraction, It is observed that the structure of these films are polycrystalline of FCC cubic structure which matched well with the standard JCPDS card no. (05-0592, a = 5.936 Å). as shown in Fig. 1, and the reflection surface (111), (200), (220), (311), (222) have been appeared, and this agree with . Obaid et al.[8] and Choudhury et al [9]. However, as the thickness was increased from 400 to 600 nm the extra peaks disappeared and the intensity of the peaks attributed to PbS improved as shown in Fig. 1. This improved intensity with well-defined sharper peaks indicates a higher crystallinity of the prepared material. The grain size of the films as a function of thickness was determined by using Scherrer formula. It is clear from Table. 1, that the estimated average size increased with an increase in the thickness. The lattice constant of the films are approximately 5.936 A which match perfectly with the standard data. This lattice constant value is very similar to the bulk PbS indicating that films grow on the glass substrate without stresses at the interface. However, the increasing of thickness produces an increase in the grain size of PbS thin films, approximately 32 -44 nm for the thickness (400, 600) nm respectively, and this agree with Abass et al. [3,10].

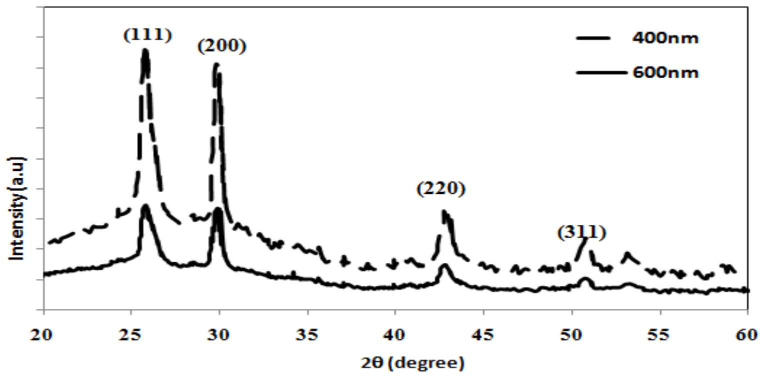

Fig. 1. The X-ray diffraction for PbS thin films at different thickness.

Table. 1 X-ray diffraction data for PbS films for (200).

Thick.(nm)	d_{stand} (A°)	D (nm)	A (A°)	I/I_o
400	2.969	32	5.935	90
600	2.969	44	5.935	90

The surface morphology of PbS thin films were determined by Atomic Force Microscope. It is well known that the atomic force microscopy (AFM) is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software The 2D and 3 D AFM images in an area of 2x2 μm of the PbS films deposited at 20°C with different thicknesses, are shown in Fig. 2. It can be observed that the surface morphology of the PbS films are compact, uniform, and have good adherence to the substrate. No evidence of cracking observed, and it has larger number of grain size and is homogeneously distributed, which indicates the crystalline nature of the film. These results are in good agreement with XRD characteristics. The crystal morphology and molecular orientation change with thickness due to the change of molar concentration. The average grain size increases with thickness as in Table. 2 from 91.12-108 nm, the grain density reduced indicating the smaller grains agglomerate together to form larger grains of crystals. the surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness. Also the root mean square (rms) roughness of the film at different thickness are shown in Table. 2, it is increases with increasing thickness which means largest surface area, the best choice for solar cell making. From the application point of view, the higher efficiency devices are obtained from the film of greater roughness, and this is agreement with other literatures. [8-11].

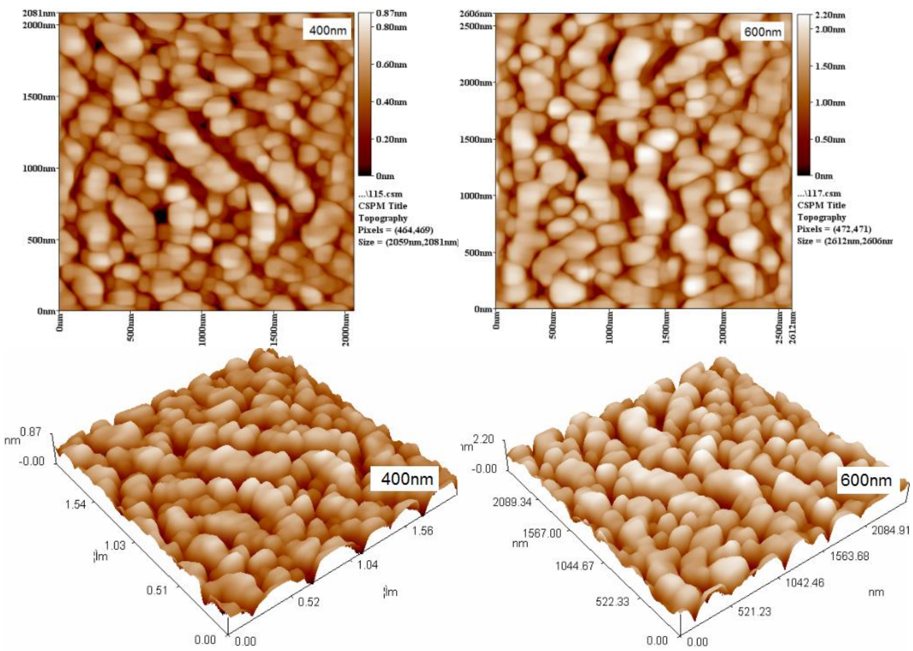

Fig. 2. Two and three-D of AFM of PbS thin films with different thicknesses (400, 600)nm.

Table. 2. Grain size average and roughness of PbS thin films at different thicknesses.

Thickness (nm)	Roughness Average (nm)	Grain Size (nm)
400	0.158	91.11
600	0.408	108

The dark electrical conductivity of PbS films was studied in the temperature range 303 to 473 K. Fig. 3 Shows the variation of log of σ with reciprocal of temperature, (1000/T). It shows that the conductivity (σ) increases exponentially with the increase of the temperatures, indicating semiconducting nature of films, the similar results is observed by the researchers. [12,13]. The thermal activation energy was calculated using the relation

$$\sigma = \sigma_0 \exp(E_a/KT) \tag{2}$$

where, σ is conductivity at temperature T, σ_0 is a constant, K is Boltzmann constant (8.62×10^{-5}eV/K) and E_a is the activation energy required for conduction. The activation energy was varied from 0.371 to 0.251 eV as thickness changes from 400 to 600 nm. These observations may be due to size effects that are arising because of quantum confinement of charge carriers within the particles is positive, indicating the films are of p-type. These results are agreement with other researchers. [11-14].

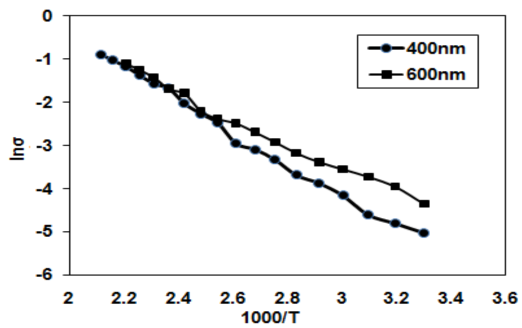

Fig. 3 The Ln σ versus 1000/T for for PbS thin films at different thickness.

From the Hall measurement, the type of charge carriers, carrier concentration (n_H), Hall mobility (μ_H) drift velocity (υ_d) has been calculated as in Table 3. It was noticed from this table that the films of all samples have positive Hall coefficient. It can be observed from this calculation that both the conductivity increases with increasing of thickness, and the carrier's concentration, mobility and drift velocity increases with increasing of thickness due to increase the grain size as we see in XRD and AFM.

Table. 3. Electrical properties parameters

Thickness (nm)	$\sigma_{R.T}$ x10^{-2} (Ω.cm)$^{-1}$	R_H x10^4 (cm^3/c)	n_H x10^{19} (cm)$^{-3}$	μ x10^{-2} (cm^{-2}/V.s)	υd x10^{-2} (cm/s)	Type
400	0.658	5.039	3.149	0.130	1.305	p
600	1.28	8.976	5.610	0.142	1.425	p

The capacitance-voltage technique is a useful tool to obtain information about the doping concentration profile of the lightly doped side of a p–n junction diode. The variation of capacitance as a function of reverse bias voltage for PbS/Si heterojunction at different thickness are shown in Fig. 4, It is observed that the capacitance decreases with increasing the reverse bias.

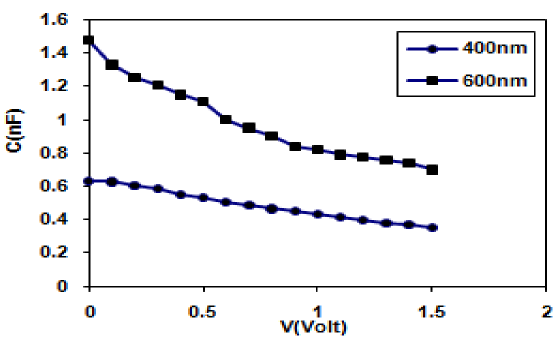

Fig.4. The variation of capacitance as a function of reverse bias voltage for PbS/Si HJ at different thickness

The inverse capacitance squared was plotted against applied reverse bias voltage for PbS/Si as in Fig. 5 The intersection ($1/c^2=0$) of the straight line with the voltage axis represents the built-in voltage. [15], and Table 4 represents the value of built-in voltage. It is observed from this Table that the value of built in voltage is in general decreases with increasing thickness as a result of the increase in capacitance value and the decrease of depletion width. Also from the same figure, one can deduce the carrier concentration from the slope of the straight line from equation 1. Table 4 represents these values which increase with increasing thickness and this value is in agreement with other literatures. Also BAROTE et a.l [15] have found that the value of barrier height is 0.745V from C-V measurements.

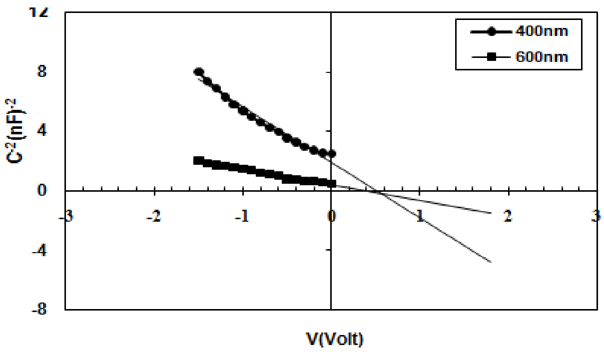

Fig.5 The variation of $1/C^2$ as a function of reverse bias voltage PbS/Si HJ at different thickness.

Table. 4. The variation of zero bias capacitance, depletion region width, built in voltage and carrier concentrations for PbS/Si HJ .

Thick.(nm)	$N_D\times10^{15}$ cm^{-3}	$C_0\times10^{9}$ Farad	V_{bi} Volt	W µm
400	3.01	0.63	0.5	7.5
1600	8.5	1.48	0.4	3.2

One of the important parameters of HJ measurement is a current- voltage characteristic which explains the behavior of the resultant current with the applied forward and reverses bias voltage. Fig. 6 shows I-V characteristics for PbS/Si HJ at forward and reverse bias voltage for different thickness. Also one can observe from this figure that the value of forward current is increases with increasing of thickness, which attributed to decrease in the depletion width (as we see in c-v characteristics), and to improve in crystal structure by increasing thickness which attributes to increase in crystallite grain size, because the increasing of thickness will cause rearrangement the interface atoms and reduce the dangling bonds which leads to improve the junction characteristics [15].Fig. 6 shows a clear rectification indicates that the junction is anisotype. The rectification factor (R.F) indicates the ratio between forward and reverse current at certain applied bias voltage, and Table 5 explains the value of rectification factor at (1Volt). The Table also shows an increase in rectification with increasing thickness, and this is attributed to improve in crystal structure, and the diffusion increases when thickness increased , Also there is a decrease in depletion width by doping with thickness which leading to increase in reverse saturation current, and this value agreement with other literature Barote et al.[15]. One can calculate the reverse saturation current from intercept the straight line with the current axis at zero voltage bias, from this figure the reverse saturation current increase with increasing thickness. From the first region, the ideality factor (β) of PbS/Si HJ can be calculated by the relation. [16,17]

$$\beta = (q/k_B T)[V_F/\ln(I_F/I_S)] \tag{3}$$

Where V_F is the forward bias voltage, I_F and I_S are the forward bias and the saturation currents respectively, the ideality factor usually has a value greater than unity, and it describes the deviation of the diode characteristics from those of the ideal diode. Table 5 explains the value of ideality factor for PbS/Si HJ at different thickness. The physical meanings of the ideality factor are greater than (2) is that the tunneling play their role with the recombination emission. [16,17]. We can see that the value of ideality factor was varies between 1.821- 1.715. These β values are in agreement with Barote et al.[15].

Table.5. The values of rectification factor at (1volt) and ideality factor and tunneling constant.

Thick.(nm)	R.F	β
400	4.618	0.821
600	6.912	0.715

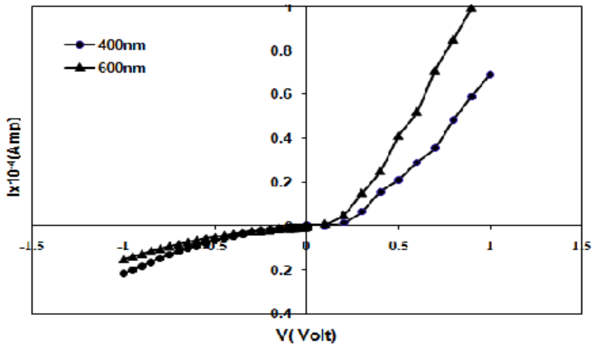

Fig. 6. The I-V characteristics for PbS/Si HJ at forward and reverse bias voltage at different thickness.

The photocurrent is considered as the important parameter, which play an effective role in photodetectors and solar cells. The prepared HJ strongly depends on the reverse bias voltage. [15]. Fig. **7** show the photocurrent of PbS/Si HJ at different thickness as a function to reverse bias voltage under different incident light power density. The current under reverse bias conditions is affected by illumination. [16,17]. Under UV illumination photons are mainly absorbed in the PbS layer (as seen from the transmittance and absorption spectra) and good response to UV illumination under the reverse biased condition can be seen from Fig. **7** due to the photogeneration of additional electron-hole pairs in the depleted PbS region. The magnitude of photocurrent increases with the increasing applied reverse bias due to enhanced carrier collection. The width of the depletion region increases with the increasing of the applied reverse bias voltage, which leads to separation of the electron-hole pairs and then increases the photocurrent. The photocurrent is a function of the generation and diffusion carriers. [13-17]. Also from this figure, we can observe that the photocurrent increases with increasing of the incident light density due to the increasing of the number of incident photon light. Also, from this figure the photocurrent increases with increasing of thickness, and this is attributed to good crystalline for the films which will decrease the grain boundary and after that the mobility increases. [13], and this is leading to increase the photocurrent. Similar results have also been observed by Barote et al.[15].

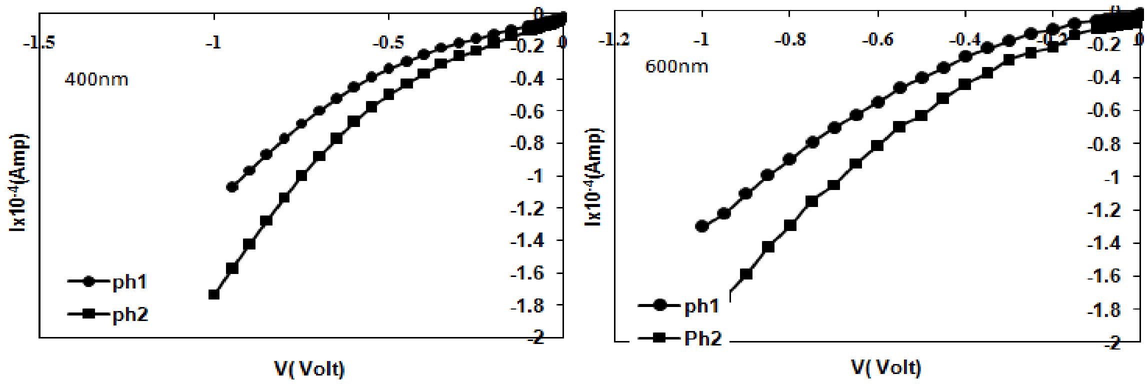

Fig. 7. I-V characteristics under illumination for PbS/Si HJ at different thickness

4. Conclusion

nanocrystalline PbS thin film at different thickness have been fabricated successfully by chemical bath deposition technique on glass and Si substrates The XRD shows that the films exhibit crystalline cubic structure oriented in (111) and (200) direction. From AFM the morphology of these films has larger number of grain size and are homogeneously distributed, compact and uniform , which indicates the crystalline nature of the film, the grain size and surface roughness of these films is increase with increasing of thickness. The Electrical properties confirm the p-type nature of PbS. The electrical conductivity and therefore activation energy are observed to be thickness dependent. It is observed that the capacitance decreases with increasing the reverse bias, while it increases with increasing thickness. The width of depletion layer decreases with increasing thickness. From the inverse capacitance squared plot against applied reverse bias voltage PbS/Si HJ at different thickness. The plots reveal a straight line relationship which means that the junction was an abrupt type. It is found that the value of built in voltage is in general decreases with increasing thickness. Also the carrier concentration increases with increasing of thickness**.** It is observed that the capacitance decreases with increasing the reverse bias, while it increases with increasing thickness. The width of depletion layer decreases with increasing thickness. From the inverse capacitance squared plot against applied reverse bias voltage, the plots reveal a straight line relationship which means that the junction was an abrupt type. It is found that the value of built in voltage is in general decreases with increasing thickness. From C-V measurements, the carrier concentration increases with increasing of thickness. The current voltage characteristics of the junction have rectification characteristics, and the value of current increases with increasing thickness.

References

[1] S. Seghaier, N. Kamoun, R. Brini, A.B. Amara, Materials Chemistry and Physics, **97**, 71 (2006).

[2] J.J. Valenzuela-J´auregui, R. Ram´ırez-Bon, A. Mendoza-Galva´n, M. Sotelo-Lerma, Thin Solid Films, **441**, 104 (2003).

[3] L.F. Koao, F. B. Dejene, and H.C. Swart, Int. J. Electrochem. Sci., **9**, 1747 (2014).

[4] D. Kumar, G. Agarwal, B. Tripathi, D. Vyas, V. Kulshrestha, J. of Alloys and Comp., **484**, 463 (2009)

[5] C. Wang, W. X. Zhang, X. F. Qian, X. M. Zhang, Y. Xie, Y. T. Qian, Mater. Lett. **40**, 255 (1999).

[6] L. F. Koao, F. B. Dejene, H. C. Swart, SAIP’2011 Proceedings, the 56th Annual Conference of the South African Institute of Physics, edited by I. Basson and A.E. Botha (University of

South Africa, Pretoria), ISBN: 978-1-86888-688-3 (2011), 151.
[7] C. Kaito, Y. Saito, K. Fujita, Jpn. J. Appl. Phys. **26**, 1973 (1987).
[8] A. S. Obaid, M. A. Mahdi, Asmiet Ramizy, and Z. Hassan, Advanced Materials Research **364**, 60 (2012).
[9] N. Choudhury, B. K. Sarma, **46**, 261 (2008).
[10] M. Abass, E..Al-Fawadi, and A-K. Al-Samuraee, Preparation of Nanocrystalline PbS Thin Films by Chemical Bath Deposition, Materials Science and Technology Proceeding, Pittsburgh, Pennsylvania 2637 (2009).
[11] U. Ubale, A. R. Junghare, N. A. Wadibhasme, A. S. Daryapurkar, R. B. Mankar, V. S. Sangawar, Turk J Phys, **31**, 279 (2007).
[12] S. Cheemadan, K. Keerthana, M. C. Santhosh Kumar, J. Environ. Nanotechnol, **2(**4), 28(2014).
[13] Mosiori, Cliff Orori, Njoroge, Walter N., Okumu, John, International Journal of Advanced Research in Physical Science (IJARPS), **1(**1), 25 (2014).
[14] A Hussain, A Begum and A Rahman, A Begum and A Rahman, Indian J Phys, **86(**8), 697 (2012).
[15] M. A. Barote, A. A. Yadav, T. V. Chavan, E. U. Masumdar, Digest Journal of Nanomaterials and Biostructures, **6**(3), 979(2011).
[16] B.L.Sharma, R.K.Purohit, Semiconductors Heterojunctions, Academic Prees, Inc, Oxford, NewYork, 1-15 (1974).
[17] G.Milnes & D.L.Feucht," Heterojunctions and Metal Semiconductors Junctions, Academic Prees, London (1972).