ZnSe/Porous Si/Si(p-type) Heterojunction Investigation
دراسة خواص المفرق المتباين نوع ZnSe/PSi/Si(P-type)

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Abstract:

In this research n-ZnSe films were deposited on glass and porous Si (P-Type) substrates by thermal evaporation in vacuum (10^{-5})(using Edward coating system 306)with thickness 200nm. All the films prepared at different annealing temperatures were studied by X-ray diffraction method and shown that ZnSe films at T_a=303K have polycrystalline structures,while we show that the films have single crystal at (T_a=343,363K).Optical measurements indicated that films have a direct energy gap in the range of (2.61-2.55eV) for films at room temperature and increases at different annealing temperatures. The effect of annealing on structural properties is observed. Hall Effect measurements showed that ZnSe films have a negative conductivity, also the concentration of charge carriers (n) and Hall mobility increases with increasing of annealing temperature. Porous Si (P-type) with (100) orientation and resistivity ($1*10^{-4}$ ohm cm) is fabricated by photochemical etching process. Multijunction of ZnSe/Porous Si/Si(p-type) diode device were fabricated, electrical properties of fabricated junction is investigated by current density- applied voltage(J-V) measurements and from (C-V) measurement the built in voltage can be found. The effect of annealing temperatures on the heterojunction is observed

Keywords: Porous Silicon heterojunction, Porous silicon

الخلاصة //

تعتبر سبيكة ZnSe من المواد الكهروضوئية المهمة ذات فجوة الطاقة العالية ،تم ترسيب اغشية ZnSe من النوع بترسيبها على قواعد من الزجاج والسيليكون المسامي (PSi)(P-type) بطريقة التبخير الحراري في الفراغ (10^{-5} torr) (باستخدام جهاز Edward coating system 306)وبسمك (t=200nm)اظهرت نتائج حيود الاشعة السينية ان أغشية ZnSe متعددة التبلور عند درجة حرارة الغرفة T_a=303K واحادية التبلورعند درجات حرارة تلدين T_a=343,363K ولمدة 30min. اشارت القياسات البصرية لأغشية ZnSe ان المركب له فجوة طاقة مباشرة تتراوح بين (2.55-2.661eV) عند درجة حرارة الغرفة وتزداد بزيادة درجة حرارة التلدين .اظهرت قياسات تأثير هول ان اغشية ZnSe ذات توصيلية سالبة وان كثافة حاملات الشحنة (n) والتحركية لحاملات الشحنة تزداد بزيادة درجة حرارة التلدين ايضا. تم تحضير السيليكون المسامي بطريقة الحفرالكيميائي-الضوئي لشرائح سليكون ذات نوع (P-type)باتجاه (100)ومقاومية ($1*10^{-4}$(ohm cm)) كما تم تصنيع المفرق الهجين n-ZnSe/PSi ودراسة الخصائص الكهربائية لهذه النبيطة من خلال فحوصات خصائص تيار – فولتية وكذلك خصائص (السعة-فولتية) ومن خلالها حساب فولتية جهد البناء الداخلي ومن ثم دراسة تاثير التلدين على خصائص المفرق المتباين.

Introduction:

There is a strong need for the development of photovoltaic cells with low cost, high efficiency, and good stability. In thin film technologies, there exists a common problem with conversion efficiency due to poor materials quality; the photogenerated electrons and holes cannot travel very far before recombination (short free-carrier diffusion lengths) and are hence lost for power conversion. If the solar cell can be made using nanoscale heterojunctions, then every photogenerated carrier will have less distance to travel, and the problem of recombination can be greatly reduced. With nanoscale diffusion lengths for the photogenerated carriers, the materials constraints can be relaxed, and low cost deposition routes become acceptable.[1,2]

A basic proposed structure for a nanostructure single-junction solar cell is consist of a nanostructure substrate that is coated with semiconducting layers through possibly deposition techniques, such as chemical bath deposition or spray pyrolysis. Another related design involves first depositing the semiconductor absorber material in a planar geometry, then etching a periodic array of nonporous, and finally using thermal evaporation or any techniques to fill in the nonporous with an opposite polarity window layer to form the p/n junction. The absorber material could be composed of silicon, GaAs, CdTe, CIGS, ZnSe or virtually any other solar cell material, since this layer can be deposited on a planar substrate and subsequently nanostructure.[1,2] Heterostructures of II-VI compound semiconductors exhibiting wide band gap are extensively studied for optoelectronic applications, such as light emitting diodes or laser diodes [1-3]. A number of techniques [4-8] are employed in the formation of high quality thin films such as, chemical vapor deposition, molecular beam epitaxy, pulsed laser, evaporation, and sputtering. However, there is an interest to investigate other approaches, which could open new or supplementary possibilities in terms of device properties, structure or engineering. High efficient devices can be obtained by electrodeposition such as electrodeposited cadmium telluride solar cells or electrodeposited wide band gap sulfide or oxides buffer/window layers[9-10]. Within direct wide-band semiconductor materials, the zinc chalcogenides compounds have been the objects of numerous studies concerning thin film deposition [11-13]. Zinc selenide (ZnSe) is considered as an important technological material due to their potential applications in various optical and electronic devices. It is an II – VI direct and wide band gap (2.7 eV) [14] semiconductor studied widely because of its potential use in semiconducting and optoelectronic devices and as window material for thin film heterojunction solar cells. The thermal evaporation deposition technique has been found to be a useful method to prepare polycrystalline semiconducting films for the use in photovoltaic cells. Thermal deposition technique seems to be an inexpensive, low temperature method that could produce good quality films for device applications. The attractive features of this method are the convenience for producing large area devices and possibility to control the film thickness, morphology and stoichiometry of the films by adjusting the deposition parameters. In this paper, we report the deposition of n-ZnSe thin films on glassy substrate and porous Si (P-type), it has been study the effect of temperature on I-V characteristic of the prepared junction, Optical transmission techniques were employed for characterizing the deposited films.

2-Experimental Details:

Thin films of ZnSe were deposited by thermal evaporation technique (under a vacuum pressure of the order 10^{-5} torr) on glass and porous silicon PS (P-type) substrates with thickness (200 nm).

The PS layer prepared by photochemical etching process that is usually achieved in Hydrofluoric acid (HF) with concentration 36% and ethanol with (1:1 percentage) for 15 min. etching time, and with optical power densities(0.55Watt/cm^2). The irradiation has been achieved using ordinary light source of tungsten halogen lamp (100w) power. The thickness of PSi was determined by using the equation ($r=m_1-m_2/m_1-m_3$)where r: is porosity thickness m_1,m_2 is the weight of wafer Si before and after etching and m_3 is the weight of PSi after removing porous layer by KOH, where the thickness of PSi under fixed etching and irradiation time is (15□m). In this work monocrystalline (100)-oriented highly doped P^+-type Si wafers with resulting electrical resistivity of about ($1x10^{-4}$ □.cm) during etching process the tungsten lamp (100 Watt) is exposed to in front of Si which immersed in above solution. Al/ZnSe/PSi/Si structures were fabricated by vacuum thermal evaporation of Aluminum electrodes. Junction was fabricated in order to carry out complementary I-V and C-V measurements. The structure of the PSi sample is shown in figure (1).

Fig.(1) Optical micrograph of the porous Silicon(1200X)

3- Results and discussion:

X-ray diffraction (XRD) studies were made on the films deposited at room temperature and those annealed to T_a=343 and 363K for 30min.XRD pattern of the films deposited are shown in Fig.(2).It is observed that the films exhibit cubic structure with peaks corresponding to the (111),(220) reflections, for the films deposited at T_a=303K,while sharp peak are observed (single crystal structure) for the films annealed at T_a=343K and become more sharper for the samples at T_a=363K these because of more arrangement of atoms with geometrical forms when the annealing temperature increases..

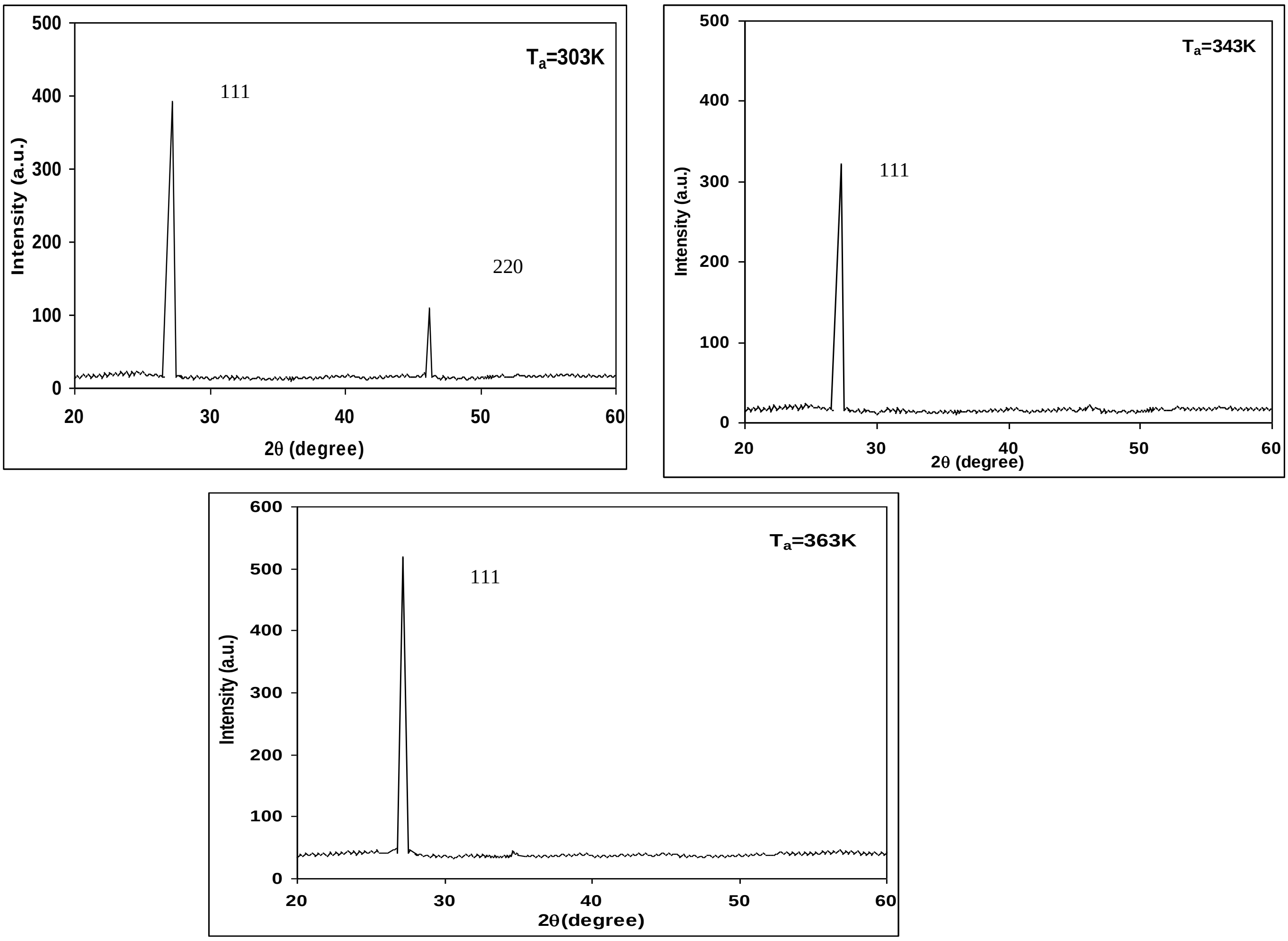


Fig. (2) X-ray diffraction of ZnSe films prepared at T_a=303K, 343K and 363K

Optical absorbance measurements were made on the films deposited on the glass substrates in the wave length range 300-1100 nm at room temperature and which annealed for 30 min at 343 and 363K to ascertain the nature of the band gap. Substrate absorption, if any was corrected by placing an identical uncoated glass substrate in the reference beam. The absorption coefficient (□) at various wavelengths has been calculated using the equation [17]:

□=2.303 A/t ………………..(1)

Where A is the absorbance value at a particular wavelength and t is the thickness of the film. The direct band gap of the films were determined by plotting a graph between $(□h□)^2$ vs. h□. Extrapolation of the linear region to the h□ axis gives the band gap of the material. Fig.(3) shows the $(ah□)^2$ vs. h□ graph for the films deposited at room and annealing temperatures. An absorption coefficient of 10^4 cm^{-1} was observed. The plots are linear, extrapolation of the plot to the h□ axis yields the band gap in the range of 2.61 – 2.55 eV for the films deposited at room and different annealing temperatures. It is noticed that the optical energy gap decreases with increasing annealing temperatures.

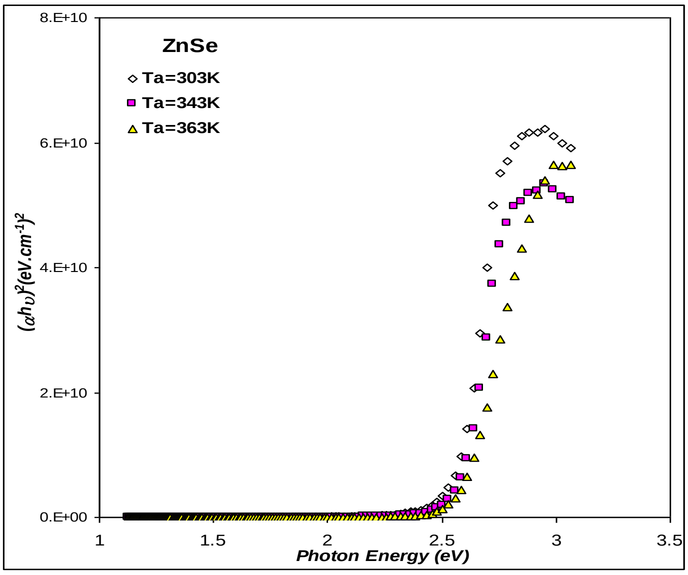


Fig.(3) Variation of$(□h□)^2$versus photon energy for ZnSe thin films at different annealing temperatures.

Hall effect results from applying magnetic field (B_z) along a rectangular sample normal to the direction of current (I_x),the charge carriers will tend to be deflected to one side, then building up potential gradient perpendicular to magnetic field and current, this effect was used to determined the type and the density of charge carriers(n).Hall coefficient is given.

$$R_H = \frac{V_H A}{I_H B_z W} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where A is the area of film, B_z applied magnetic field=0.257 Tesla. The density of charge carriers is given by the relation: $n=1/eR_H$ and the mobility of charge carriers is given by the relation □=□ R_H where □ is the conductivity. From equation (2) Hall measurements showed that the films of ZnSe thin film at T_a=303K is n-type i.e. the conduction is dominated by electrons. referred that R_H is negative this is obviously due to the excess in Se atom in ZnSe compounds act as donor atoms, the density of charge carriers(n) and the mobility were measured also. Table (1) declared that (n) increased by increasing annealing temperature, many reports affirmed that (n) increased when semiconductors were thermally treated. In general the Hall mobility of charge carriers is observed to increase by increasing annealing temperature; this is attributed to lowering of potential barriers and increasing of electrical conductivity.

Table(1) illustrates values of R_H,*n* and μ for ZnSe films deposited at R.T and different annealing temperature.

T_a (K)	R_H(cm^3/C)	n(cm^{-3})	μ (cm^2/v.s)
303	-1540	$4.05x10^{15}$	1.3×10^{-4}
343	-778.21	8.03×10^{15}	3.36×10^{-4}
363	-770	8.11×10^{15}	2.28×10^{-3}

Figure(4) shows the variation of inverse capacitance as a function of reverse bias voltage in the range (0-1) Volt at frequencies equal (f=1 kHz), at different annealing temperature equal to T_a=343K and T_a=363K.the plots reveal a straight line relationship which means that the junction is of an abrupt type [18] the interception of the straight line with the voltage axis ($1/C^2=0$) represents the built-in voltage, it can observed from table (2) that the V_{bi} increase with increasing of annealing temperature this may be due to decrease in energy gap by increasing annealing temperatures.

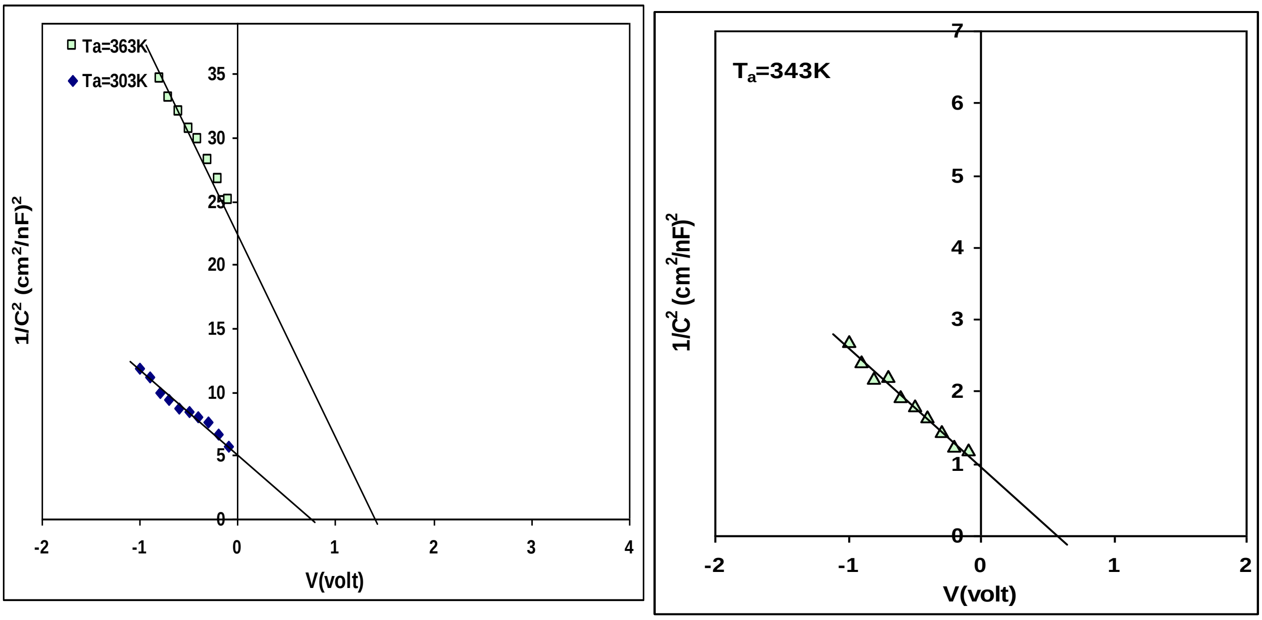


Fig.(4) ($1/C^2$) as a function of the reverse bias voltage for ZnSe/PSi/Si HJ having different T_a temperatures.

The current–voltage characteristics are important parameter to identify the significance of the various components under reverse and forward bias as well as other important parameters.

Fig.(5) shows the I-V characteristic for ZnSe/PSi/Si HJ at dark forward bias voltage within the range (0-1 Volt). These curves demonstrate the behavior of the current with the forward bias voltage. There are two regions for the forward current curves the first region for the voltage range (0-0.3Volt) which the recombination current is dominate and the second region (V>0.3 volt), the variation is of exponential type and it is due to the tunneling current [19]. The initial part of Fig.(5) could be approximated by an expression of the type $I \sim exp(qV/ßk_BT)$ where (ß) is the ideality factor. So from the logarithm of the initial part of the forward current, the ideality factor (ß) could be calculated. From the second region in Fig.(5) the tunneling constant (A_t) can be calculated using $A_t=[dLn (I_f/I_{s2})]/dV$ [20].

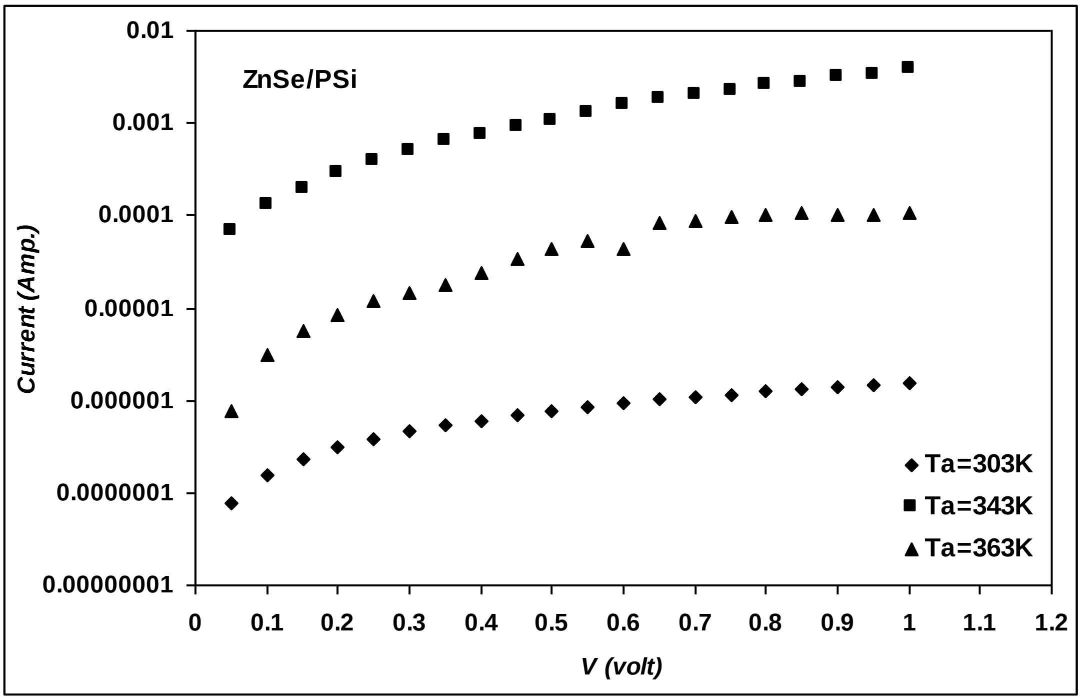


Fig.(5) I-V characteristic at dark forward bias voltage on semilogarthmic scale for ZnSe/PSi/Si HJ at different annealing temperatures.

Table (2) reveal that the ideality factor decreases from 5.54 to 4.85 when the sample annealed to 343K then increased to 7.02 at T_a=363K.

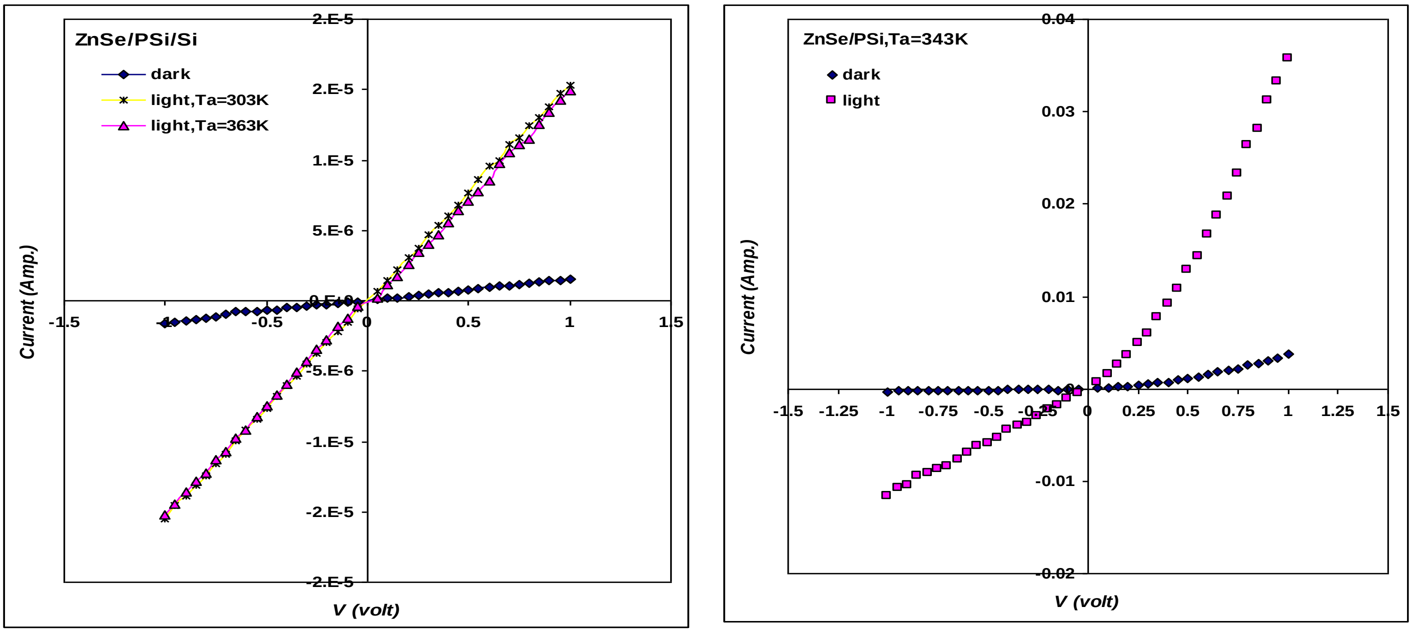
In general, the forward dark current is generated by the flow of minority carriers. The applied voltage injects majority carriers which decreases the built-in potential, as well as the width of the depletion layer. The majority and minority carrier concentration is higher than the intrinsic carrier concentration (n_i^2<np) which generate the recombination current at the low voltage region (0-0.3 Volt). This is because the excitation of electrons from valence band to conduction band will recombine them with holes that are found at the (V.B). This is observed by the little increase in the recombination current at low voltage region [21]. While the tunneling current occurs at the high voltage region (V>0.3 Volt).

Table (2) the tunneling, ideality factors, V_{bi} and energy gap for ZnSe/PSi/Si HJ and ZnSe films

T_a(K)	A_t $(Volt)^{-1}$	□	V_{bi}(V)	E_g(eV)(ZnSe films)
303	4.14	7.14	0.6	2.55
343	2.72	9.40	0.8	2.58
373	0.68	10.05	1.6	2.61

For the structures with ZnSe/PS/c-Si layers, I-V curves measured in the darkness exhibit a typical ohmic behavior (at a bias up to one volt). The positive direction of voltage in this figure (forwarded current) corresponds to a positive bias applied to P-Si. The reverse branch displays current saturation, which is always clearly pronounced. Analysis of the forward current gives the value of the series resistance of the sample amounting to several kiloohms and the tunneling factor at small bias of approximately 4.14 to 0.68 Volt-1 .

Under illumination, the I-V curves (see Fig.6) is a typical ohmic behavior for the samples which prepared at T_a=303K and 363K while atypical photodiode for samples prepared at T_a=343K.The ratio of photocurrent measured under illumination and in the darkness is one to two orders. The photocurrent increases with reverse bias very slowly. The open circuit voltage (V_{oc}) is about 0.07 Volt, and the sign of V_{oc} corresponds to the depletion band bending of P-Si.



Fig(6)I-V Characteristic under illumination for different annealing samples.

Conclusion:

The energy gap of n-ZnSe thin films increases with the increase of annealing temperatures, the junction of n-ZnSe/PSi/Si heterojunctions performed successfully. From C-V measurements the V_{bi} is calculated and it is found that the V_{bi} increases with increasing annealing temperature, the I-V characteristic showed that the junction look like ohmic behavior at annealing T_a=303 and 363K,while at T_a=343K the junction have a photodiode properties. Also, the junction is of the type of abrupt HJ.

References:

[1] E. Krause, H. Hartmann, J. Menninger, A. Hoffmann, Ch. Fricke,R. Heitz, B. Lummer, V. Kutzer, and I. Broser, “J. Cryst. Growth” Vol.138,No.75 (1994).
[2] G. J. Yi, Radomsky, and G. F. Neumark, “J. Cryst. Growth” Vol.138,208 (1994)
[3] A. P. Samantilleke, I. M. Dharmadasa ,K. A. Prior. K. L. Choy,J. Mei, R. Bacewicz and A. Wolska, “J. Mater. Sci. Mater. Electron.” Vol.12, 661 (2001)
[4] M. C. Harris Liao, Y. H. Chang, Y. F. Chen and J. W. Hsu, J.M. Lin and W. C. Chou, “Appl. Phys. Lett.” Vol.70,No.28 (1997).
[5] Huanyoug Li and Wanqi Jie, “J. Cryst. Growth” Vol.257, No.110 (2003)
[6] N. Sankar and K. Ramachandran, “J. Cryst. Growth” Vol.247, No.157 (2003)
[7] E. Guziewicz, M. Godlewski, K. Kopalko, E. Lusakowska, E.Dynowska, M. Guziewicz, M. M. Godlewski, and M. Phillips, “Thin Solid Films”Vol. 446, No.172 (2004)
[8] A. Rizzo, M. A. Tagliente, L. Caneve and S. Scaglione, “Thin Solid Films”Vol. 368,No.8 (2000)
[9] Cesar A. Estrada, P. K. Nair, M. T. S.Nair, Ralph A. Zingaro and A. Meyers, “J. Electochem. Soc.” Vol.141,No.802 (1994)
[10]C. Wang, W. X. Zhang, X. F. Qian, X. M. Zhang, Y. Xie and Y. T. Qian, “Mater. Chem. Phys.”Vol. 60,No.99 (1999)

[11]I. M. Dharmadasa, A. P. Samantilleke, J. Young and M. H.Boyle, R. Bacewicz and A. Wolska, “J. Mater. Sci. Mater. Electron.” Vol.10,No.441(1999).

[12]C. Natarajan, M. Sharon, C. Levy Clement and M. Neumann Spallart, “Thin Solid Films” Vol.237, no.118 (1994)

[13]G. Riveros, H. Gomez, R. Henriquez, R. Schrebler, R. E. Matrotti and E. A. Dalchiele “Sol. Energy Mater. Sol. Cells” Vol.70,No. 255 (2001)

[14] S.T. Lakshmikumar and A. C. Rastogi, “Thin Solid Films” Vol.256, 150(1995).

[15] T.Mahalingam and A.Kathalingam “J.New Material for Electrochemical systems” Vol 10,P.15-19,(2007).

[16] K.R.Murali,K.Thilakvathy,and S.Vasantha “chalcogenide Letters”Vol.5,No.6 P.11-116,(2008).

[17] T.H.Yeh,A.E.Blakesee, “J.Electrochem Soc” Vol.110,No.1018(1963).

[18] F.C.Jain,and M.A.Mehely, “Appl.Phys.lett.” Vol.27 ,No.1 , (1975) , P.(36-38).

[19] Y.Gaing and R.Hong“Adv.Mater”Vol.15, No.14,(2003),P.1195.

[20] B.L.Sharma and R.K.Durohit, “Semiconductor Heterojunctions” Newyork, (1974).

[21]A.M.Green“Solar Cells”translated by Y.M. Hassan,Univ. of Mosul, (1989).