Porous Silicon effect on the performance of CdS nanoparticles photodetector

Mymana W. Eesa, Manal M. Abdullah
Department of Physics, College of Science, Baghdad University, Baghdad, Iraq
E-mail: maymanawaleedalrawi@gmail.com

Abstract

Cadmium sulfide photodetector was fabricated. The CdS nano powder has been prepared by a chemical method and deposited as a thin film on both silicon and porous p- type silicon substrates by spin coating technique. Structural, morphological, optical and electrical properties of the prepared CdS nano powder are studied. The X-ray analysis shows that the obtained powder is CdS with predominantly hexagonal phase. The Hall measurements show that the nano powder is n-type with carrier concentration of about (-5.4×10^{10}) cm^{-3}. The response time of fabricated detector was measured by illuminating the sample with visible radiation and its value was 5.25 msec. The specific detectivity of the fabricated detector is found to be $(9\times10^{11}$ W^{-1} .Hz$^{1/2}$.Cm^{-1}). The responsivity was (0.03A/W).

Key words
CdS nano particle, thin film, photo detector, porous silicon, responsivity, I-V characteristic.

Article info.
Received: Jun. 2016
Accepted: Sep. 2016
Published: Dec. 2016

تأثير تنميش السليكون على اداء كاشف الجسيمات النانويه كبريتيد الكادميوم

ميمنه وليد عيسى، منال مدحت عبدالله
قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم تصنيع كاشف ضوئي من كبريتيد الكادميوم بالحجم النانوي. حضر المسحوق بطريقه كيميائية ثم رسب كغشاء رقيق على قواعد السليكون والسليكون المسامي بواسطة تقنية الترسيب بالتدوير. درست الخصائص التركيبية والسطحية والبصرية والكهربائية لكبريتيد الكادميوم النانوي. تحليل الاشعة السينية بين أن مسحوق كبريتيد الكادميوم النانوي المحضر ذو تركيب سداسي ومن قياسات هول وجد ان المسحوق النانوي من النوع المانح وبتركيز حاملات شحنة حوالي -5.4×10^{10} سم$^{-3}$. تم قياس زمن استجابة الكاشف المصنع بعد اضائتة بالاشعة المرئية فكانت قيمته 2,5ملي ثانية. وجد ان تحسس الكاشف هو 9×10^{11} واط$^{-1}$.هرتز$^{1/2}$.سم$^{-1}$ واستجابية 0.03 أمبير.واط$^{-1}$.

Introduction

Nanotechnology has been an interesting field of research gained much importance from last two decades [1]. Nanotechnology is an engineering of functional systems at the molecular level, covers a broad range of topics and focuses on controlling and exploiting the structure of materials, mainly semiconductors, on a large scale below 100 nanometers [2, 3].

In particular, the confined dimensions result in a quantization of the bulk electronic bands and a widening of the gap (called a blue shift) between the valence band and conduction band, which is particle size dependent [4].

The Photo detectors are fabricated from various semiconductor materials, which are used as an optical receiver to convert light into electricity [5], since the band gap needs to be smaller than the energy of photons detected. Photon absorption generates electron-hole pairs which are subsequently separated by the applied electrical field. Nanostructure materials such as CdS have been successfully used in a number of applications such as in optoelectronics, solar cells, X-ray detectors and photo detector devices[6]. CdS is a II-VI semiconductor which is insoluble in water but soluble in dilute mineral acids. It exhibits intrinsic n-type of conductivity caused by Sulphur vacancies due to excess Cadmium atoms, with direct band gap (2.42 eV) and exciting binding energy of 28 meV.

CdS has high absorption coefficient and considerable energy conversion efficiency [7]. It attains three types of crystal structures namely wurtzite, zinc blend and high pressure rock-salt phase. Among these, wurtzite is the most stable phases and can be easily synthesized [8].

We present a photodetector, based on silicon (Si) and porous silicon substrates. CdS nanoparticles films are deposited by spin coating method.

The preparation method, the characterization of the prepared material the characteristic of the morphological, optical and detector properties are also presented in this work.

Experimental work

Chemical synthesis is used to prepare the CdS nanoparticles which were coming in three separated steps:

1- The preparation of (S- paraffin oil) solution with concentration 0.1 M:

1 mmole of Sulfur (S) is dissolved in 10ml of paraffin oil, the mixture was heated up to 220°C with stirring till dissolution is complete and the color of the solution change from yellow to nearly brown, which indicate the formation of S-Paraffin oil.

2- The preparation of Cd complex solution with concentration of 0.1M:

2 mmole of Cadmium Chloride is dissolved in 20 ml of the solution of (Paraffin : Olic acide), have volume ratio as 5:3 The mixture was heated to 160°C with stirring to get the complete dissolution of $CdCl_2$. The period for mixture heating to form the Cd complex solution is about 1 hour.

3- Mixing the cadmium and sulfur with mole ratio 2:1; mixing the S-Paraffin solution and Cd- Paraffin + Oleic acid complex. The reaction process takes about 6 hours using 3-neck flask with magnetic stirrer. The complex of Cd solution is heated up to 220 °C for 20 min with Argon gas flow through the solution, then the S-Paraffin solution is injected gently with stirring into the hot reacted mixture, the heat is held at 300 °C, then the reaction mixture is cooled down and absolute ethanol is added to it at room temperature to quench the reaction. A yellow precipitate is formed meaning that the CdS nanostructure was formed. The CdS nanostructure then washed three times by ethanol and centrifuged, the last treatment is washing and centrifuged by toluene (fast process).The precipitate dried at room temperature to get CdS nanosparticles powder [9].

To manufacture the photodetector, 1x1 cm^2 P-type Silicon wafer (1.5***Ω***.cm and 508±15µm thickness) is used as a substrate. Also the substrate is photo-chemically etched in diluted (10%) HF acid for manufacturing another detector in order to study the role of silicon etched substrate. Tungsten halogen lamp of 250 watts was used as the photo etching source. Etching time was chosen to be 10 minutes [10, 11]. After the etching process, the sample has been rinsed with ethanol and stored in a glass container filled with methanol to avoid the formation of oxide layer above the porous Silicon film. The CdS nanostructure is deposited on the substrate with thickness of 1 µm to obtain the photo detector. A micro mask of (0.4 mm) electrodes spacing is used to deposit the Aluminum electrodes on the surface of the detector as shown in Fig.1.

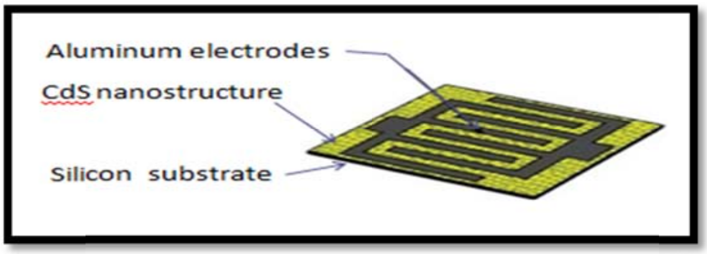


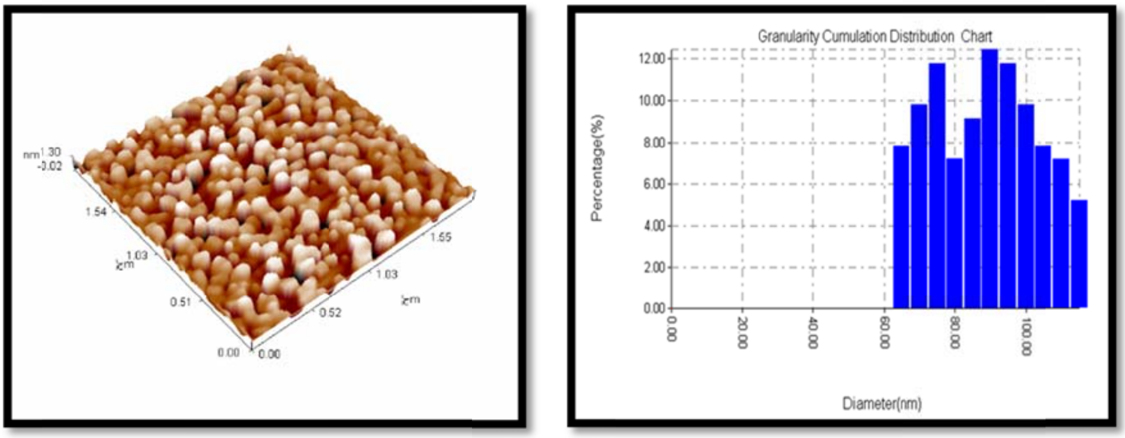
Fig.1: CdS photodetector device.

Results and discussion

The morphology of CdS structure has been investigated using AFM, SEM and X-ray.

a. Atomic force microscopic analysis

Fig.2a shows a 3D magnified picture of the sample surface, where we can see the nanostructure of the rough surface with the average roughness of 0.27 nm. Fig.2b is a panel diagram presents the height profiles measured along the sample surface with an average diameter of 86.20 nm.



(a) (b)

Fig.2: The AFM test for CdS nanostructure. (a): 3D photo of the sample surface. (b): a panel diagram of the height profiles measured along the sample surface.

b. X-ray diffraction

XRD patterns of the prepared CdS nanostructure shows the presence of the diffraction peaks corresponding to the (100), (002), (101), (220) planes. All the peaks in the XRD pattern can be indexed as hexagonal wurtzite structure. Fig. 3 shows the XRD of the prepared CdS nanostructure. These results are comparable to the values obtained by R. Meshram, 2012 [12].

The presence of small peaks in x-ray diffraction reveals the formation of nano-crystalline CdS films (also proved by AFM study).

The peaks are not sharp indicating that the average crystalline size is small. Due to size effect the peaks in the diffraction broaden and their widths become large as the particles become smaller.

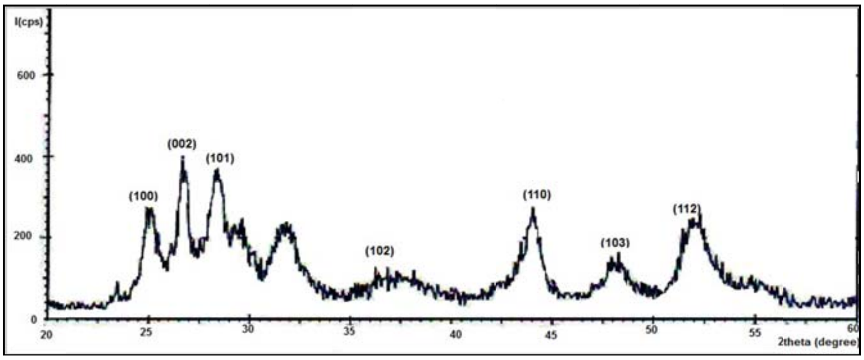


Fig.3: XRD of CdS nanostructure.

c. Scanning Electron Microscopy (SEM)

Fig.4. the image of CdS nanostructure shows the spherical clusters of CdS nanostructure, while the grain size estimated was about 20nm.

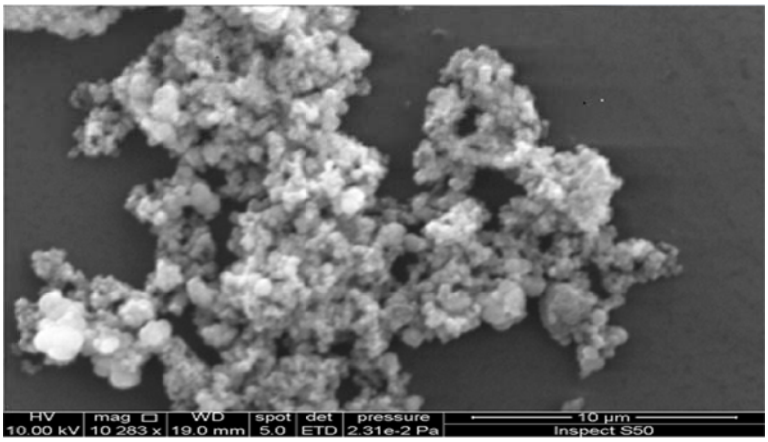


Fig.4: SEM of CdS nanostructure.

Optical properties of CdS nanostructure

The optical properties of the CdS nanostructure have been measured by the UV-VIS spectroscopy and photoluminescence PL spectrum. The absorption spectrum shows two peaks at 410 nm and 455 nm as shown in Fig.5. The absorption spectrum shows a blue shift relative to the peak absorption of bulk CdS indicating quantum size effect.

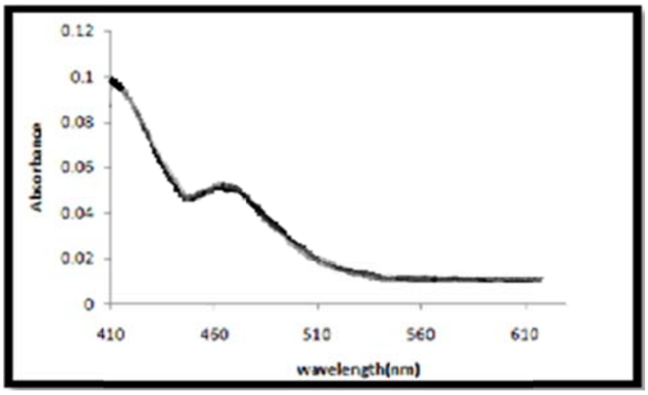


Fig.5: The absorption spectrum CdS nanostructure.

The optical band gap energy (Eg) of the semiconductor is calculated from Tauc relation. A plot of $(\alpha h\nu)^2$ versus hν shows intermediate linear region, the extrapolation of the linear part can be used to calculate the Eg from intersect with (hν) axis as shown in Fig.6.

The resultant values of Eg for CdS is found to be about (2.7eV) this value show a good agreement with the values presented by other workers[13, 14].

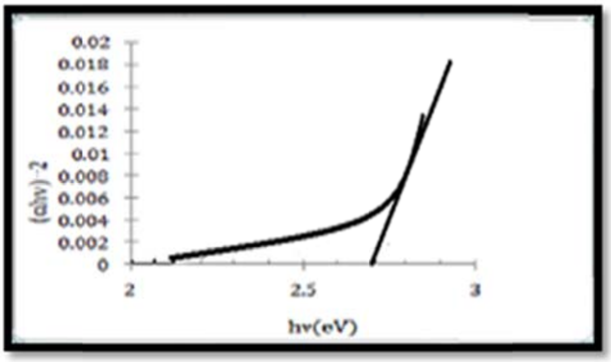


Fig.6: The energy gap of CdS nanostructure.

At room temperature PL spectra of sample is shown in Fig.7. The sample is excited with 300 nm source. Two peaks of Gaussian shape are fitted in the PL spectra and denoted as subbands I and II which are centered at about 460 nm and 565 nm, respectively. According to previous studies, generally there are two PL emissions of CdS nanostructure, namely band-edge and surface-defect emissions. Band-edge emission is attributed to the radiative recombination of excitons in the nanostructure. The PL peak energy of such band-edge emission is usually slightly lower than the band-gap energy of the CdS nanostructure. It is known that the band-gap energy of the nanostructure is related to the quantum confinement effect of excitons in the nanostructure. In the “quantum confinement region,” which is defined as the region with particle crystallited size smaller than 4 times the Bohr exciton radius about 12 nm for CdS, the excitons in the particles are “squeezed” and the band-gap energy increases noticeably as the size of the particles decreases.

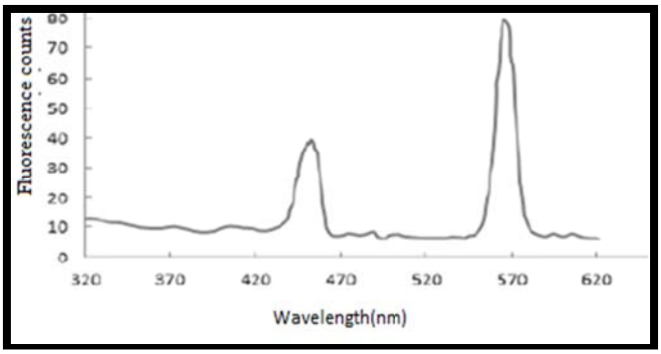


Fig.7: PL spectrum of CdS nanostructure.

In this case, the PL peak positions of the band-edge emission of the nanostructure are strongly size-dependent and usually in the wavelength range of 450–600 nm for CdS.

Some ultra small about 4 nm CdS nanostructure even have a band-edge emission peaked at about 400 nm. When the crystallite size of the CdS nanostructure becomes larger, the confinement of excitons becomes weaker. There is almost no exciton confinement when the crystallite size is about 50 nm, thus resulting in band-edge emission with size-independent PL peak positions at about 450 nm, a wavelength that is slightly smaller than that corresponding to the band-gap energy of bulk CdS.

On the other hand, the surface-defect emission is caused by surface states such as Sulfur vacancies, oxygen vacancies and defects in the CdS nanostructure. The PL peak positions of the surface-defect emission are usually in the range wavelength of 500- 600 nm [15].

Electrical properties of CdS nanostructure

a. Hall effect

The Hall Effect setting type (HMS3000) was used to obtain Table 1 which contains the electrical properties of CdS (conductivity, carrier mobility, charge concentration).

Table 1: Hall measurement for CdS nanostructure

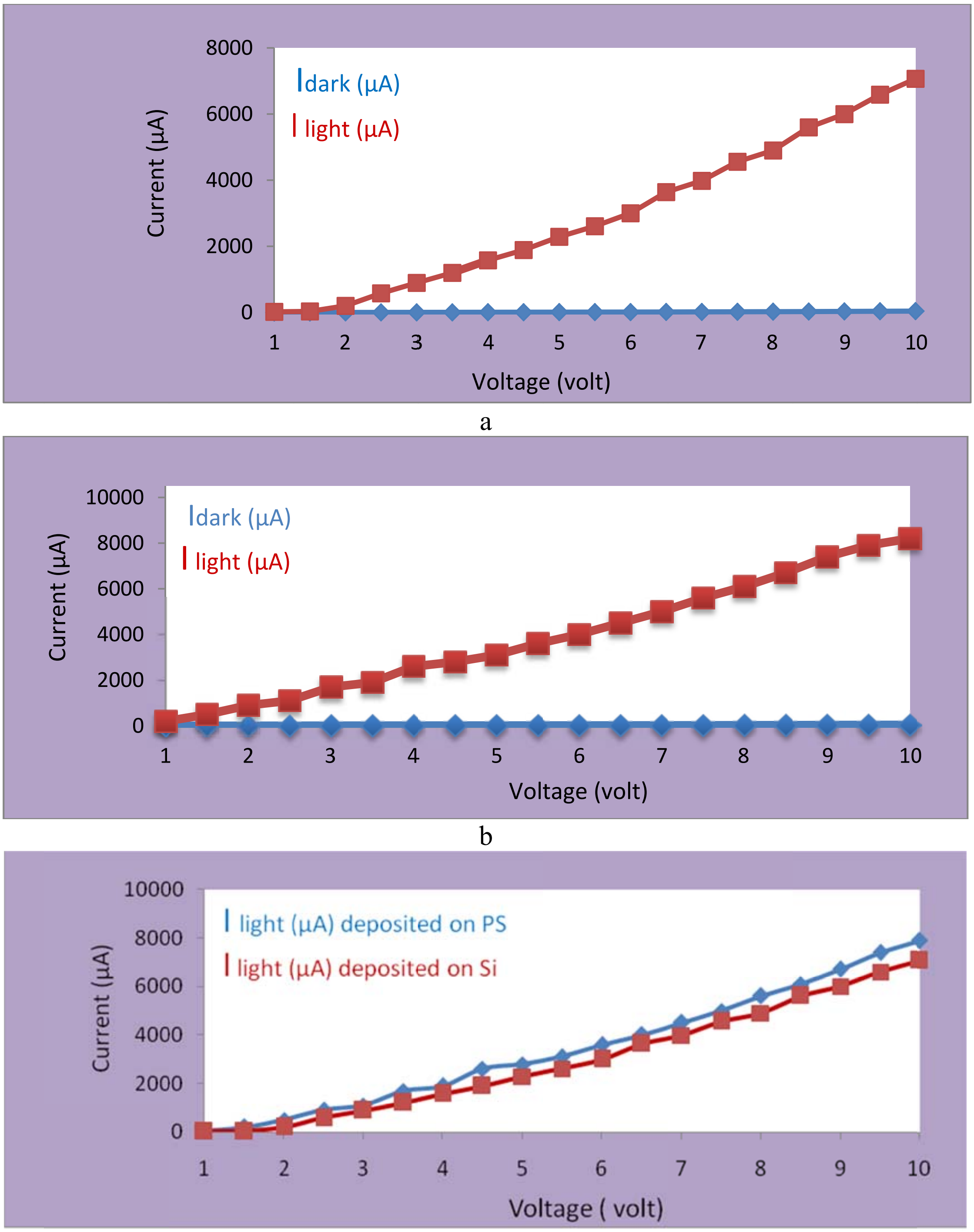
Materials	**Si**	**PS**	**CdS**	**Si+CdS**	**PS+CdS**
Bulk concentration (1/cm^3)	**3.7×10^{17}**	**1.06×10^{23}**	**-5.45×10^{10}**	**-2.49×10^{13}**	**-7.89×10^{14}**
Conductivity (1/Ω.cm)	**5.75**	**1.31×10^{6}**	**4.814×10^{-8}**	**10.4**	**6.93×10^{-6}**
Mobility (cm^2/V.s)	**96.7**	**77**	**5.512**	**6.14×10^{5}**	**5.48×10^{-2}**
resistivity (Ω cm)	**1.7**	**7.61×10^{-7}**	**2.077×10^{7}**	**9.58×10^{-2}**	**1.44×10^{5}**

I-V Measurement

The currrent–voltage (I-V) characteristics of the fabricated photodetector as a function of the baise voltage at dark and under illumination of Tungsten halogen lamp of 250 watts were tested.

The overall increase in current was observed at room temperature. Fig. 8 shows the I-V Characteristics of CdS nanostructure photo detectors based on both Silicon substrate and porous Silicon substrate. The current-voltage curves are the most commonly used characterization tool for the devices[16].

The photocurrent exhibits a linear response with light intensity and with bias voltage. The linear behavior may be related to the ohomic nature of the detector. All samples used in the experiments of the photoresponsivity measurements of the prepared detectors are carried out under identical experimental conditions. The conditions are; the distance between the light source and the measured sample, the wavelength and the power of the light source the distance between the electrodes mask, and the applied bias voltage. It can be observed that the dark current is very low compare with the photocurrent (illumination by visible light). In the other hand, the photocurrent when the CdS deposited on PS is higher than when it's deposited on Si.



c

Fig.8: I-V characteristics of CdS photo-detector. (a: CdS deposited on silicon, b: CdS deposited on porous silicon, and c: the comparison between them).

It can be observed the increasing in the photocurrent of the fabricated CdS photodetector on porous silicon layer at etching time of 10min as a function of the bias voltage. The CdS /PS structures have good potential to improve the performance of a CdS photoconductor device.

Table 2 shows the increase on the photoelectric gain which is obtaining from divided photocurrent to dark current when CdS deposited on Silicon and on porous Silicon.

Table 2: The measurement of photoelectric gain for CdS photodetector

Composition	**Si+CdS**	**PS+CdS**
Gain	**18**	**66**

Table 3 shows the figure of merit for CdS nanostructure photodetector. The photoconductive gain G, Which is calculated from the ratio between the photocurrent at the same bias voltage, is given by calculate T_r (transit time). T_r the equation $G=t/T_r$. Also the carrier life time t was calculated after = $l^2/\mu.V_B$, using the value of gain G and mobility for CdS as found from Hall measurement. l=0.04 cm and V_B =10V.

Table 3: The figure of merit for CdS nanostructure photodetector.

Composition	**T (ms)**	**I_n (Amp)**	**R_λ (Amp/W)**	**NEP (Watt)**	**D $(Watt)^{-1}$**	**D* $(Watt^{-1}. Hz^{1/2}.cm)$**
Si+CdS	**5.2**	**1×10^{-10}**	**0.03**	**1.04×10^{-12}**	**9×10^{11}**	**9×10^{11}**
PS+CdS	**2.1**	**3.9×10^{-12}**	**0.04**	**8.2×10^{-12}**	**9.9×10^{12}**	**9.9×10^{12}**

The addition of the etching process to this devise has decreased the response time from 5.2 ms to 2.1ms. This mean that addition is beneficial for enhancing the devise.

Conclusion

CdS have been prepared in this work as a nano size regime with a predominantly hexagonal phase. Optical absorption property of CdS nanostructure showed a blue shift in their absorption band edge (410 nm) from that of bulk (517 nm), it is explained due to the quantum size effect. X-ray diffraction analysis confirms the formation of hexagonal wurtzite structure of CdS with average grain size of 6.62 nm. AFM images depict the presence of spherical nanostructure. The CdS nanostructure photodetector has responsivity of (0.03Amp/W) and response time of (5.2 ms). Thus; the present method is an efficient for the preparation of nano-crystalline CdS nano-structural photo detectors. The photoelectric gain has improved from 18 to 66 by substrate changes from Si to PS. And this is success the enhancement of devise.

References

[1] G. Kauri, T. Singh, A. Kumar, International Journal of Education and Applied Research, 2, 1 (2012) 2310-9173.

[2] Y. Fu, M. Qiu, "Optical Properties of Nanostructures", Amazon Giveaway, Group by Pan Stanford, 8, 2011, 312p.

[3] Z. Lin Wang, Y. Liu, Z. Zhang, "Handbook of Nanophase and Nanostructured Materials", Kluwer Academic/Plenum Publishers, 1 (1), (2002) 1200p.

[4] M. Di Ventra, S. Evoy, J.R. Heflin, "Introduction to Nanoscale Science and Technology", Springer US, 978(1), 2004, XIII-611 p.

[5] J. D. Vincent, "Fundamentals of Infrared Detector Operation and Testing", Wiley, New York, 1990.

[6] J. Piprek. "Semiconductor Optoelectronic Devices: Introduction to Physics and Simulation". Academic Press, 2013, 279 p.

[7] J. I. Pankove, "Optical Processes in Semiconductors", Courier Corporation, (2012) 448 p.
[8] V. Singh, P. Chauhan, Journal of Physics and Chemistry of Solids, 70, 7 (2009) 1074-1079.
[9] O. A. Ibrahim, S. S. Ahmid, R. K. Ibrahim, K. M., O. N. Naji, Certified International Journal of Engineering and Innovative Technology, 4, 1 (2014) 2277-3754.
[10] M. A. Abdul Majeed, N. B. Hasan, G. H. Mohammed, American Journal of Condensed Matter Physics, 5, 3 (2015) 76-79.
[11] I. M. Mohammed, A. H. Shnieshil, International Journal of Application or Innovation in Engineering & Management, 2, 9 (2013) 2319-4847.
[12] R. S. Meshram, B. M. Suryavanshi, R. M. Thombre, "Structural and optical properties of CdS thin films obtained by spray pyrolysis", 3, 3 (2012) 1563-1571.
[13] O. O. Akinwunmi, G. O. Egharevba, E. O. Bolarinwa, Journal of Modern Physics, 5, 10 (2014) 257-266.
[14] B. A. Ezekoye, K. O. Ighodalo, V. A. Ezekoye, T. M. Emeakaroha, J. I. Ezema, P. O. Offor, Academic Journals, 10, 13 (2015) 403-412.
[15] Y. Lei, W. K. Chim, H. P. Sunand G. Wilde, Applied Physics Letters, 86, 10 (2005) 103-106.
[16] S. A. Hasoon, I. M. Ibrahim, R. M. S. Al-Haddad, Sh. S. Mahmood, International Journal of Current Engineering and Technology, 4, 2 (2014) 2347-5161.