

## Optoelectronic properties of ZnO/PS/n-Si Heterojunctions

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### Abstract:

In this work a colloid of nanocrystalline ZnO particles is prepared by chemical method, and then sprayed on porous silicon substrate which is prepared by electrochemical etching under a current density of  $15\text{mA/cm}^2$  for 10 min. The initial radius of the ZnO particles is found to be (2.2 nm). FTIR spectra exhibit the presence of Zn – O bond which indicates the formation of ZnO particles. Also spectra reveals the formation of  $\text{SiH}_x$  ( $x=1-2$ ) and Si-O bond which indicates the presence of porous layer. High performance rectifying was obtained, with high photoresponsivity of 0.54 A/W at 400 nm. The corresponding quantum efficiency was 166.7%. The results show that ZnO on porous silicon (PS) structures will act as good candidates for making highly efficient photodiodes.

**Keyword:** ZnO nanoparticles , ZnO/PS heterojunction, PS device.

### الخلاصة:

في هذا البحث تم تحضير عالق البلورة الدقيقة لجزيئة اوكسيد الخارصين ZnO بالطريقة الكيميائية ، وبعد ذلك تم رشه على سيليكون مسامي محضر بطريقه وجود الاظهار الكهروكيميائي تحت كثافة تيار  $10\text{mA/cm}^2$  لزم من 10min . وجد ان نصف القطر الاولي لجزيئات ZnO هو 2.2nm . يظهر من طيف FTIR اصرة Zn-O والتي تشير لتكوين جزيئة ZnO . وايضا ان الطيف يكشف تكوين اصرة  $\text{SiH}_x$  ( $x=1-2$ ) واصرة Si-O والتي تشير الى وجود الطبقة المسامية . تم الحصول على كفاءة تقويم عاليه مع استجابيه ضوئيه عاليه تصل ( 0.54A/W ) عند ( 400nm ) . هذا يقابل كفاءة كمية ( 166.7% ) . تبين النتائج ان اوكسيد الخارصين على تراكيب السليكون المسامي سيعمل كبديل جيد لصنع دايودات ضوئية بكفاءة عالي

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#### Introduction:

Formation of stable rectifying junctions with porous silicon (PS) [1] with good forward reverse characteristics is one of the most challenging problems for proper exploitation of the material in the device industry. Vacuum deposited Au [2] and Al [3], sputter – coated indium tin oxides [4] and conducting polymers [5] have been used with limited success for fabricating light – emitting diodes and photo detectors, we have recently shown that deposition of  $\text{SnO}_2$ : Sb:  $\text{Tb}^{3+}$  on PS from an aqueous solution gives significantly better rectifying or Ohmic contacts due to the filling of pores by the deposited material [6]. Deposition of a film by a similar technique which is both electrically conducting and optically transparent could be lead to the fabrication of improved PS based photodiodes and electroluminescent devices. In this work ZnO colloid is prepared by wet chemical method deposited by spray on porous silicon gives photodiodes with excellent rectification and photo response properties.

#### Experiment:

PS was formed by an anodic etching bath with the electrolyte consisting of a mixture of HF and ethanol in the ratio 1: 2 by volume. The substrates were (1.5- 4  $\Omega\text{cm}$ ) n-type (111) Si wafers. Anodization was performed for 10min under a current density of  $15\text{mA}/\text{cm}^2$  then the sample

were washed in deionizer water and dried in air.

ZnO colloid was deposited on the porous silicon surface from spray. Colloid of ZnO nanoparticles was prepared by wet chemical method. It involved 50 ml of 0.14 m  $\text{LiOH}\cdot\text{H}_2\text{O}$  solution was added to 50mL of 0.1 m  $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$  solution. The solution first cooled to  $0^\circ\text{C}$  before the hydroxide solution was added slowly to the zinc solution while stirring.

Optical transmission spectra for colloid was recorded a UV/VIS Cecile-7200 dual beam spectrophotometer, the (8400S, SHIMADZU) Scans of the FTIR measurements are performed over range between (400-4000)  $\text{cm}^{-1}$  for porous silicon and (200-500)  $\text{cm}^{-1}$  for ZnO. The thickness of film is measured with Fizeau fringes. Dark and light (I-V) measurements were done by using a Keithley- 616 digital electrometer and Tektronix CDM 250 multimeter were used to measure the corresponding current . Spectral photoresponsivity measurements were performed using a light source and a monochromator with spectral range (300-1200) nm.

#### Results and Discussion:

Results of optical transmittance spectrum of the ZnO colloid prepared are presented in figures (1), One can notice that ZnO colloid have high absorption for UV light but transmits visible light. The mechanism of UV absorption is that material involves the use of photon energy to excite

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electron from the valence band to the conduction band [7]. The energy gaps  $E_g$  of ZnO colloid is calculated as follows [8]:

$$E_g = \frac{hc}{\lambda_{cf}}$$

Where  $h$  is the Plank constant.  $c$  is the velocity of light and  $\lambda_{cf}$  is the threshold (cutoff) wavelength of the transmission spectrum of the investigated samples as shown in figures (1). The gap energy  $E_g$  is inversely proportional to the square of the particle radius  $R$  [9]. According to the effective mass approximation; one can use the energy position to estimate the average particle size, with effective masses of electrons ( $m_e = 0.28 m_0$ , where  $m_0$  is the free electron mass) and hole ( $m_h = 0.59 m_0$ ) is taken from reference [10]. This was obtained of 2.2 nm for prepared dots.

Figure (2) shows the FTIR spectra of p-type porous silicon prepared by electrochemical etching, the peaks between 3000 to 3650  $\text{cm}^{-1}$  is the SiO-H stretching vibration; while a peak at  $\sim 2000 \text{ cm}^{-1}$ , 2100  $\text{cm}^{-1}$  and 2200  $\text{cm}^{-1}$  is related to Si-H<sub>2</sub> and Si-H respectively. The band between 1000 to 1250  $\text{cm}^{-1}$  is the Si-O-Si stretching vibration. So that Si-O-Si structure with vacancies ( $\nu$  (Si-O-Si) = 1080  $\text{cm}^{-1}$ ) called "Not bridge oxygen hole center" (NBOHC), as the surface structure responsible for PL emission [11]. A peak at  $\sim 977 \text{ cm}^{-1}$  is related to SiH bending vibration, then a peak at

$\sim 900 \text{ cm}^{-1}$  is SiH bending vibration. A peak at  $\sim 856 \text{ cm}^{-1}$  is related to SiH<sub>2</sub> wagging vibration mode, while a peak at  $\sim 840 \text{ cm}^{-1}$  is related to Si-O-Si and a peak at  $\sim 862 \text{ cm}^{-1}$  is due to SiH<sub>3</sub> symmetric bond, then a peak at  $\sim 660 \text{ cm}^{-1}$  is due to SiH deformation mode and peak at  $\sim 610 \text{ cm}^{-1}$  is related to the Si-Si bond vibration. The peak around  $\sim 750 \text{ cm}^{-1}$ , and  $\sim 1092 \text{ cm}^{-1}$  is related to NO<sub>3</sub> wagging vibration modes [12] while peaks at  $\sim 460 \text{ cm}^{-1}$  and  $\sim 470 \text{ cm}^{-1}$  are related to SiO-Si mode, a peak at  $\sim 850 \text{ cm}^{-1}$  is related to SiH<sub>2</sub> wagging vibration mode. This result agreed with the results of Sacleto et al [13].

Figure (3) show the FTIR spectrum of ZnO colloid. The absorption peak around  $\sim 420 \text{ cm}^{-1}$ , &  $\sim 412 \text{ cm}^{-1}$  corresponds to bending of Zn - O [14, 15].

Figure (4) represents the I-V characteristic of ZnO/PS/n-Si under various levels of illumination. The I-V characteristic for forward and reverse bias for ZnO/PS/n-Si is represented by double schotky heterojunction mode in which the current increased in both directions. It has been understood from studies that the visible photon energy transmitted through the ZnO layers and absorbed mainly in the depletion region, creating electron - hole pairs that depletion generator the photocurrent under reverse bias [16], due to the depth limit of light penetration, while figure (5) shows the variations of responsivity as a function of

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wavelength for ZnO/PS composite. The spectral responsivity of structures is measured in the wavelength range from 300 to 1100 nm. It's found that the maximum value obtained was 0.59A/W at 400 nm wavelength, and other is 0.15A/W at 1100 nm. Figure (6) shows the variation of quantum efficiency (which is defined as the number of carriers per photon or

$$h \frac{I_{ph}}{f} \text{ where } f \text{ is photon flux) as a}$$

function of wavelength for ZnO/PS/p-Si devices prepared, which was 166.7%, this come from the avalanche effect inside the porous silicon and later is generated by the voltage drop in porous silicon which is intrinsic and as narrow as silicon wire [17]

## Conclusion

Highly transparent ZnO colloid has been prepared by chemical wet method. The optical transparency of the film is above 80% in the wavelength range of (200 – 350) nm. Characterized heterojunction photo – diodes made from ZnO colloid on porous silicon show very good spectral response. The simplicity for making these diodes makes them very attractive for their application as a possible substitute of conventional silicon photo detector.

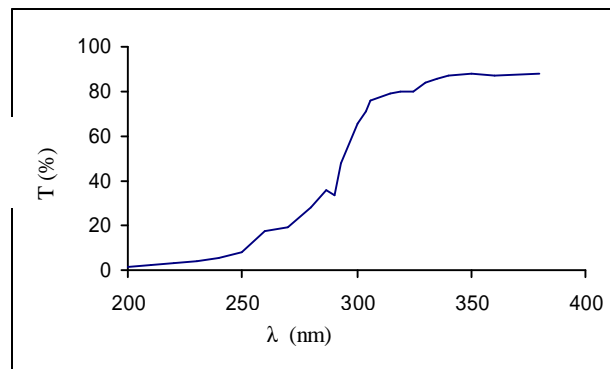
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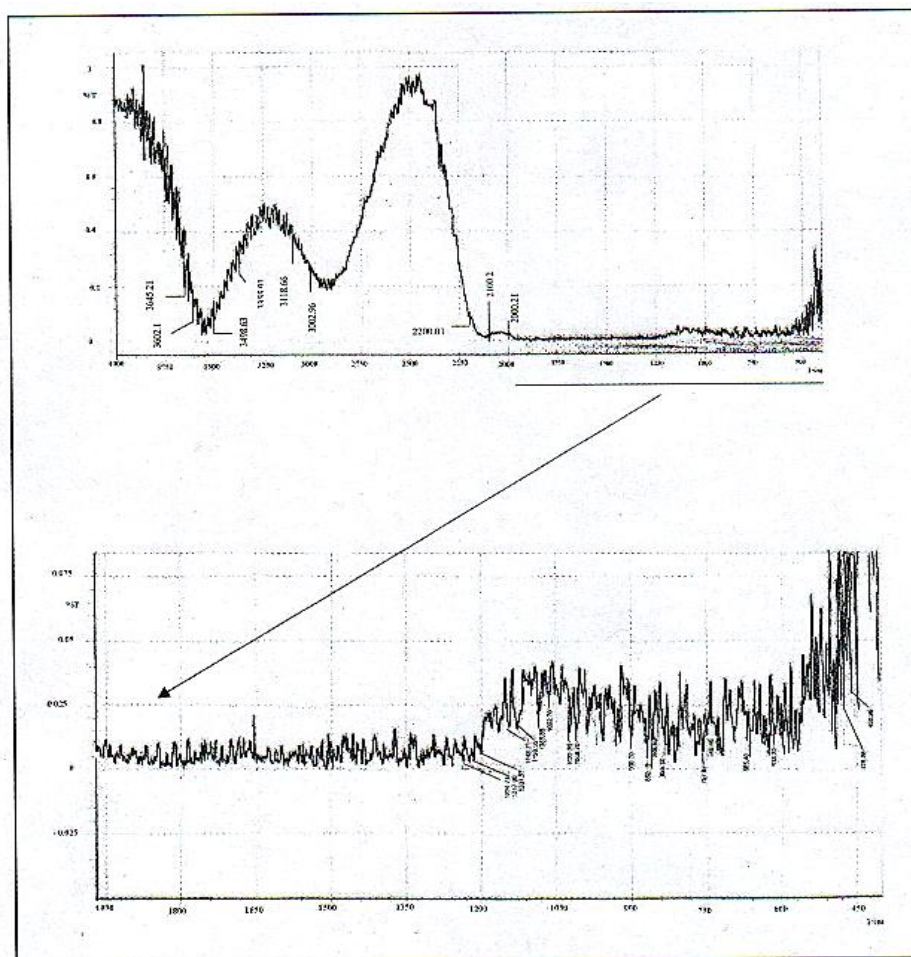
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**Figure (1): Transmission of ZnO colloid**



**Figure (2): FTIR spectrum of PS/n-Si**

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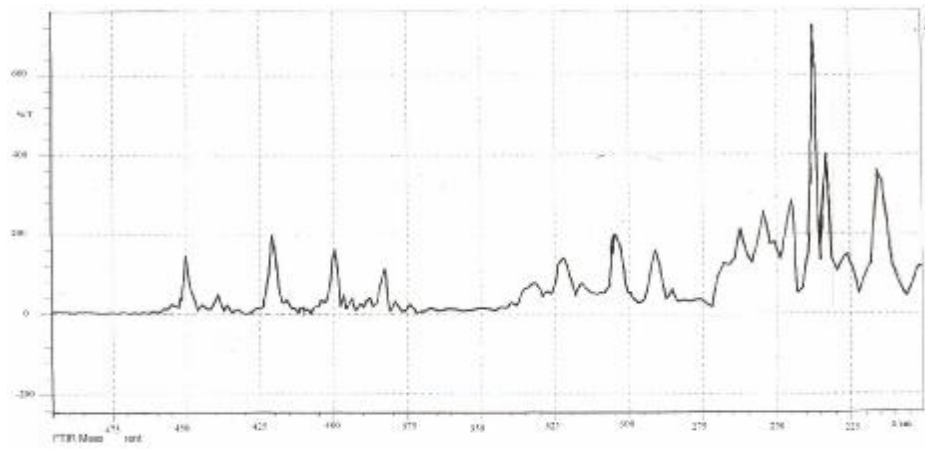


Fig. (3): FTIR spectrum of ZnO colloid

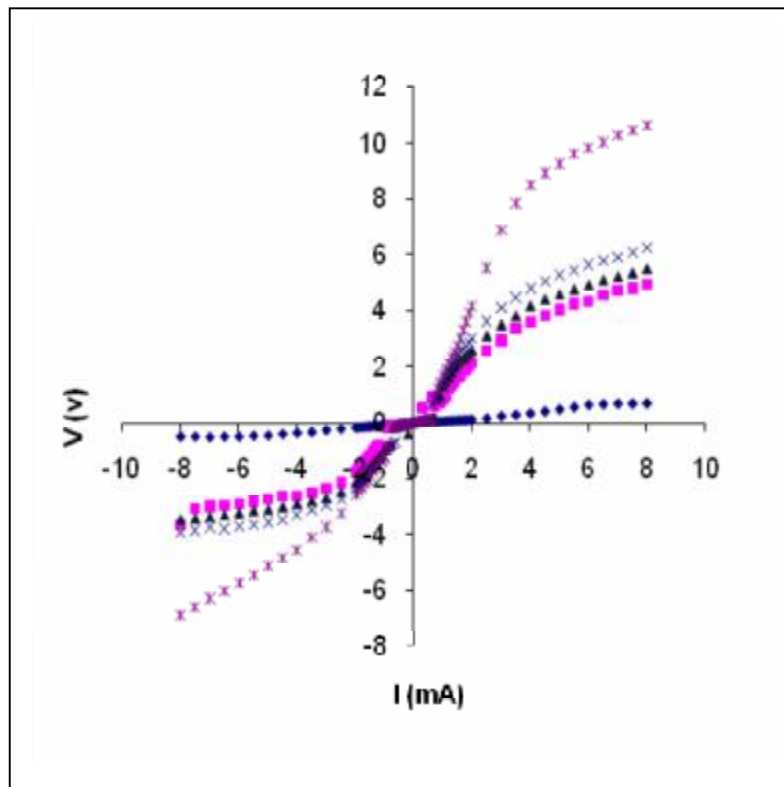
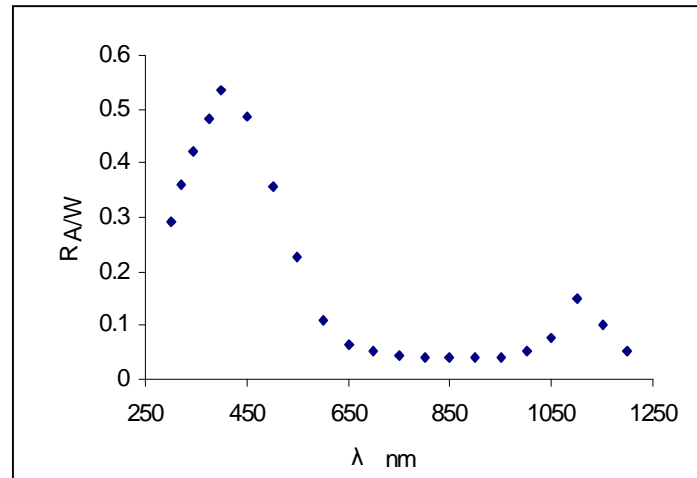
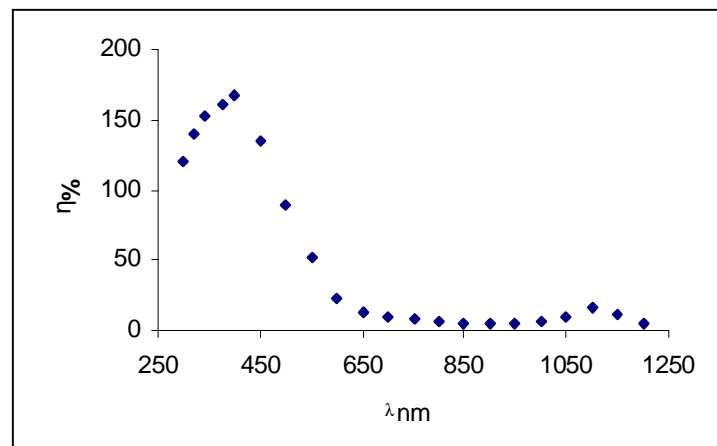


Fig.(4) I-V characteristic of ZnO/PS/n-Si under several of levels of illumination:( $\diamond$ ) dark current, ( $\blacksquare$ )  $41.5 \text{ mW/cm}^2$ , ( $\blacktriangle$ )  $90 \text{ mW/cm}^2$ , ( $+$ )  $240 \text{ mW/cm}^2$  & ( $*$ )  $400 \text{ mW/cm}^2$

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**Fig. (5): Spectral responsivity of ZnO/ PS/p-Si sample****Fig. (6): Quantum efficiency of ZnO/ PS/p-Si sample**