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ZnO/Porous-silicon photovoltaic UV detector

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Abstract

A P-type Zinc Oxide (ZnO) /porous-silicon photovoltaic device was fabricated to detect fast ultraviolet (UV) radiation pulses. The photovoltaic UV detector, based on the deposition of the ZnO wide-band gap semiconductor material on nanospikes silicon layer to form a heterojunction, has fast response time to the UV pulses. The current-voltage characteristic, the capacitance variation with the applied voltage and the ideality factor of the heterojunction were studied. The operation of the detector under the reverse bias of -2 volts has successfully detected an ultra fast nitrogen laser pulses at 385 (nm). The traced output signals have a rise time of 1(µsec) with photoresponsivity of about 0.8 A/W.

Keywords: ZnO, heterojunction; UV detector; porous silicon layer; photovoltaic detector.

I. INTRODUCTION

The photodetector for the ultraviolet (UV) radiation has attracted a great interest due to its wide range of applications. The first priorities of application were given to the environmental monitoring, missile warning system and to the solar astronomy [1, 2]. In the last decade the silicon photodiode covered the UV detection region. The silicon ultraviolet photodetector has many dramatic limitations, such as the law quantum efficiency in the deep UV spectrum due to passivation layer. The other limiting factors are the age reduction of the silicon photoresponse when exposed to radiation of much higher energy than its energy gap and the sensitivity of the silicon to the visible spectrum [3].

ZnO is a direct, wide band gap semiconductor material [4]. This material has a potential application in the detection of the UV spectrum [5]. The UV detector based on polycrystalline ZnO thin film shows law photoresponsivity and long response time of the order of few minutes [6]. Since the one-dimension ZnO nanostructures are characterized by presence of deep level surface traps, the ZnO detector exhibits long life time of the photo carriers [7]. Despite a great deal of research on ZnO UV detector, most of the work concentrated on the improvement of the micro mask electrodes [8-10]. The improvement of the photoresponsivity of the ZnO UV detector was carried out by the surface treatment of the ZnO thin film. The covering of the ZnO film surface with nanosheet of different types of polymers has highly improved the detector photoresponsivity [6]. Coating the ZnO film surface with polyamide nylon was found to improve the photoresponse of the photoconductive detector to four orders of magnitude, but still the response time is slow and it was in few seconds range [11]. The deposition of the ZnO nanofilm on Porous-silicon layer has highly enhanced the resistivity of the ZnO nanofilm leading to fast response in UV region

In this work, a photovoltaic ZnO UV detector is fabricated. The ZnO nanofilm deposited on Porous-silicon layer has formed a heterojunction with the silicon nanospikes layer. The operation of this heterojunction detector under a reverse bias has improved the speed of response of the ZnO UV detector and a pulses of 1 µs rise time and 10 µs fall time were displayed after illumination the ZnO photovoltaic detector with high repetition rate UV nitrogen laser.

II. EXPERIMENTAL WORK

The n-type Si wafer was used as a starting material in photochemical etching. The resistivity of the wafer was 0.05 Ω.cm and its thickness was 500 µm. Samples of dimension of 2x2 cm were cut from the wafer and rinsed with acetone and methanol to remove dirt. In order to remove the native oxide layer on the samples, they were etched in dilute (10%) Hydrofluoric acid (HF). After cleaning the samples, they were immersed in HF acid of 50% concentration in a

Teflon beaker. The sample were mounted in the beaker in such a way that the current required for etching process could complete the electrical circuit between the irradiated surface and the bottom surface of the Si sample A 100W Tungsten halogen lamp integrated with convex ellipsoidal mirror was used as the photon beam source. The irradiation time for the photo-etching was taken to be 30 minutes. The choice of this time depends on the electrical properties of the prepared samples. At the end of the photochemical etching process, the samples were rinsed with ethanol and stored in glass containers filled with methanol to avoid the formation of oxide layer above the nanospikes film. The morphology of the nanospikes surface produced by photochemical etching on Si wafer was studied using Scanning Probe Microscope (SPM).

ZnO thin films, prepared by chemical spray pyrolysis method, were deposited on porous silicon substrates heated to 400 $^{\circ}$C. The spray solution of 0.1 M morality was prepared by dissolving Zinc Chloride ($ZnCl_2$) of 98% purity in 100 ml distilled water. The substrate which was heated to 400 ^{o}C was kept at this temperature during the spray time. The prepared mixture ($ZnCl_2 + H_2O$) was sprayed by the spray nozzle, with the help of nitrogen as the carrier gas. The spraying time is controlled to be about 4 sec. The time interval between successive sprays was 12 sec in order to restore the previously set spraying temperature 400 ^{o}C. The chemical spray pyrolysis experimental setup is similar to the standard one which is shown in Figure1 [12].

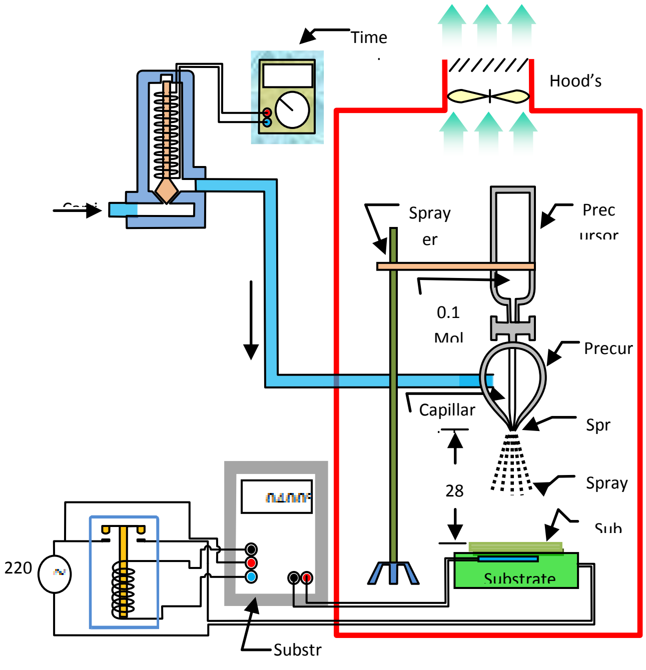

Figure 1: Schematic representation of the spray pyrolysis deposition system

The optimum experimental conditions for obtaining homogeneous ZnO thin film at 400 ^{o}C were determined by the spraying time, the drying time, the height of and the flashing gas pressure [11]. The measured thickness of the prepared ZnO films on porous silicon layer was measured by interference method and it was of the order of (800 nm). The morphology of the ZnO film was scanned using Scanning Probe Microscope (Type AA3000 SPM) from Angstrom Advance Inc. The micro mask of (400µm) electrode spacing was used to deposit the electrical electrode on the ZnO layer surface. The photoresponsivity of ZnO photovoltaic UV detector at 2V bias voltage was carried with 365 nm wavelength nitrogen laser of about 400 ps pulse duration. The electrical circuit applied in the measurements of the detector parameters is shown in Figure 2

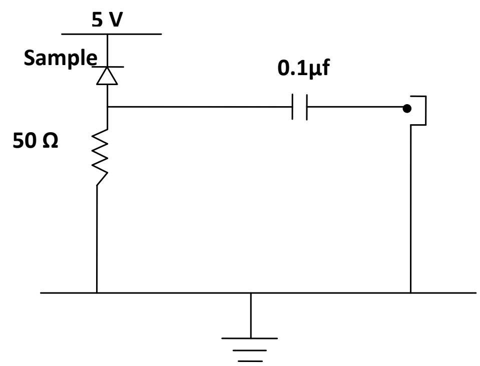

Figure2: the operation diagram of ZnO photovoltaic detector

III. RESULTS AND DISCUSSION

The morphology of the porous silicon layer is tested by the (SPM) and the surface image is shown in Figure3. The figure shows that the nanospikes distribution for ZnO sample of 30 – minute etching time is nearly uniform and it is of few nanometer heights and of about 10 nm in depth. The formation of the nanospike layer increased the resistivity of this layer to order of 10^5 **Ω**.cm [12]. The increase of resistivity of the nanospikes layer may be attributed to several reasons; the capturing of the charges carriers by the traps at the nanospikes; the diffusion of the impurity atoms to the electrolyte, or to the wall of the pores and may be due to the passivation of the impurity atoms with hydrogen [12]. The morphology of the ZnO film deposited on porous silicon (PS) is shown in Figure4. It can be noticed from the figure that the nanocrystallites were formed on the surface of the ZnO sample deposited on porous silicon. The dimensions of the nanocrystalline structures of the ZnO nanofilm surface were measured and they were found to be in the range of (20-50 nm).

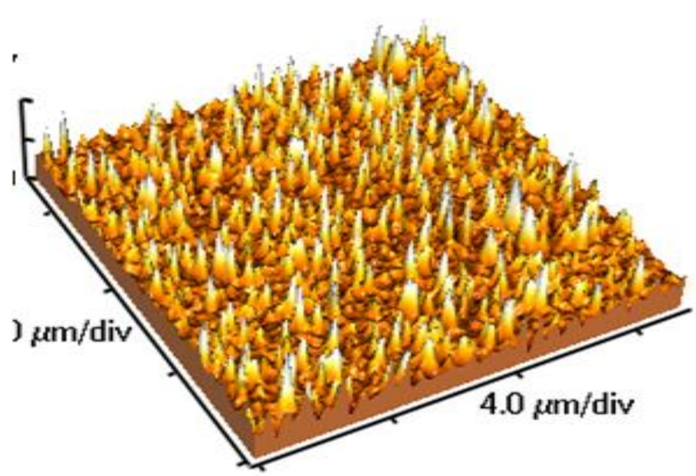

Figure 3: scanning probe Microscope morphology of the porous silicon sample

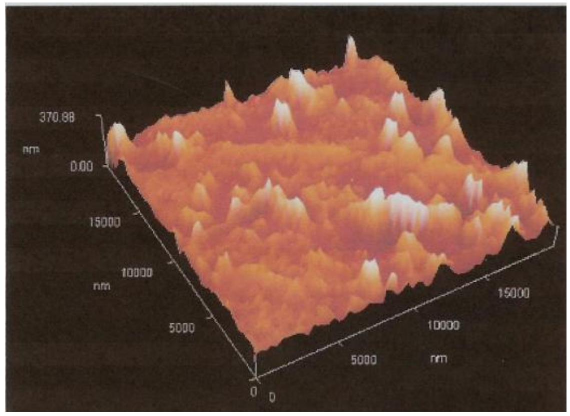

Figure 4: scanning probe Microscope micrograph of ZnO thin film deposited on PS

The X-ray diffraction (XRD) patterns of the n-ZnO film prepared by spray pyrolysis technique deposited on nanospike layer of n-silicon substrate has been shown in Figure 4. Obviously ZnO has hexagonal (wurtzite) polycrystalline structure. The (002) and (201) diffraction peaks of ZnO observed at 2Θ= 36.48 °and 2Θ= 69.74° respectively and (400) peak of Si is observed at 2Θ=71.02°. The grain size (g) on the surface of the ZnO film can be estimated using Scherrer's formula, then the crystalline size is estimated of about 86.25 nm.

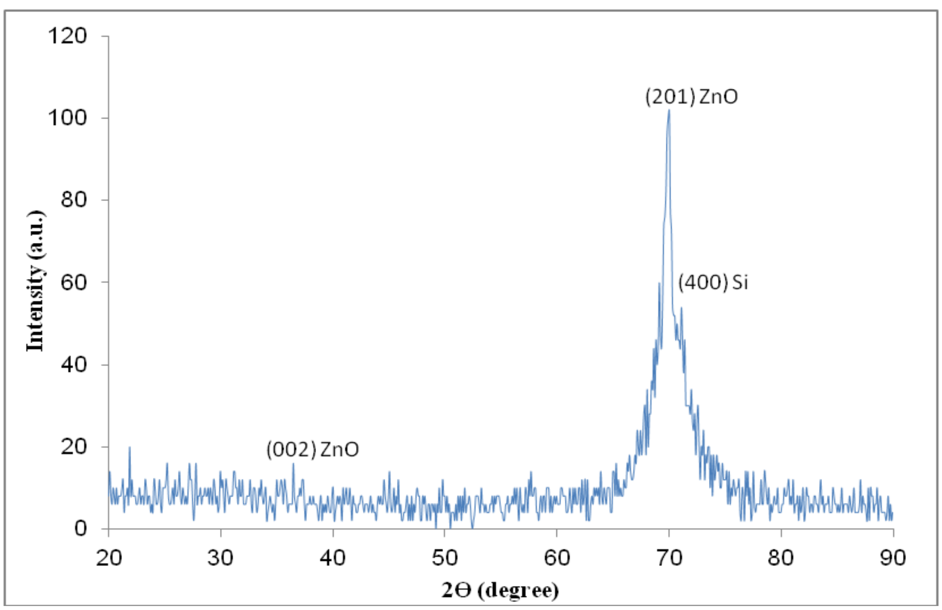

Figure 5: The X-ray diffraction of the ZnO on porous silicon

The room temperature photoluminescence (PL) spectrum of the prepared ZnO film on porous silicon layer is shown in Figur e6. The spectrum displays two luminescence peaks around 370 nm and 430 nm. The first peak (near – band edge) is due to the intrinsic band to band transition which corresponds to 3.35 eV and it is originated from the recombination of the free exciton. The second peak is due to donor - acceptor pair emission at 2.88 eV with a relatively high intensity ratio with respect to the first peak. The deep level broadening luminescence was observed at 540 nm with low intensity compared with the band to band transition peak and the donor – acceptor emission. The quenching of the broad band intensity around 540 nm may be attributed to the improvement of the crystallization structure of the ZnO film deposited on the nanospikes silicon layer. This result gives a good evidence of the reduction in the surface state formation when ZnO deposited on porous silicon.

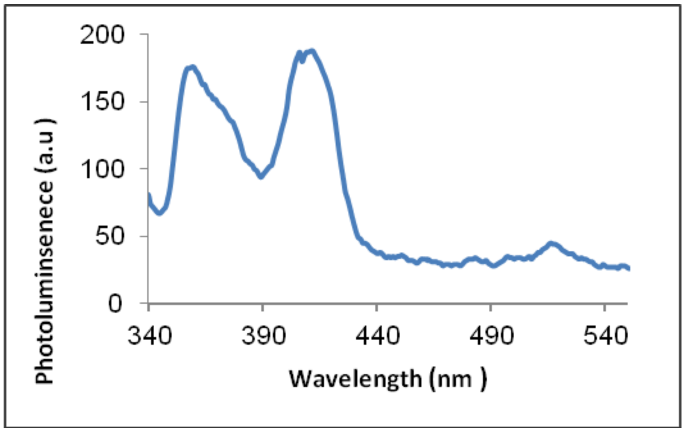

Figure 6 : The Photoluminescence spectrum of ZnO film on PS layer.

The absorption spectrum of the ZnO surface is shown in Figure7. The figure shows high absorption coefficient in the UV region, whereas it is transparent in the visible region. Assuming direct transition and referring to Tauce relation, the dependant of $(\alpha h\nu)^2$ on $h\nu$ is plotted as in Figure8 [13].

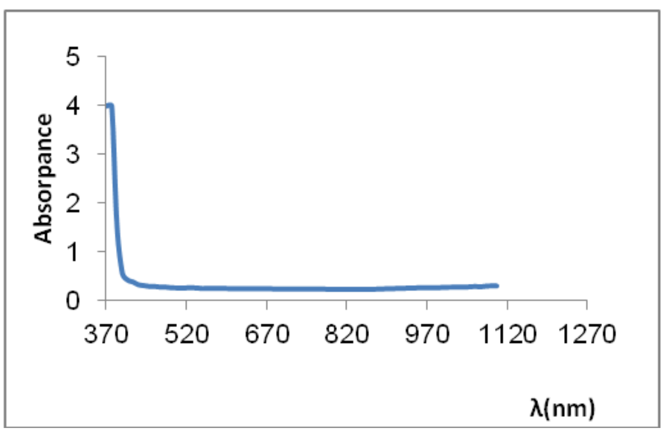

Figure 7: The UV-VIS absorption spectrum of ZnO thin film

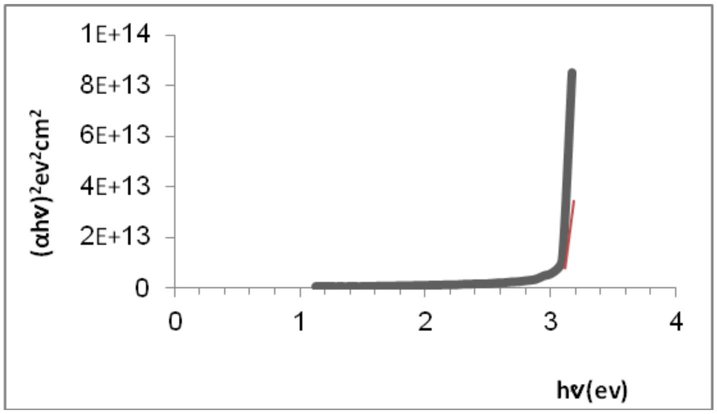

Figure 8: plot of $(\alpha h\nu)^2$ vs. hν ZnO thin film

The extrapolation of the linear part of the above plot to $(\alpha h\nu)^2=0$ gives the energy gap value of ZnO film, which was found to be about (3.1eV),this value is not far away from the value extracted from the luminescence spectrum. The energy gap structure of the deposited ZnO nanofilm on the porous silicon layer is shown in Figure9, whereas the device structure of p-ZnO/p-Si is illustrated in Figure 10.

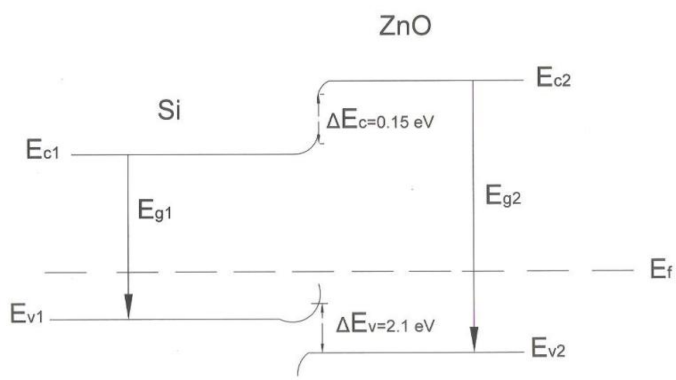

Figure 9: p-p heterojunction

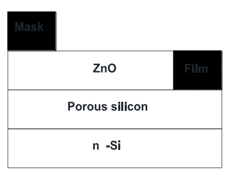

Figure 10: the based structure of p-Zno/p+-Si .

III.1 The I -V characteristic

The deposited ZnO nano film on the high resistivity nano spikes silicon layer forms a p-p heterojunction which was illustrated by Figure9. The formed heterojunction is characterized through the I-V characteristic measurements shown in Figure11**.**

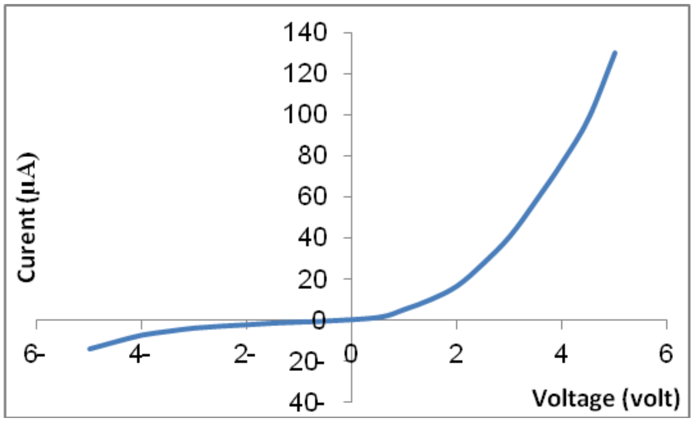

Figure 11: I-V Characteristic without illumination of UV source

It can be noticed from this figure that the junction exhibits rectifying behavior. This rectifying behavior is attributed to heterojunction potential barrier at the ZnO/ Porous-silicon interface. The formation of the heterojunction structure is referred to the difference in energy gap between the ZnO and Porous-silicon .The ideality factor of the formed junction was determined from the plot of lnI-V following the relation :

$$I = I_s\left(e^{ev/kt} - 1\right) \qquad (1)$$

and it was found to be about 1.1 for the diffusion current region and 3.3 for the recombination current region as shown in Figure12.

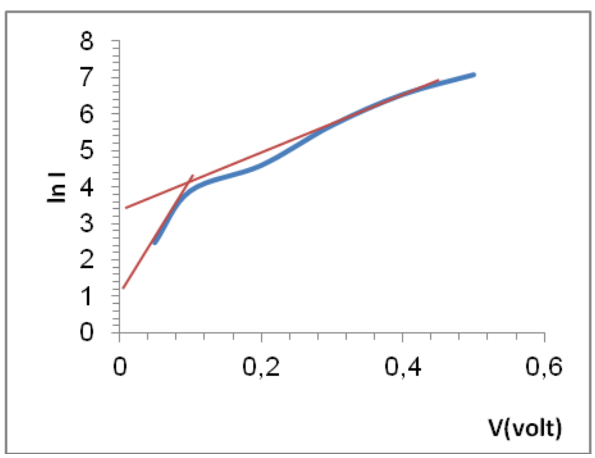

Figure 12: I-V Characteristic without illumination of UV source

Since in p-n junction, the barrier height seen by electron and holes are the same and equals to the built in potential (V_{bi}), in heterojunction, the barrier seen by electron and holes are different and do not equal to

(V_{bi}). In this case the conduction – valance band offsets, is shown in Figure9, is considered leading to a large rectifying ratio can exist in the p-p heterojunction. The diode under a reverse bias exhibits a voltage dependent capacitance caused by variation in the stored charge at the junction. The cutoff frequency, which represents the limit of the photodetector response time is related to the junction capacitance and to the load resistance, by the relation:

$$f = \frac{1}{2\pi C R_L} \tag{2}$$

In case of our fabricated detector sample the junction capacitance C is found to be about 1nF under reverse bias voltage of -2v and for $R_L \approx 50\Omega$; the cut off frequency is found to be about 3.3 MHz leading to a response time of the order of 300 ns. The output UV nitrogen laser signal detected by the fabricated ZnO/PS-Si photodetector is shown in Figure13**.** It can be noticed from the figure that the detected pulse has 1 µs rise time and the fall time of about 5 µs.This result indicates that the fabricated photovoltaic detector is fast and can be useful to work with high speed UV sources.

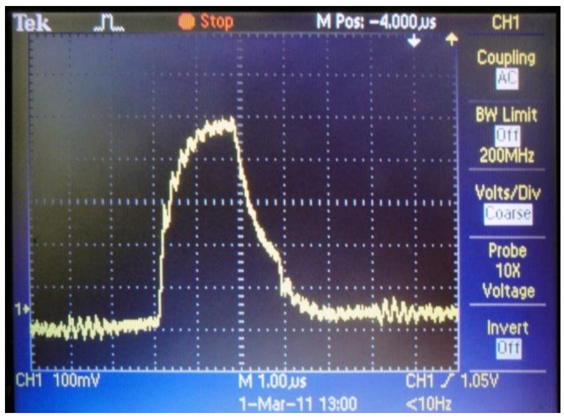

Figure 13: detector to UV source photo response time of fabricated ZnO

III. 2 The C-V characteristics

The capacitance-voltage(C-V) characteristic is useful in obtaining the required information about the formed junction. The potential barrier at the junction, the carrier concentration, the presence of the traps in the device material and the junction width are the most parameters determined from the C-V study. The plot of $1/c^2$ versus reverse bias voltage of the ZnO/PS-Si layer at a frequency of 1MHZ is shown in Figure 14.

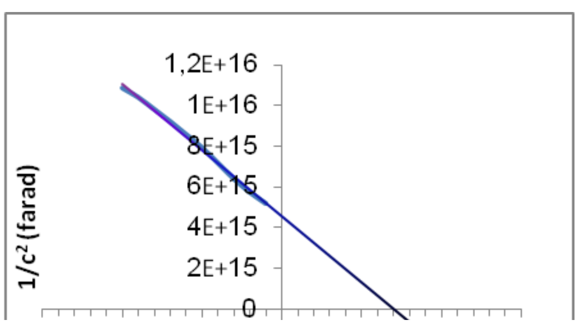

Figure 14 : 1/c2 vs. v of the ZnO on porous silicon

The output result should yield a straight line and the extrapolation of this plot gives the value of the built in potential V_{bi} which was found to be about (0.7 V). The effective acceptors concentration (n_d) in the ZnO nano layer is calculated from the relation;

$$n_d = \left(\frac{2}{e\varepsilon_s\varepsilon_o A^2}\right)\left(\frac{\Delta V}{\Delta \frac{1}{C^2}}\right) \quad (3)$$

Using the values of ε_s for ZnO to be 5.5, the slope $V/1/C^2$ of about $1.092*10^{15}$ as extracted from Figure13. And for the junction active area of the order of (3mm) the value of n_d was found to be about $5.1*10^{17}$ cm^{-3}. This value is in a good agreement with the value found by Hall measurements of our samples. The width of the depletion layer (W) for the
ZnO deposited on Porous-silicon is related to the n_d , ε and the built in potential V_{bi} , as:

$$W = \left(\frac{2\varepsilon_s \quad V_{bi}}{e.n_d}\right)^{\frac{1}{2}} \quad (4)$$

Using the values of V_{bi} and n_a as mentioned before the estimated depletion layer value was found to be 980 nm.

IV. CONCLUSION

The heterojunction ZnO /porous Silicon was fabricated by deposition of ZnO semiconductor material on nanospikes layer of etched Silicon substrate. The device was found to be p-ZnO/p-Si junction. The ideality factor of the junction was found to be 1.1 at the diffusion current region. The fabricated device was tested as a photodiode to detect ultrafast nitrogen laser and has shown 1 µsec rise time and 21 µsec fall time.

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