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Fabrication and Characteristics of Fast Photo Response ZnO/Porous Silicon UV Photoconductive Detector

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Abstract

Fast response time UV photoconductive detector was fabricated based on ZnO film prepared by thermal chemical spray pyrolysis technique. The ZnO nanofilms are grown on the porous silicon (PS) nanosurface which has drastically reduced the response time of the ZnO UV detector from few seconds to few hundreds of microseconds. The surface functionalization of the ZnO film deposited on porous silicon (PS) layer by polyamide nylon has highly improved the photoresponsivity of the detector to 0.8 A/W. The normalized detectivity (D*) of the fabricated ZnO UV detector at wavelength of 385 nm is found to be about 2.12×10^{11} $cm \cdot Hz^{1/2} \cdot W^{-1}$. The ZnO film grown on the porous silicon layer was oriented in the c-axis and it is found to be a p-type semiconductor, which is referred to the compensation of the excess charge carriers in the ZnO film by the nanospikes silicon layer.

Keywords: Porous Silicon, P-ZnO/PSi Junction, Nanostructure Materials, Photoconductive Detectors, Recombination and Trapping

1. Introduction

The ultraviolet (UV) photoconductive detectors have attracted a great interest due to its wide range of applications. Most of the applications are concentrated in the environmental monitoring, missile warning system, and solar astronomy [1,2]. In the last decade, the silicon material was covered the UV detection region. The silicon ultraviolet photodetectors have many dramatic limitations, like the low quantum efficiency in the deep UV range due to the passivation layer. The other limiting factor is the age reduction of the Si photodiode exposed to radiation of much higher energy than the Si band gap [3].

The ZnO is a wide and direct band gap semiconductor material, which has a potential application in the UV detection [4]. The UV detector based on polycrystalline ZnO thin film shows low responsivity and long response time which is of the order of few minutes [5,6]. Since the one-dimension ZnO nanostructures are characterized by presence of deep level surface trap states, the ZnO detector exhibits long lifetime of the photo carriers [7]. Despite a great deal of research on ZnO UV detector, most of the research concentrated on the improvements of the micro mask electrodes, in order to enhance the performance of the ZnO photoconductive detectors [8-10].

The improvement of the photoresposivity of the ZnO UV detectors 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 improved the detector performance [11,12]. Coating the ZnO film surface with polyamide nylon has improved the photoresponsivity of the photoconductive detector to about 2.24 A/W, but the response time still in few seconds [13]. Most of published works concerning the enhancement of the response time are concentrated on fabrication of photodiodes [14]. In this work, a simple and highly reliable technique is used to fabricate high speed photoconductive ZnO UV detector of reasonable photoresponsivity by depositing the ZnO nanofilm on nanospikes silicon layer.

2. Experimental Work

N-type Si wafer of 0.05 Ω·cm resistivity was used as a

starting material in the photochemical etching. The samples of 2 × 2 cm^2 dimensions 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 diluted (10%) HF acid. After cleaning the samples they were immersed in HF acid of 50% concentration in a Teflon beaker. The samples were mounted in the beaker on two Teflon tablets in such a way that the current required for the etching process could complete the circuit between the irradiated surface and the bottom surface of the Si sample.

Tungsten halogen lamp of 100 Watts integrated with diacnamic ellipsoidal mirror was used as the photon beam source. The photoetching irradiation time was chosen to be 30 minutes.

At the end of the photochemical etching process, the samples were rinsed with ethanol and stored in a 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 is studied using Scanning Probe Microscope. The nanospikes silicon layers were used as a substrate for the ZnO photoconductive detector elements.

The ZnO nanofilms were prepared by chemical spray pyrolysis technique. The films were deposited on porous silicon layer heated to (400˚C). A 0.1 M Spray solution is prepared by dissolving Zinc Chloride ($ZnCl_2$) of 98% purity in 100 ml distilled water. The above mixture solution was placed in the flask of the atomizer and spread by controllable pressurized nitrogen gas flow on the heated substrats. The spraying time was 4 seconds, which is controlled by adjustable solenoid valve. The heated substrate was left for 12 sec after each spraying run to give time for the deposited (ZnO) layer to be dry. The optimum experimental conditions for obtaining homogeneous ZnO thin film at (400˚C) were determined by the spraying time, the drying time and the flashing gas pressure.

The thickness of the prepared films was measured by laser interferometer technique. The thickness of the films was found to be in the range between (800 - 1000 μm). The morphology of the film was scanned using Scanning probe Microscope (type AA3000) from Angstrom Advanced Inc. working in tapping mode. The micro mask of (0.4 mm) electrode spacing was used to deposit the gold electrical electrodes on the film surface. The variation of photoresponsivity of ZnO Photoconductive UV detector with the bias voltage was carried out under the illumination with UV diode of 2.5 m Watt power and of 385 nm wavelength. The operation circuit diagram of ZnO photoconductive detector and the schematic cross section of the fabricated ZnO porous silicon detector are shown in **Figures 1(a)-(b)**.

The response time of the prepared detector was tested through illuminating the fabricated detector with a nitrogen laser type (LN 120 C frm) from laser photonics company. The laser output pulses of 337.1 nm wavelength, has energy of 10 μJ and 0.3 ns pulse duration. The ZnO photocondutive detector output signal was displayed by digital oscilloscope of 200 MHz model TDS 202413 from Tektronix.

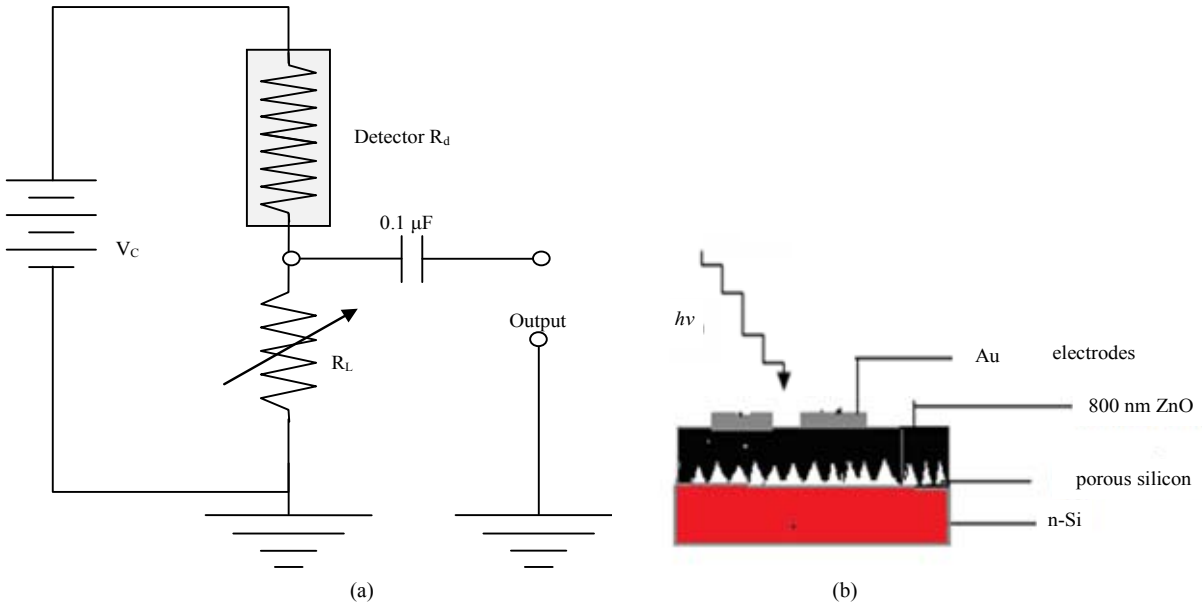

Figure 1. (a) The operation circuit diagram of ZnO photoconductive detector where; R_d is the detector element, R_L is the load resistance and V_C is the bias voltage; (b) Schematic cross section of the fabricated ZnO porous silicon detector.

3. Result and Discussion

3.1. The Surface Morphology Studies

The morphology and the line scanning of the porous silicon layer etched in 30 minutes is illustrated through the micrograph of the scanning probe Microscope, as shown in **Figure 2**.

The figure shows that the nanospikes distribution for the 30 minutes etching time is uniform and it is of about 2 nm heights, and around 1.5 nm dimensions. The formation of the nanospikes layer increased the resistivity of the silicon porous layer to the order of $10^5\,\Omega\cdot$cm. This can be attributed to several reasons; the capturing of the charge 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 [15,16]. The surface morphology of the ZnO film deposited on (PS) is shown in **Figure 3**. It can be noticed from the figure that the nanostructure formed on the surface of the ZnO sample deposited on PS is very clear. The size and distribution of the nanocrystalline structure of the ZnO nanofilms, deposited on the silicon nanolayer, are affected by the silicon nanospikes substrate in size and distribution.

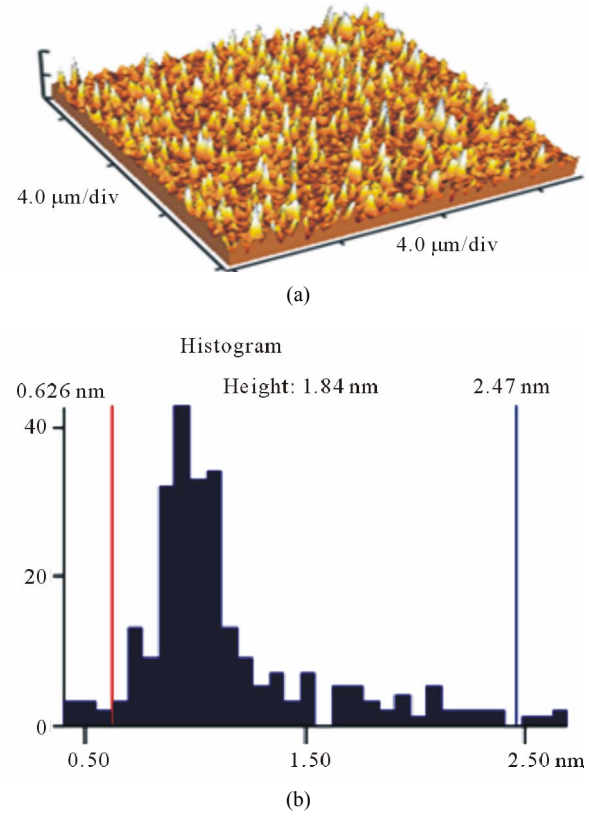

Figure 2. (a) Scanning probe Microscope image of porous silicon layer of 30 sec; (b) The histogram of the PS layer.

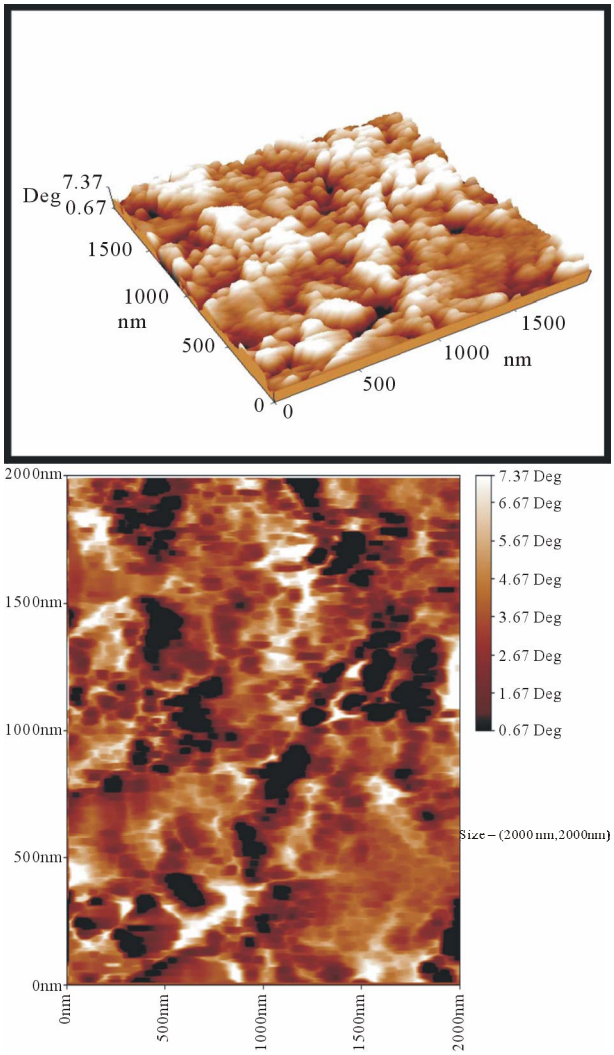

Figure 3. 2D and 3D Scanning Probe Microscope images of ZnO thin film deposited on PS.

3.2. Structural Characteristics

The X-ray diffraction (XRD) pattern of the 800 nm thick ZnO nanofilm deposited on nanospike layer of n-type silicon substrate is illustrated in **Figure 4**.

The figure shows the (100), (002), and (101) peaks occurred at 2θ values of 33°, 34.4° and 36.25° respectively, with full width at half maximum (FWHM) of (002) peak of about 0.15°. The broadening peak around 69.8° is attributed to the silicon nanospikes layer which has been observed by other authors [17].

3.3. Optical and Electrical Properties

The room temperature photoluminescence (PL) spectrum

of the prepared ZnO film on porous silicon layer is shown in **Figure 5**.

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.

The absorption spectrum of ZnO nanofilm deposited on glass substrate is shown in **Figure 6**. The figure shows high absorption coefficient in the UV region, whereas it is transparent in the visible region.

The variation of the photoconductive response of the fabricated photoconductive detector as a function of the bias voltage at dark and under illumination with UV source of 2.5 mWatt radiation power is illustrated in **Figure 7**.

It was found from the I-V measurements of the fabri cated detector that the dark current was about 10 μA at 10 V bias whereas the photoconductive current was 2100 μA. This result reflects a good UV radiation sensitivity with photoconductive gain (G) of more than 200.

The measured gain was calculated from the ratio of carrier life time to carrier transit time. The correction

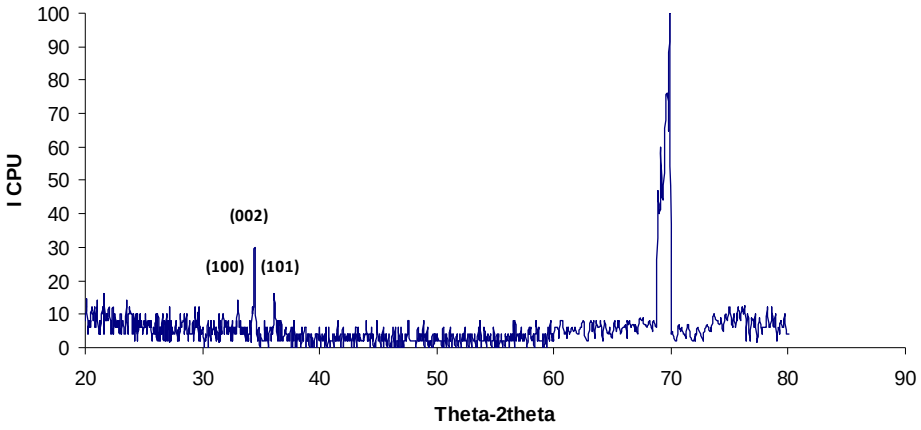

Figure 4. The XRD pattern of ZnO thin film on PS.

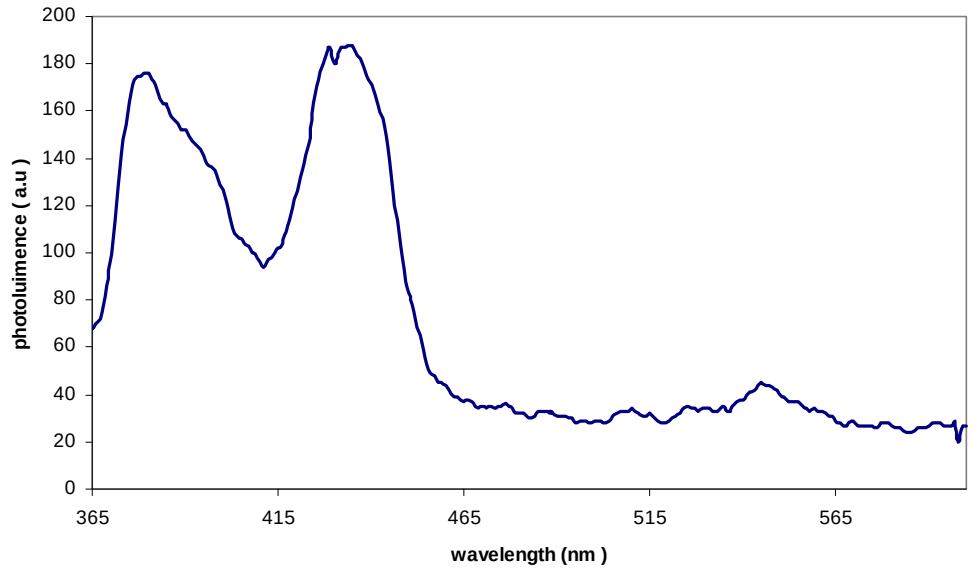

Figure 5. The Photoluminescence (PL) spectrum of ZnO thin film deposited on PS.

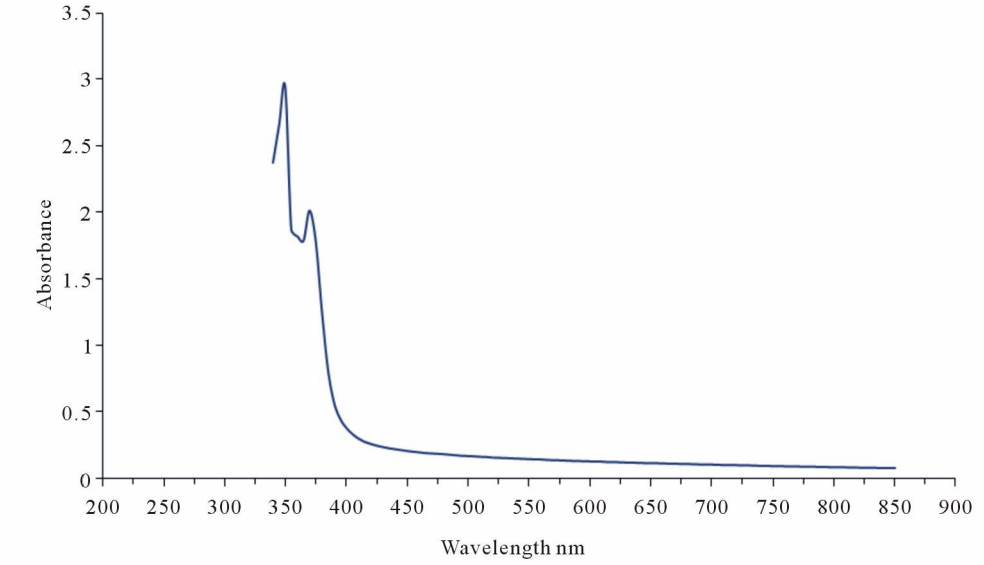

Figure 6. The absorption spectrum of ZnO thin film on glass substrate.

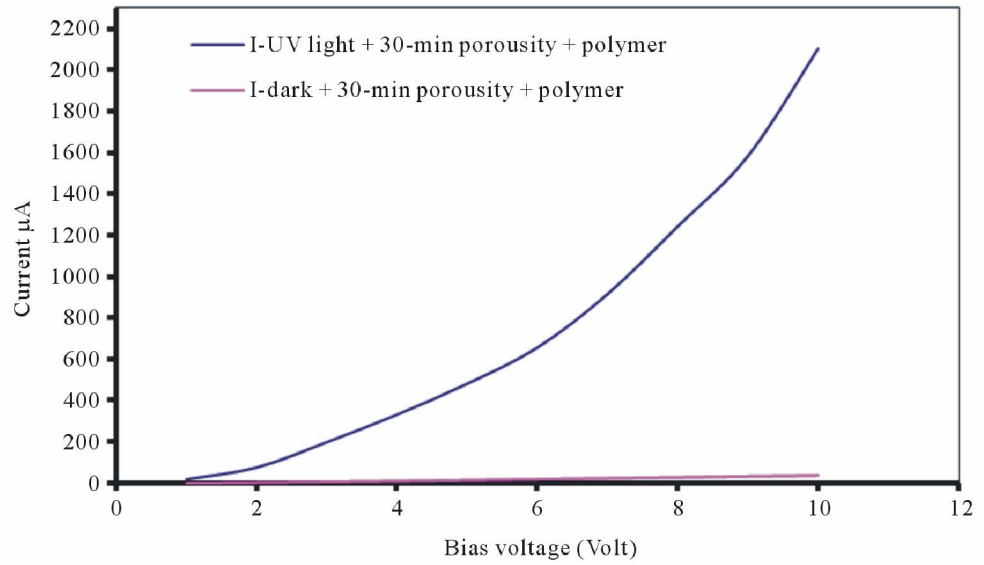

Figure 7. The variation of the photocurrent of the fabricated ZnO UV detector on porous silicon layer as a function of the bias voltage.

factor include the trap saturation and the carrier bimolecular recombination at the high light intensity which is usually shortening the carrier life time was ignored .this is because the gain was measured at low intensity which is in order of (I - 10^{-4} W/cm^2) [18].

The photoconductive gain (G) which is calculated from the ratio between the photocurrent to the dark current at the same bias voltage is given by; $G = \tau / T$ where τ = is the charge carries life time, and T is the transient time between the detector electrodes. The transient time is related to the electrode spacing and the carrier mobility by the relation; $T = L^2 / \mu V$, where L is the electrodes spacing, μ is the carrier mobility and V is the bias voltage. Using the values of G = 200, μ = 43.89 cm^2/V·s as found from Hall measurements, L = 0.04 cm and v = 10 V the carries life time (τ) was found to be about 730 µs. This value is very close to the experimental value obtained in this work from the transient measurements of the pulsed N_2 laser using the fabricated ZnO UV detector element. The specific detectivity D^* which is some time called the normalized detectivity, is the reciprocal of the Noise Equivalent Power NEP normalized to the detector area of 1 cm^2 and a noise electrical band width Δf of 1 Hz, and it can be written as:

$$D^* = R_\lambda \left(A\Delta f \right)^{1/2} \Big/ I_n \quad (1)$$

where R_λ is the photoresponsivity of the photoconductive detector in (A/W), A is the detector sensitive area and I_n is the noise current which is estimated from the dark current by the following relation:

$$I_n = \left(2eI_d \Delta f \right)^{1/2} \quad (2)$$

where I_d is the dark current, e is the electronic charge and Δf is the noise bandwidth. The value of dark current of about 10 μA at the bias voltage of 10 V, lead to noise current of about 1.8×10^{-12} A, at $\Delta f = 1$ Hz. Using the value of photoresponsivity $R = 0.8$ A/W, $A = 0.23$ cm^2 and $I_n = 1.8 \times 10^{-12}$ A, the specific detectivity of the fabricated ZnO UV detector deposited on porous silicon layer is found to be 2.12×10^{11} cm·Hz$^{1/2}$·W^{-1}. The value of photoresponsivity ($R = 0.8$ A/W) was found with the ZnO film coated by nano layer of polyamide nylon. This polymer layer is working as antireflecting coating and highly improves the ZnO photoconductive detector response to the UV radiation [13].

The response time of the fabricated ZnO UV detector on PS layer was tested with nitrogen laser of 0.3 ns pulse duration and 10 μJ energy.

The trace of the output pulse on the digital oscilloscope of 200 MHz band width is illustrated in **Figure 8**. It can be noticed from the traced signal that the rise time (10% - 90%) was of the order of 180 μs and the fall time (1 - 1/e) was about 750 μs. The slow decay time is due to slow escape of holes from tarps. Hole captured into the hole traps may be emitted back into the valance band according to a time constant depends on energy separation between the corresponding hole traps and the edge of the valance band. Traps in a wide band semiconductor such as ZnO are extremely deep which are centered around 540 nm in abroad peak as shown in **Figure 5** illustrated in this work. The deep traps have slow response and this may explain the slow fall time of the output pulse as shown in **Figure 8**.

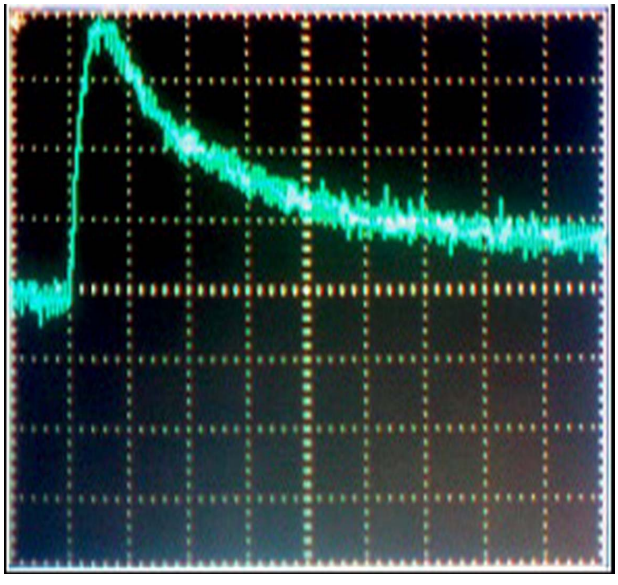

Figure 8. The photoresponse time of fabricated ZnO UV detector to the nitrogen laser. The time base on x-axis is 250 μs/div.

The long tail accompanied with the pulse is due to sample heating by the high repetitions rate N_2 laser illuminate the ZnO photoconductive detector. Comparing this result with the response time measurements for the ZnO photoconductive detector deposited on glass substrate, prepared by the same technique, and working in the same conditions, it is found that the speed of response of the new detector is four orders of magnitude faster than the sample prepared on glass substrate [13].

The huge observed reduction in the response time for the ZnO photoconductive detector deposited on porous silicon compared to the one deposited on glass substrate can be attributed to the improvement in the electrical properties of the ZnO film deposited on porous silicon.

The improvement of the electrical properties of the ZnO film deposited on porous silicon is highly influenced the performance of the ZnO UV detector. This improvement can be noticed from the Hall measurement of this film compared to same measurement for the film deposited on glass substrate as in the **Table 1**.

The table shows that the ZnO film deposited on glass substrate is n-type semiconductor, whereas the film deposited on PS layer has shown p-type behavior with Hall coefficient of 6.63×10^4 m^2/C and carrier mobility of 43.89 cm^2/V·s.

This behavior indicates that the porous silicon substrate is beneficial to improve the crystalline quality of ZnO film in lattice mismatch heteroepitaxy due to its sponge-like structure [19]. The above result was checked by depositing ZnO films on porous silicon layers formed by different photochemical etching time and the results are show that all the ZnO films deposited on nanospikes silicon layers are p-type with different carriers mobility depending on the etching time.

Table 1. The Hall measurements of ZnO film deposited on porous silicon and glass.

Parameter	ZnO on Porous silicon	ZnO on glass
Bulk concentration cm^{-3}	9.405E+13	–5.222E+18
Resisitivity (ρ) Ω·cm	1.512E+3	6.368
Average Hall coefficient (R_H) m^2/c	6.63E+4	–1.195
Mobility(μ) cm^2/V·sec	43.89	0.1877

The silicon nanospikes tips may be working as a compensator reducing the carrier concentration in the ZnO deposited film which changes its polarity from n-type to p-type. The same result was found by Vanmaekelbergh and Liljeroth for ZnO film deposited on silicon substrate [20]. The capturing of the excess charge carriers in the ZnO film by the silicon nanospikes layer reduced the surface charge density leading to increase the surface resistivity of the deposited ZnO film. The ZnO nanocrystals grow around the silicon nanospikes having a size similar to the nanospikes dimension. Thus the size of ZnO nanocrystals are reduced when the film is deposited on porous silicon compare to its size when the film deposited on glass. The nanocrystalline size reduction may help in improvement of the speed of response of the ZnO UV detector. The reduction in nanocrystalline dimension helped in maximizing the surface to volume ratio. The increase of the surface to volume ratio led to the increase in the overlap of the electron and hole wave functions. Since the increasing of the overlap functions account for the reduction in the carriers recombination life time, the speed of response of the ZnO UV detector is improved for the ZnO nanofilm deposited on nanospikes silicon layer. The charge carriers recombination mechanisms in semiconductor nanocrystals were intensively studied by many authors [21-23].

4. Conclusions

The fast response ZnO UV detector prepared by chemical spray pyrolysis technique was fabricated. The ZnO films deposited on chemically etched silicon substrate show a p-type behavior rather than n-type when they are deposited on glass substrates .The p-ZnO film show high carrier mobility leading to high speed UV detector. The functionalization of the ZnO film surface by polyamide nylon highly improved the photoconductive gain of the detector. The fabricated detector was tested to detect fast nitrogen laser pulses. The output signal was characterized by 180 μs rise time and 750 μs fall time. These results indicate that the deposition of ZnO nanofilm on porous silicon is recommended for improving the response time of the fabricated ZnO UV Photoconductive detectors.

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