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Fast Response ZnO/porous Silicon UV Photoconductive Detector

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Abstract: Zinc Oxide (ZnO) UV detector thin films have been prepared on nanospikes silicon layer with different etching time by spray pyrolysis using 0.1 M aqueous solution of Zinc acetate. The Hall measurements for ZnO films grown on the porous silicon layer, show that they were oriented in the c – axis and it is found to be a p – type semiconductor. This behavior may attribute to the compensation of the excess charge carriers in the ZnO film by the nanospikes silicon layer. The ZnO layer type, resistivity and the carrier mobility were measured with different etching time to the n-type silicon wafer. The optimum etching time for the fabrication of fast ZnO UV photoconductive detector was determined. The deposited ZnO film was coated by nanosheet of polyamide polymer to improve the photoresponsivity of the detector to 2.24A/W. 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 about 180 μs. The final device was tested with high speed pulsed nitrogen laser.

Keywords: Porous silicon, ZnO/P-Si junction; nanostructure materials; photoconductive detectors.

1 Introduction

Zinc oxide (ZnO) is an important electronic and photonic material because of its wide-bind semiconductor with a band gap of about to 3.37eV and large exciton binding energy of 60meV of excitons at room temperature [1-3]. Since ZnO gap energy lies in the ultraviolet (UV) range, ZnO is suitable for UV detection by using its photoconductivity properties [4]. The UV photodetector has a wide range of applications and it attracted great interest during the recent years. Most of the applications are directed toward the environmental monitoring, solar astronomy, and missile warning systems [5,6]. Growing high quality ZnO film on Si substrate has been promising for its low cost and the advantage in Si –based integration of optoelectronic devices [7]. Many different techniques such as chemical vapor deposition, organic chemical vapor deposition (MOCVD), plasma-assisted molecular beam epitaxy (PA-MBE), pulsed laser deposition (PLD), and spray pyrolysis technique have been used to growth the ZnO [8-10]. The UV photoconductive detector based on polycrystalline ZnO thin film shows low photo responsivity and long response time which is on the order of few minutes as mentioned by many authors [11,12]. 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 [13]. 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 [14-16].

The improvement of the photoresponsivity 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 highly improved the detector performance [17, 18]. 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 [19]. Most of published works concerning the enhancement of the response time are concentrated on fabrication of photodiodes [20]. 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 (porous) silicon layer.

2 Experimental Works

N-type Si wafer of 0.05 Ω.cm resistivity was used as a starting material in the photochemical etching. The samples of 2 x 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 concave ellipsoidal mirror was used as the photon beam source. The photoetching irradiation time, were (30, 60,90) 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. A 0.1M Spray solution is prepared by dissolving the zinc acetate Zn $(CH_3COO)_2.2H_2O$ with a molarity of 0.1 M and molecular weight equal to 219.49 gm / mole dissolved in distilled water. The above mixture solution was placed in the flask of the atomizer and spread by controllable pressurized nitrogen gas flow on the preheated substrates. The films were deposited on porous silicon layer heated to (400 ºC).
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 ºC were determined by the spraying time, the drying time and the flashing gas pressure. This method was used to prepare a film of thickness in order of 1μm. The thickness of the prepared films was measured by a laser interferometer technique. The morphology of the film was scanned using Scanning probe Microscope (type AA3000) from Angstrom Advanced Inc. The Micro mask of o.4mm electrode spacing was used to deposit the aluminum electrical electrodes on the film surface. The Hall Effect setting type (HMS3000) was used to measure the resistivity (ρ), charge carrier concentration (n) and carrier mobility (μ). Their values are listed in Table (1).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 mwatt power and of 385 nm wavelength. The measuring circuit is shown in Fig 2.1.

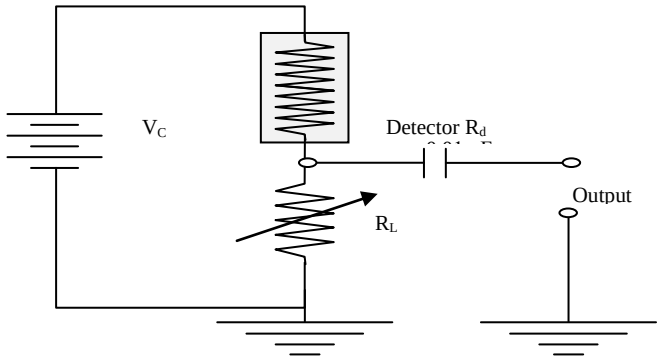

Figure 2.1:The operation circuit diagram of ZnO photoconductive detector, where; R_d is the detector element, R_L is the load resistance and V_C is the bias voltage.

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 50 μJ and 0.3 ns pulse duration. The testing circuit characterized load resistance R_L of 1KΩ and coupling capacitor of 0.01μF to give time constant of 10μs. This is sufficient to allow the output signal of the prepared detector when it is illuminated by the Nitrogen laser. The ZnO photoconductive detector output signal was displayed by digital oscilloscope of 200 MHz model TDS 202413 from Tektronix.

3 Results and Discussion

3.1 The Surface Morphology Studies

The morphology of the porous silicon layer after 90 seconds photochemical etching time is illustrated through the micrograph of the Scanning Probe Microscope shown in Fig.3.1. The figure shows that the nanospike distribution is uniform and it is of few nm heights and of about 10 nm in depth relative to the surface of the silicon substrate. The formation of the nanospikes layer increased the resistivity of the silicon porous layer to the order of 10^5Ω.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 [21,22]. The surface morphology of

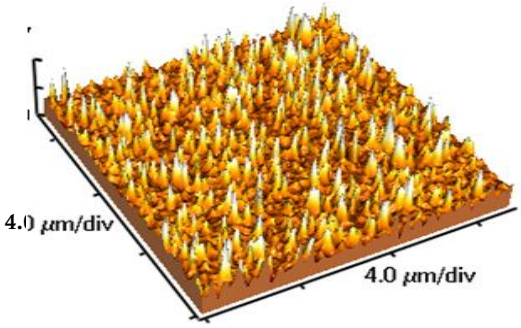

Figure 3.1: Scanning probe Microscope micrograph of porous silicon.

the ZnO film deposited on (PS) is shown in Fig.3.2. 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 a mirror to the silicon nanospikes substrate in size and distribution.

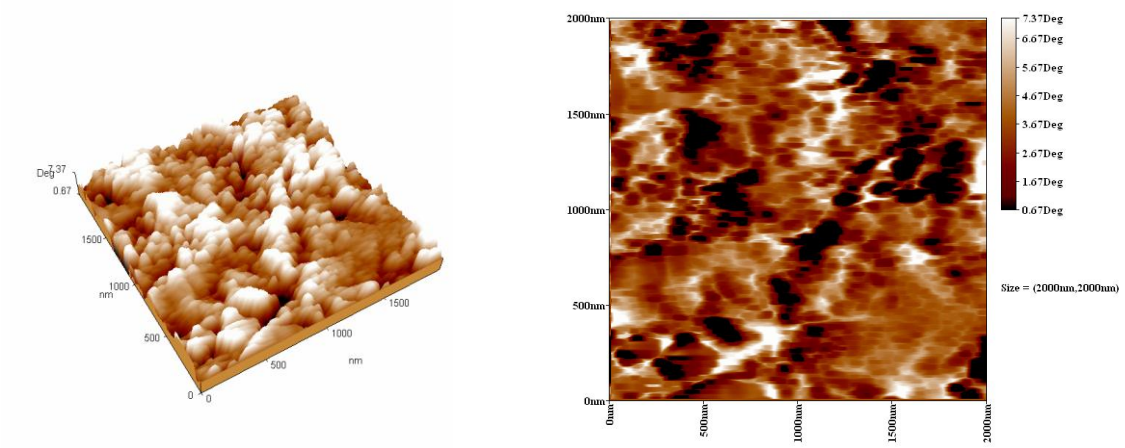

Figure3. 2: 2D and 3D Scanning Probe Microscope images of ZnO thin film deposited on PS.

3.2 Structure Characteristic

The crystalline structure of 1μm thick ZnO nanofilm deposited on nanospike layer of n – type silicon substrate was studied by X-ray diffraction using XRD- 6000- Schemadzu system. The XRD pattern of a ZnO nanofilm is illustrated in Fig 3.3. The figure shows the (100), (002), and (101) peaks occurred at 2Θ values of 31.7°, 34.4° and 36.25° respectively,with full width at half maximum (FWHM) of (002) peak of about 0.15°.

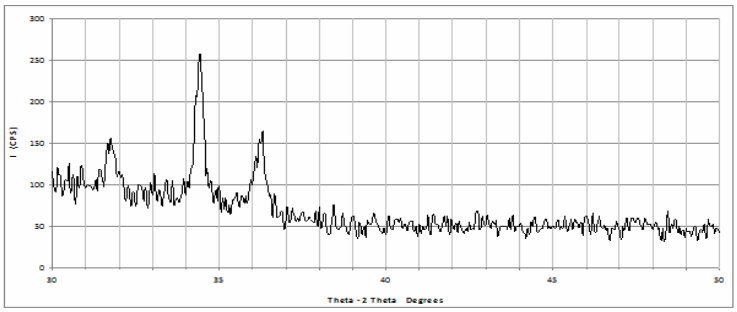

Figure3.3: The XRD pattern of ZnO thin film on glass.

3.3 Optical and electrical properties

The optical properties of ZnO nanofilms have been studied in this work. The absorption spectrum of ZnO nanofilm deposited on glass substrate is shown in Fig3.4. The figure shows high absorption coefficient in the UV region, whereas it is transparent in the visible region. Assuming direct transition, the dependence of $(\alpha h\upsilon)^2$ on the photon energy hυ is plotted as in Fig3.5.

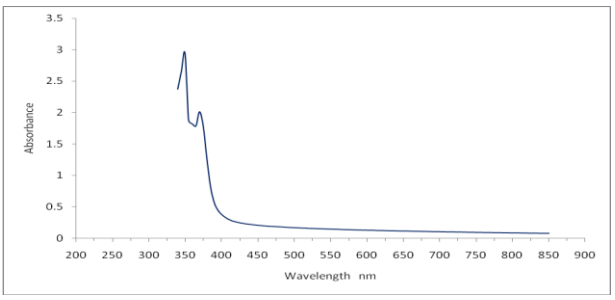

Figure3.4: The absorption spectrum of ZnO thin film on glass substrate.

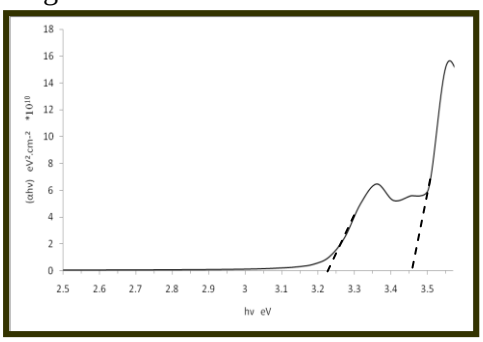

Figure3.5: Plot of $(\alpha h\upsilon)^2$ vs. photon energy (hυ) for ZnO thin film of

The extrapolation of the linear part of the above plot to $(\alpha h\upsilon)^2 = 0$ give the energy gap value of the ZnO film, which was found to be about 3.22 eV, and 3.46 eV [3,15]. The above two values may be related to the nanostructured ZnO film and to bulk ZnO material respectively.

The current-voltage (I-V) characteristics of the fabricated photoconductive detector as a function of the bias voltage at dark and under illumination for uncoated ZnO/PS samples were illustrated in Fig3.6. The radiation power of the UV source was 2.50 mw and the etching times (30, 60, 90min).

It was found from the I-V measurements that the dark current was about 10 μA at 5V bias voltage. The photo current is increased under illumination by 385nm UV light and it reaches to 440 μA for uncoated ZnO /PS samples, which lead to photoconductive gain (G) of about 50. Whereas the polymer (polyamide nylon) coated ZnO/PS samples, shows high increase in the photoconductive current reaching a value of 1500 **μ**A as shown in Fig3.7. This increase in the photoconductive current for the samples coated with nanosheet (polyamide nylon) was explained by Suhail et.al [19]. These results reflect a good UV radiation sensitivity with photoconductive gain of more than 150.

The response time of the fabricated ZnO UV detector on PS layer was tested with nitrogen laser of 0.3 ns pulse duration and 50μJ energy. It can be noticed from the traced pulse shape that the rise time was of the order of 180μs and the fall time was about 750μs. The slow decay time is due to slow escape of holes from the 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.

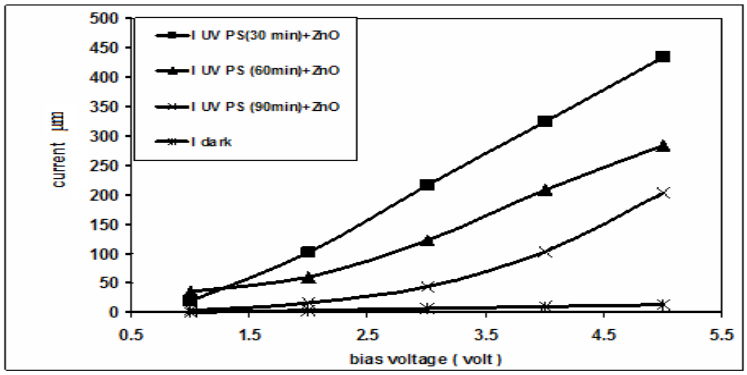

Figure3.6: The variation of the photoresponsivity of the fabricated ZnO UV detector on porous silicon layer at different etching time as a function of the bias voltage.

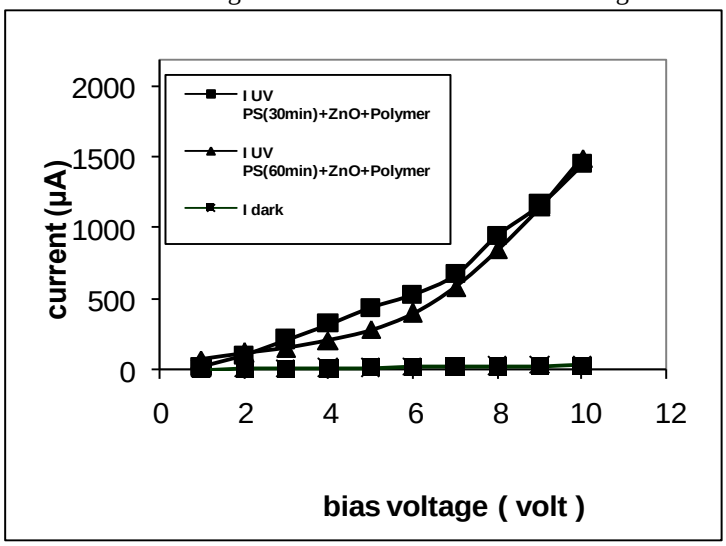

Figure3.7: The variation of the photoresponsivity of the fabricated ZnO UV detector on porous silicon layer at different etching time coated with polyamide nylon polymer as a function of the bias voltage.

The deep traps have slow response and this may explain the slow fall time of the output pulse as shown in Fig3.8. 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 [19].

The huge observed reduction in the response time for the ZnO photoconductive detector deposited on porous silicon may 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 these films compared to same measurement for the film deposited on glass substrate as in the table I. The table shows that the ZnO film deposited on glass substrate is a n-type semiconductor, were as the film deposited on PS layer has shown a p-type behavior. This behavior may be indicate 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 [23].

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

Parameter	ZnO on Porous silicon (30 min)	ZnO on Porous silicon (60min)	ZnO on Porous silicon (90min)	ZnO on glass
Resisitivity (ρ)	$2.864x10^{3}$ Ω. cm	6.923 Ω. cm	1.401×10^{4} Ω. cm	6.368 Ω. cm
Average Hall coefficient (R_H)	$8.985x10^{5}$ m^2/c	3.108×10^{4} m^2/c	1.364×10^{6} m^2/c	- 1.2 m^2/C
Mobility(μ)	3.317×10^{2} $cm^2/$ v.sec	4.489×10^{3} $cm^2/$ v.sec	9.738×10^{1} $cm^2/$ v.sec	0.1877 Cm^2 / v.sec
Bulk concentration	6.947×10^{12} cm^{-3}	2.008×10^{14} cm^{-3}	4.576×10^{12} cm^{-3}	-5.22×10^{18} cm^{-3}

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 [24].

The capturing of the excess charge carriers in the ZnO film by the silicon nanospikes layer reduced the surface charge density leading to increase in the surface resistivity of the deposited ZnO film. The improvement in the speed of response of the ZnO UV detector deposited on nanospikes silicon layer may be attributed to the reduction in the nanocrystalline size of the deposited ZnO film. The reduction in nanocrystalline dimension helped in maximizing the surface to volume ratio, which lead to the increase in the overlap of the electron and hole wave functions. Since the increasing of the overlap functions account

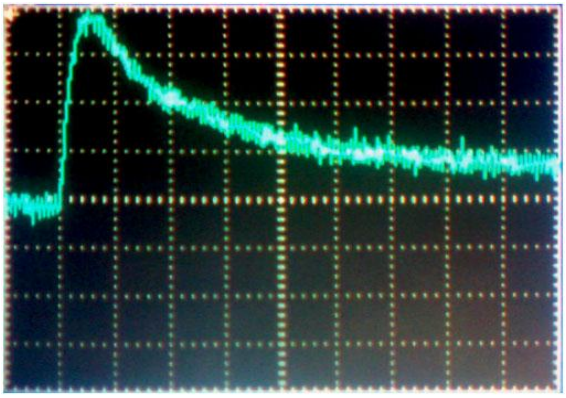

Figure3.8: The photoresponse time of fabricated ZnO UV detector to the nitrogen laser. The time base on x-axis is 250 μs/div.

for the reduction in the carriers recombination lifetime, 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 [25- 27].

4. Conclusion

The ZnO UV detectors prepared by chemical spray pyrolysis technique were fabricated on photochemical etched silicon substrates. The fictionalization of the ZnO film surface by polyamide nylon highly improved the photoconductive gain. The ZnO UV photoconductive detector deposited on porous silicon shows an acceptable photoresponsivity compared to the ZnO UV detectors deposited on glass substrate. The speed of response of the ZnO UV detector element deposited on porous silicon reach 180μs which is six orders of magnitudes faster than that of ZnO photoconductive detector element deposited on glass substrate.

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