



Improvement Of The Photoresponse Of The Solar Blind ZnO Photoconductive UV Detector

A.M. Suhail*, E.K.Hassan, S S.Ahmed and M.K.M Alnoori

Department of Physics, College of Science, University of Baghdad/ Iraq.

E-mail: Abdulla_shl@yahoo.com, Eman_kahreem@yahoo.com,
and soudadbassam@gmail.com

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Abstract: The UV solar blind photoconductive detector was fabricated using ZnO film prepared by thermal chemical spray pyrolysis technique. The ZnO thin film was grown on quartz substrate heated to 400 °C. The studies of the films structure and optical properties showed that the films are n- type with optical band gap of around 3.1-3.3 eV .The aluminum Interdigitated electrodes were evaporated on the film to fabricate the UV photoconductive detector. The photoresponsivity was measured under illumination of the ZnO film by 1 mwatt, 385nm UV radiation from GaN UV- led and it was 2.24 A/W. The photoresponse enhancement was improved by coating the ZnO film with 200 nm of PVC, PVA, and polyamide polymers using spin coating technique. The polymer nanolayer highly increased the photoresponse of the fabricated ZnO UV detector to a factor of 10⁴ with respect to the uncoated ZnO film . The results show that the ZnO film coated with polyamide polymer gives the highest responsivity rather than the PVA and PVC polymers.

Keywords:UV detector, ZnO thin film, polymer ZnO composite, spray pyrolysis.

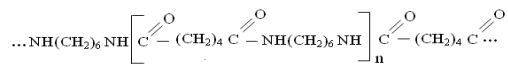
1. INTRODUCTION

The ultraviolet (UV) photodetector has a wide rang 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 [1, 2]. The silicon ultraviolet photodetectors have many dramatic limitations, like the low quantum efficiency in the deep UV range due to passivation layer. The age reduction of the Si photodiode exposed to radiation of much higher energy

than the Si band gap is one of the limitation factor in use of Si as a UV detector [3].

The UV detector based on polycrystalline ZnO thin film, shows low responsivity and of long response time. The response time ranging from a few minutes to several hours [4] and the photoresponsivity is low as well [5]. Since the one dimension ZnO nanostructures are characterized by presence of deep level surface trap states, ZnO exhibits large life time photocarrier [6] and it usually exhibits lower photosensitivities than the photodiodes.

Despite a great deal of research on the ZnO UV detector, most of the research concentrated on the improvement of the micro mask electrodes [7-9]. The surface treatments by coating the ZnO film surface with different types of polymer show high improvements in the detector performance [10, 11]. In this work the photoresponsivity is highly increased, and the response time is improved as well through the treatments of the film surface by coating the prepared ZnO nanofilms samples by special type of nylon (polyamide).



2. EXPERIMENTAL WORK

The ZnO nanofilms were prepared by chemical spray pyrolysis technique. The films were deposited on quartz substrates heated to 400 °C. The spray solution is prepared by mixing Zinc acetate {Zn (CH₃COO)₂·2H₂O}, isopropyl alcohol with purity 95% and distilled water in a volume ratio 3 : 1 at (0.2 M) .

The above mixture solution was placed in the flask of the atomizer and spread by controlled

nitrogen gas flow on the heated substrates. The chemical spray pyrolysis experimental setup is similar to the standard one [12] as shown in Fig.1 the spraying time was 4 sec. which

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. In order to get a film of proper thicknesses (500 nm-1200 nm) many layers deposited of ZnO are required. The optimum experimental condition for obtaining homogeneous ZnO thin film at 400 °C were determined by the spraying time, the drying time and the flashing gas pressure.

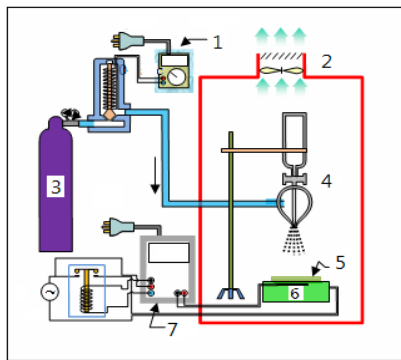


Fig. 1 Schematic representation of the spray system:(1) time controller (2) Hood's ventilation fan (3) N₂ gas cylinder (4) atomizer (5) substrate (6) substrate heater (7) substrate temperature controller [12].

The crystalline structure of the ZnO film was studied by X-Ray diffraction using XRD-6000-Shemadzu system. The X-ray diffraction pattern of a ZnO film of 500 nm thickness is illustrated in Fig.2. The spectrum indicates that the ZnO film is a polycrystalline structure. The grains are highly oriented along the (002) direction implying that the crystal orientation is mostly along the c-axis perpendicular to the substrate surface. The other two peaks at (100) and (101) can be noticed.

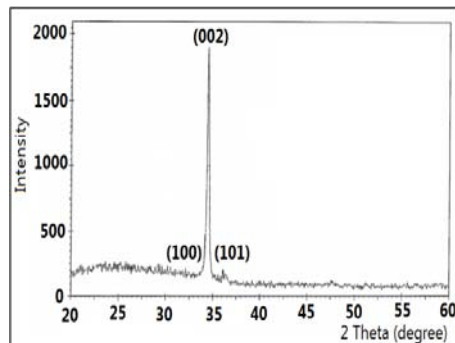


Fig. 2 X-ray diffraction for ZnO thin film on a quartz substrate.

The absorption and transmission spectra of the sample are recorded using Shemadzu UV-160/UV-Visible recorder spectrophotometer. The photoluminescence spectrum (PL) was obtained by SL 174 spectrofluorometer covering a range of (300-900) nm with line source of 320 nm wavelength and of a power of 1 mW. The Hall measurements were carried out using ECOPIA type (HMS-3000VER3.5) system with Magnetic field of 0.55 Tesla.

Interdigitated Al ohmic metal contacts were deposited on the ZnO samples on quartz substrate by vacuum evaporation to fabricate the ZnO UV detector. The Interdigitated electrodes consist of two combs of eight fingers, with distance between the fingers of 1 mm.

The experimental setup of the current-voltage (I-V) characteristics and photoresponsivity measurements is shown in Fig.3. The UV led with wavelength of 385 nm and of a power of 1 mW was used as a light source. The ZnO UV detector is operated in photoconductive mode with variable bias source, and the load resistance was chosen to be 5 kΩ referring to the maximum allowed bias current. The photo current was measured by a digital multimeter connected directly to the PC which led to direct plotting of the I-V curves and the temporal response of the ZnO UV detector. The coating of the detectors samples by different types of polymer was carried out by spin coating technique, leading to polymer layers of thickness in order of 200 nm.

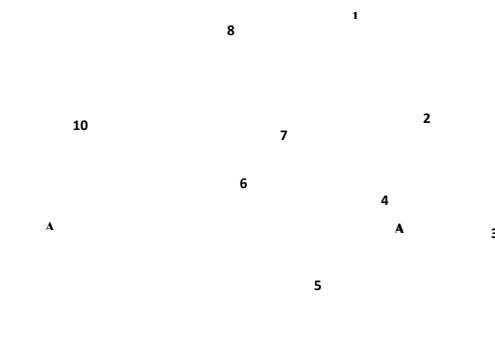


Fig. 3 Schematic diagram of the experimental setup: (1) ZnO detector(2)Variable Resistance (3) D.C Power Supply(4) PC-interfaced Digital Multimeter(5) USB interface Cable (6) Laptop PC(7) Optical Bench (8) UV-source (9) D.C Power Supply (10) Variable Resistance

3. RESULTS AND DISCUSSION

The electrical properties of the prepared film were estimated from Hall measurements as follow; the average Hall coefficient is $-1.2 \text{ m}^2/\text{c}$, the carrier mobility is $0.2 \text{ cm}^2/\text{v}.\text{sec}$. and the electron concentration is $5.2 \times 10^{18} \text{ cm}^{-3}$.

The optical properties of ZnO films which were prepared on quartz substrates have been studied in this work. The absorption spectrum, the energy gap determination, the refractive index variation with the wavelength, and the photoluminescence (PL) Spectra of the ZnO film in the spectral range (200-1100 nm), are shown in Figs. 4, 5,6 and 7.

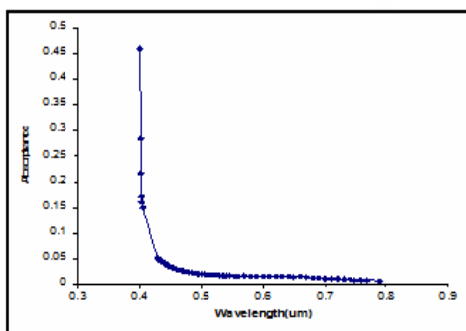


Fig. 4 Absorption spectrum of ZnO thin film.

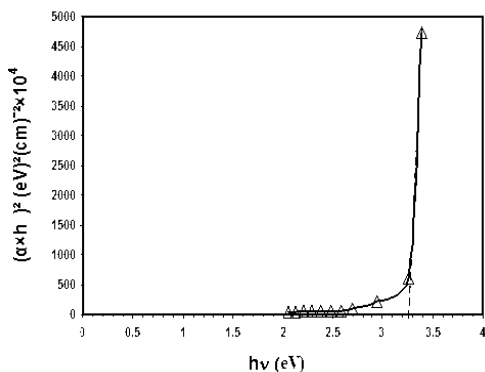


Fig. 5 Plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for ZnO thin film.

The absorption spectrum show low absorbance in the visible and infrared regions; however, the absorption in the ultraviolet region is high. Referring to the data extracted from the absorption spectrum in Fig.4, the absorption coefficient (α) was calculated as a function of wavelength. Assuming allowed transition; the dependence of $(\alpha h\nu)^2$ on $(h\nu)$ is plotted as in

Fig.5. The extrapolation of the linear part of the plot $(\alpha h\nu)^2 = 0$, gives rise on estimation of the energy gap value of the ZnO film. The value of the energy gap was found to be about 3.28eV. This value was in a good agreement with the values presented by other workers [13].

It was noticed through this work that the energy gap of the ZnO films decreases with the increasing of the film thickness from (500 nm – 1200 nm). The decreasing of the band gap with increasing the film thickness implies that the ZnO sample crystalline structure is improved with increasing the thickness. This leads to reduction in the defects concentration and negative charge carriers in the n-type semiconductor sample. This decrease of the band gap can be explained through Burstein-Moss effect and due to the many body effects [14].

The calculation of the refractive index as a function of the wavelength from the data extracted from the transmission spectrum using the envelope theory was carried out and illustrated in Fig. 6.

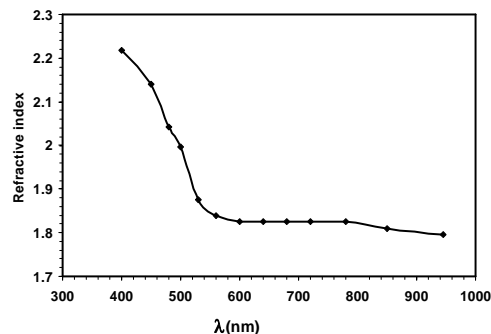


Fig. 6 The Refractive index of ZnO thin film Calculated as a function of the wavelength (λ).

The optical fluorescence spectrum of the ZnO film illuminated by 320nm UV line is shown in Fig. 7.

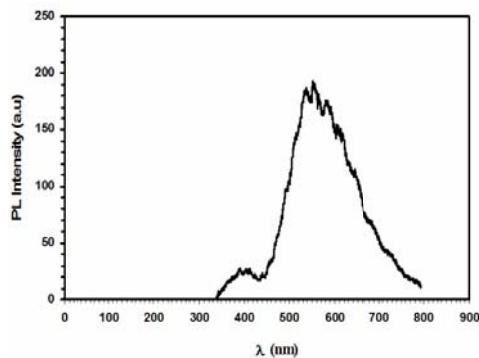


Fig. 7 Photoluminescence spectrum of ZnO thin film of 900 nm thickness [13].

The PL spectrum displays two major luminance peaks at 380 nm and around 556 nm. The first peak (near-band edge) is due to the intrinsic band-to-band transition which corresponds to 3.28 eV; it is originated from the recombination of the free excitons. The second peak in the visible band is related to the extrinsic deep defects transitions such as oxygen vacancies, and it is in a good agreement with the results measured by many other authors [15, 16]. The broad green-yellow emission peak that is dominated at 556 nm (≈ 2.23 eV) is a good evidence of the bonded exciton formation in ZnO with a binding energy of 60 meV. The high binding energy enables the finding of the exciton at room temperature interacting with the defect in the sample to emit the broad band in the visible region of the spectrum. The locations of the surface states in semiconductor were calculated by Suhail et.al. [17]. The intensity at the 556 nm peak is higher than that found around 380 nm peak. This is because the band-to-band transition was quenched by the defect states. The same behavior was observed by other authors [18, 19].

The current-voltage (I-V) characteristics of the fabricated device were illustrated in Fig. 8. The linear I-V curves referring to the ohmic nature of the detector. The dark current was very low under the illumination by visible light with a value of 0.1 μ A. The photocurrent is highly increased under the illumination by 385 nm UV light of 1 mW power and it reaches 25 μ A for uncoated ZnO detector samples. Whereas for the polymer coated samples the photocurrent reaches a value of about 2240 μ A at 10 V bias voltage, which leads to photocurrent gain (g) of about 2.24×10^4 , and of responsivity of the order of 2.24 A/W. The responsivity of our photoconductive detector was estimated to be 12×10^3 V/W; this value of responsivity is considered to be high with respect to the values mentioned by other authors [4,5,11]. All samples performed in the experiments of photoresponse were carried out under identical measurement condition (e.g., the distance between the light source and the measured sample, the power of the UV source, and the area of the UV light on the sample) all the measurements are taken under the visible light, because our ZnO UV detector is blind in the visible light. The maximum values of the photocurrent registered by the polymer coated

UV ZnO nanofilm photoconductive detector under the influence of 1 mW UV radiation are listed in the table.1.

Table 1 The measured photocurrent for the fabricated ZnO UV detector illuminated by 1mW UV radiation at 385 nm with 10 V bias voltage.

Sample case	Photocurrent (μ A)
Dark sample (unilluminated)	0.1
Un coated sample	25
Coated with PVC polymer	90
Coated with PVA polymer	208
Coated with polyamide nylon	2240

The above values reflect the effect of the nylon on the improvement of the responsivity and the response time of the fabricated detector.

The huge increase in the photoconductance of the ZnO UV detectors coated with nanosheet of different types of polymers can be attributed to several reasons. The first one referring to the high absorption of the UV light by the polymer nano layer which induced excited states in the polymer. The excited electrons left an unoccupied orbital (ground states) at an energy levels falling within the band gap of the ZnO semiconductor. These states can be considered as transition states for electrons of the ZnO valance band to transit to the conduction band. This hopping process may highly increase the transition probability of the valance electrons to the conduction band resulting in large increase in e-h pairs.

The other reason is the reduction in the reflected part of the incident UV radiation on the ZnO samples due to the index matching between the ZnO and the coated polymer. The refractive index of ZnO at 385 nm is about 2.2, thus the reflection part of the incident UV radiation is more than 14% for the uncoated ZnO film. The polymer coating nanosheet of refractive index of 1.5 are working as a matching index layer through $\sqrt{n_{ZnO} \cdot n_{air}} \approx 1.48$ which is not faraway from the refractive index of the polyamide nylon. This matching index is highly reduce the reflection of the UV radiation for the ZnO film surface.

Since the photoelectric current gain (g) is a function of the electrodes geometry as;

$$g = \frac{\tau \cdot \mu \cdot V}{l^2} \quad (1)$$

where τ is the carrier life time, μ is the charge carrier mobility in ZnO, V is the applied voltage, and l is the distance between the electrodes. Thus the photoelectric gain can highly be improved by reducing the electrodes spacing [11].

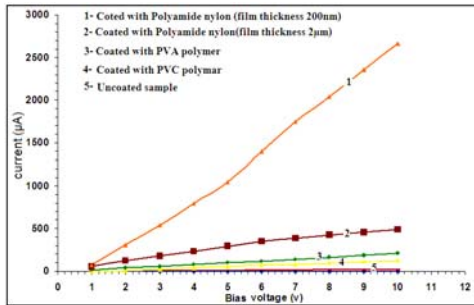


Fig. 8 The I-V characteristics of the coated ZnO samples with different coating polymers.

The dark impedance of the ZnO samples was measured at room temperature and it exceeds 2 MΩ. When the samples are illuminated by 385 nm UV radiation from the UV diode, the resistance drops to values of few kilo ohms in a time of about 50 sec as shown in Fig.9. These measurements are required for the nanofilms detectors operated in photoconductive mode, in order to determine the maximum allowed bias power.

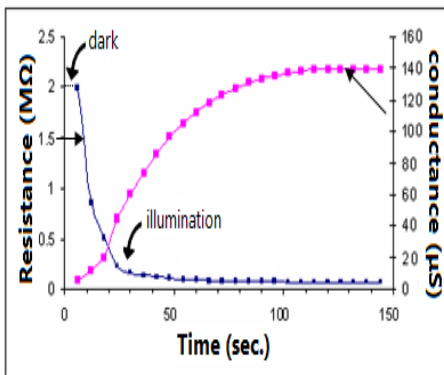


Fig. 9 The resistance variation of the fabricated ZnO UV photo sensor illuminated by UV photo diode.

The on/off state corresponding to the exposure of the ZnO film by UV light is illustrated in Fig.10. The rise time of the photocurrent was in order of 20 sec, whereas the fall time was in

order of 120 sec for all the coated polymer coated samples. These values are accepted and it is much better than the values of the rise time and the fall time recorded by Lao, et al [10]. Since these results were recorded with electrodes spacing of 1 mm, high improvement can be done if the electrodes spacing is reduced. Liu et al were found a rise time and fall time in order of few microseconds in there samples when they used electrodes mask of inter electrode spacing of 5 μm [7]. This is because the transit time of the carrier T is a function of the electrodes spacing as;

$$T = \frac{l^2}{\mu V} \quad (2)$$

thus the response time can highly be improved by improving the engineering of the electrode mask.

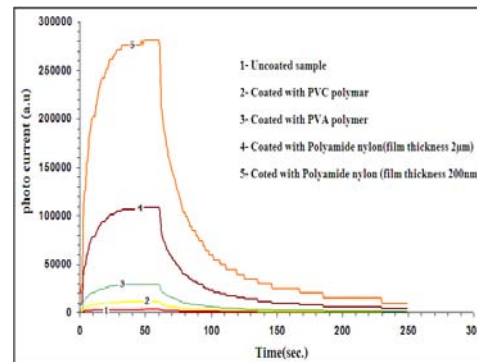


Fig. 10 The response time of the ZnO UV polymer coated detector.

The slow response and recovery time of the UV ZnO photoconductive detector may be attributed to the oxygen adsorption and desorption process [23,24]. In the dark Oxygen molecules adsorb to the ZnO nanofilm surface as negatively charged ions by capturing free electron for the n-type ZnO $[O_2(g) + e^- \rightarrow O_2^-(ad)]$. This mechanism helps in creating depletion layer of low conductivity near the film surface. Upon exposure to UV radiation at photo energy above ZnO band gap, the electron- hole pairs are generated. The generated holes migrate to the surface and discharge the adsorbed Oxygen

ions through surface electron-hole recombination $[h^+ + O_2(ad) \rightarrow O_2(g)]$. The photo-generated electrons accumulated gradually until the desorption and reabsorption of O_2 reach the equilibrium state, which results in slow current rise time.

4. CONCLUSION

The ZnO UV detector prepared by chemical spray pyrolysis technique was fabricated. The functionalization of the ZnO film surface by different types of polymers shows giant enhancement in the photoresponsivity and a good improvement in the response time. The photocurrent gain for the coated ZnO UV detectors reaches a value of 2.24×10^4 . The maximum responsivity among all the tested polymers was observed by the samples coated with the nanosheet of polyamide nylon and it was 2.24 A/W. Up to our knowledge, this responsivity value obtained with electrode spacing of 1mm is considered to be an excellent result compared to the highest registered value of 60 A/W for 1 μ m electrode spacing.

5. ACKNOWLEDGMENTS

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