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PREPARATION THE UV PHOTOCONDUCTIVE DETECTOR BY TPD:ZNO NPS BLEND

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Abstract

Physical properties includes Hall measurement , UV NPs, (I –V Measurements) and (Electro - optic properties IPCE) of ZnO NPs:TPD :PMMA Photo detectors deposited on P Si by two methods (phase segregation method and drop casting method) and compression with properties of the Presence of polymers (PMMA TPD) were distinguished using I-V Measurement by figures of merit .IPCE measures the absorption of the prepared photo detector in different wavelengths. This can be done according to the photon absorption of the monochromatic light of the incident radiation with a wavelength of 570 nm and 530 nm for the deposited film by phase segregation method and by drop casting method at current efficacy 0.09% and 0.56% respectively and for only polymers is 0.19% . In I-V characterization the photoconductive gain has improved by the method of deposition of device by drop casting method, then ZnO NPs embedded in TPD:PMMA polymer highly improved the photoconductive gain from 34 to 77 by phase segregation method and to 88 by drop casting method , The responsivity was increased from to 3.6*10-6 A/W for films prepared by phase segregation method to 8.4*10-6 A/W for films prepared by drop casting method and response time from 8.2*10-6 µs. to 8.8*10-7 µs respectively.

Keywords: Zno Nps:TPD :PMMA, Photo Detectors, Phase Segregation Method , Drop Casting Method, I - V Measurements, Electro - Optic Properties (IPCE).

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1. Introduction

Photo-detector is a system that transforms an optical signal into another type of signal, like a power or a voltage electrical signal.Only the photodetector semiconductor is discussed in this thesis. it operates by absorbing photon energy and generating electron-hole pairs as a result of the photoelectric effect . Photo detectors are classified into many categories based on their various working mechanisms or device structures ,including photoconductors, photodiodes junction, phototransistors, and charge-coupled devices (CCDs) [1]. For Spectral Response they can only respond to a specific wavelength range for any given photo detector .The first consideration when designing a photo detector is to choose the correct material that is capable of responding to the photo signal. In this work ,we focused only on ultraviolet and visible photo detectors. In the form of either a photoelectron or a hole pair, the External Quantum Efficiency (EQE) can be calculated as the proportion of the photo generated charge number to the photon incident number [2] The EQE value is the same as the gain value. For example, if the EQE is 1000 per cent, we can say the gain is 10 per cent. The gain term, even so, is usually used when the EQE is greater than 100 percent; when the EQE is far less than 100 percent, we say there is no gain. The sensitivity of the optical signal is calculated as the proportion of output current or voltage to input power. It is a key factor and can tell the available signal from a detector for a certain input signal. Noise Equivalent Power (NEP) is the signal-to-noise (S/N) ratio to be equal at the output, the input, you must use an equivalent amount of input power. It is the minimum power required to distinguish the signal from the noise. A photo detector with a smaller NEP can detect less light than a photo detector with a larger NEP[3]. The detectivity (D) defines a photo detector's capability of finding a tiny signals. The property of a linearity of a sensor is that the output signal of the sensor changes in quantity to the input We should use a large detector to detect both weak and strong light sources. In order to follow the optical signal, a photo detector should be fast enough to shoot photos at a frame rate as quick as the signal changes.[4] The time response, as shown in Fig.(1)is referred to as the impulse or square-like time[2].

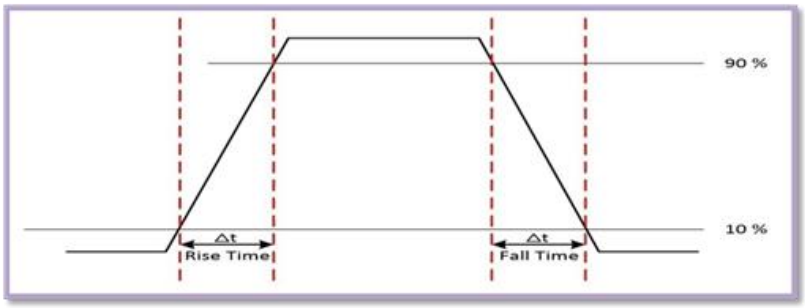

Fig1: Rise time and Fall time diagram [2].

1.1 Photoconductors

The phototransistor is based on photoconductivity. Some radiation, such as ultraviolet light and visible light, causes it to conduct. Semiconductors exhibit high conductivity when exposed to light with photon energy greater than their band gap. Semiconductor photoconductors typically sit between two conductive contact layers. These kinds of photo detectors need no amplifying device, such as the photomultiplier. Also, though, their amplitudes are high, their dynamics are low, and their response speeds are sluggish. Many initiatives have been undertaken to meet these objectives, such as the use of nanoparticles] as well as treatment with surface treatment [5, 6].

1.2 Photodiodes

Photo catalysts are used in most industrial applications because they require at least one metallic contact for effective operation. Many photolithographic films, including Schottky photosensitive, p-junction photosensitive, and Metal-Semi, have been developed. They have low dark current, fast response, and broad dynamic range However, in reverse bias, a single photon can generate one electron-hole pair, and maximum gain cannot be obtained because there is no charge injection.

1.3 The Aim of The Work

The aim of the present work is prepared and manufactured a photodetector devices with a combination of ZnONPs: TPD: PMMA at prepared time 60 µs by two different deposition methods drop casting and phase segregation , so that a device in the first method has form a photoconductive detector, and by the second deposition method is a photovoltaic detector in the form and the properties of each two detectors are compared.

2.Experimental Work

In according with the previous procedures, Zinc Oxide was prepared by reference [7]. To manufacture the photodetector, Commercially available silicon wafers made in Germany was used in this work. The wafer thickness was about 500±15µm with 76.2 mm diameter and one side polished. The crystal of the wafer was grown by Czochralski (CZ) growth method. Boron doped n-type with orientation (100) and high resistivity of 0.01-0. 02 Ω.cm. The silicon wafers were cut into small pieces with dimensions of ($2\times2^{cm^2}$). Before the electrochemical etching the samples were rinsed in ethanol to remove any contamination on the surface then followed by dipping in (40%) hydrofluoric (HF) acid and ethanol with ratio 1:1 .After electrochemical etching, the sample were rinsed with (DI) water then dipped in ethanol to ensure clearing the pores from water and left in the environmental air until they dry out. The samples were kept in plastic container filled with ethanol to prevent the formation of native oxide on the prepared sample until passing through characterizing. Etching time was constant (10 min) and the value of current density was (20 mA/cm2).The micro mask of Aluminum is deposited on the porous silicon substrate with (0.4mm) electrodes spacing .After deposition of the aluminum mask to prepare photoconductive detector, ZnONPs are combined with both N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl) benzidine (TPD)and Polymethyl methacrylate (PMMA) polymers, and this mixture is deposited on the porous silicon on which the aluminum mask is applied. The etching cell was manufactured from Teflon cell which had high resistivity to HF acid. The Silicon was placed over copper in order to provide good Ohmic contact. Another O-ring with a larger diameter was placed inside the Teflon cap used to press and fix the interior O-ring on the sample. The copper screw is connected to the contact piece at the back of the wafer. Silicon acts as an anode electrode, while the Silver mesh is used as a cathode electrode. The silver mesh should be equal to or bigger than the silicon sample, it should be placed in parallel to the sample with a distance of about 1cm away from the sample. The silver mesh was held by a silver holder. Figure (2)shows the ECE cell arrangement.

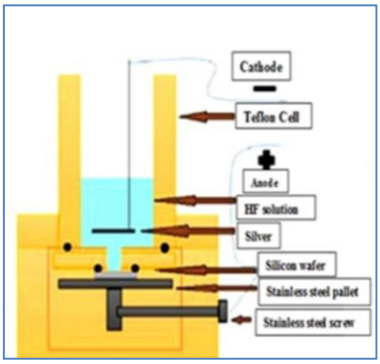

Fig (2): illustrates the cross section of anodization cell with ECE arrangement.

In this paper, two methods of material precipitation were used to manufacture the photoconductive detector which are phase segregation and casting dropping. The process of mixing the materials to manufacture the detector and the method of their deposition on the substrate will be explained:

The phase of segregation was used and it can be summarized as multi-layer film preparation by spin-coating multi-materials with a different solubility in the solution content of this solvent. Using 3.37 eV at room temperature, ZnO Bulk's band gap is wide and direct. The visible area of the defect states has more emission status. ZnO is an important material for photo detecting devices because of these features. Assistance with the TPD phase that is separated from ZnO NPs. TPD is therefore used for transporting the hole material as an inorganic-organic system which can increase emissions of ZnO. This option suggests that ZnO NPs with organic polymer electrodes can be combined to provide a hybrid technology to prevent problems of n-type ZnO. The TPD improves electrons and holes recombination of ZnO NPs[8] . Polymethyl methacrylate (PMMA) has been adopted as the host matrix for the mixture TPD:ZnO NPs and provides our organic inorganic hybrid film with the transparent host matrix. The good conductivity of TPD mechanisms used PMMA[9]. Finally, ZnO NPs is used because it contains most native defects which produce deep emission (DLE) levels at different positions within the band gap, which allows observing a rather large number of luminescence lines with different energies. This explains why in different ZnO NP samples all visible colors were observed experimentally. ZnO's common bands are blue, green, and red luminescence. The ZnO nanostructures can be used in the generation of white light [10]. TPD powder has been diluted in chloroform (50mg of TPD dissolved in 100ml of Chloroform). Until the dissolution was completed, the mixture

was pulled together PMMA chloroform powder has been diluted (70mg of PMMAdissolved in 100ml of Chloroform). Until the dissolution was completed, the mixture was put in a stirrer.
ZnO powder in chloroform has been diluted (0.1 gm of ZnO dissolved in 1ml of Chloroform). Until dissolution was complete the mixture was placed on a stirrer.
TPD chloroform solution and PMMA chloroform solution (with mole ratio of 1:1:0.1 wt%) were mixed to the ZnO - Chloroform solution. Till the dissolution was completed, a magnetic stirrer mixture was placed on. this is shown in Figure (3).
In this paper, ZnO NPs were obtained by the chemical method mentioned in ref. [7] with a reaction time of 60 minutes, and the deposition process was by two methods as mentioned above.

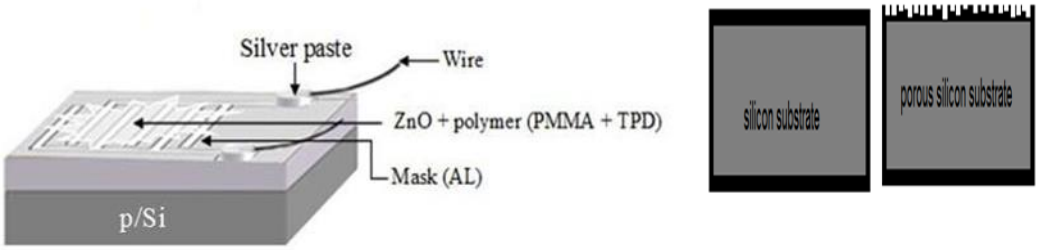

Fig . (3) Steps of the manufacturing a photoconductive detector

3.Results and Discussion
3.1Electrical properties of ZnO NPs
3.1.1 Hall Effect
The Hall measurements setting type(HMS3000) shows that the ZnO nanostructure deposited on porous glass substrate is n-type semiconductor Which is consistent with other studies[10], The Hall parameters for n-type ZnO nanostructure(resistivity, conductivity, and Hall coefficient) at reaction time (60 min) were illustrated in Table (1)

Table 1: Hall measurement on glass substrate with different reaction time.

Sample	Mobility(μ) ($cm^2/v.s$)	Resistivity(ρ) (Ω.cm)	conductivity σ (Ω.cm)-1	Carrier Concentration(n (Cm^{-3})	Hall coefficient RH($1/cm^3.C$)	Type of conductivity
ZnO NPs(60 min)	2.05E+04	3.68E-02	2.72E+01	8.26E+15	-7.56E+02	n- type

4.**Electro-Optical Properties of ZnO Photoconductor Device by (phase Segregation Method and Drop Casting Method)**
The measurements of the fabricated ZnONPs: TPD:PMMA on PSi as photoconductor device have been done. They included incident photon –current efficiency (IPCE) , the I-V characteristics, the specific detectivity , the transient time ,the response time and the gain.
4.1 Incident Photon Current Efficiency (IPCE)
In this measurement, the efficiency of the incident photon of the photoconductor device during the above reaction time (60 min) by phase segregation method and one sample by drop casting method and one sample only polymers (TPD :PMMA),and the absorption of the photodetector prepared to emit different wavelengths according to the absorption of the photon energy of the monochromatic light of the incident radiation. With a wavelength of 570nm and 530 nm for deposited film by [phase segregation method and by drop casting method] at current efficiency 0.09% and 0.56% respectively and for only polymers is 0.19%. This means that the best photo-electric response of the detector in green light to incident light radiation as mentioned in the following study [12]. From the observation of the IPCE measurement, we note from curve that there is no significant difference between PMMA: TPD and the detector prepared of adding ZnO NPs to polymers by phase segregation method. This is due to the rise of ZnO NPs in the upper layer of PMMA: TPD. Thus, the effect of ZnO NPs is limited to absorption(UV-LED) and its fluorescence to give wavelengths ranging from (350-600) nm. Except in the case of the detector prepared with a time of 60 minutes by the

phase segregation method and with drop casting method This is evident in the figure3.We notice the emergence of a peak at 470 nm, which is attributed to the transition between (V_{Zn}-Zn_i) , and we also note the presence of a peak at 570 nm and returns to the transition resulting from the TPD, which was observed to have a red shift in the peak of PMMA: TPD due to the effect of the energy gap small for silicon = 1.11 ev. In Figure (4) the case of the drop casting method shown, it represents the measurement of IPCE in the case of PMMA: TPD/ZnO NPs is in the form of composite or plan, so we notice the effect of energy transfer between ZnO with TPD and the emergence of peaks at (595, 525, 700, 800 and 895) nm, due to the transitions between Zni-Oi, a blue shift of the summit was also observed due to the effect of the large energy gap of ZnO (NPs) = 3.3 ev [11].

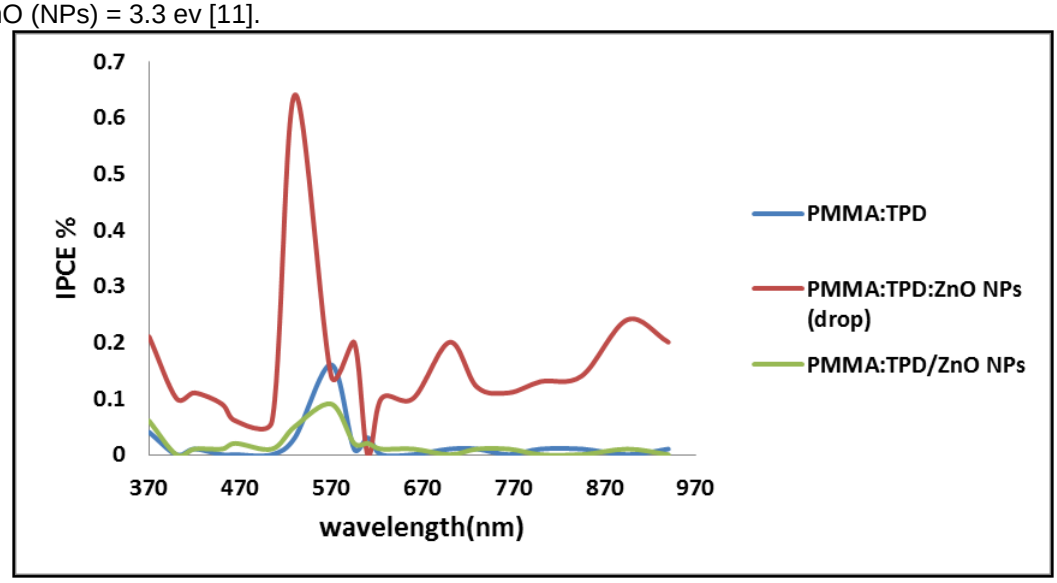

Fig (4): The relation of IPCE of the fabricated ZnO photovoltaic detector by phase segregation method on porous silicon substrate with wavelength with polymer at reaction time(60 min), (PPMA:TPD) and (TPD:PMMA:ZnONPs 60 min) deposition by by phase segregation method

4.2 Current-Voltage Measurements

The characteristics of current - voltage of the photodetector (I -V) are tested in relation to the bias tension at dark and under UV LED illumination of 10W. At room temperature, the overall current increase was observed. The I-V features of ZnONPs shown in Figure (5 a,b,c) PMMA:TPD:ZnONPs photo detector based on porous silicon substrate by drop casting method as photovoltaic detector, and other a different sample (PMMA:TPD) and (PMMA:TPD/ZnO NPs) by phase segregation method as photo conductive detector. The voltage-curves are the most frequently used tool for characterizing devices. Figure.(5c) represents I-V in the case of deposition by the method of drop casting. It is clear that the change in the light current is due to the shedding of its voltages. And in its presence and in the case of the presence of light (UV) the behavior behaves exponential, and we notice a gradual increase in current and then the behavior behaves similar to the absence of light, which means an increase in the current in the trap area charge current.

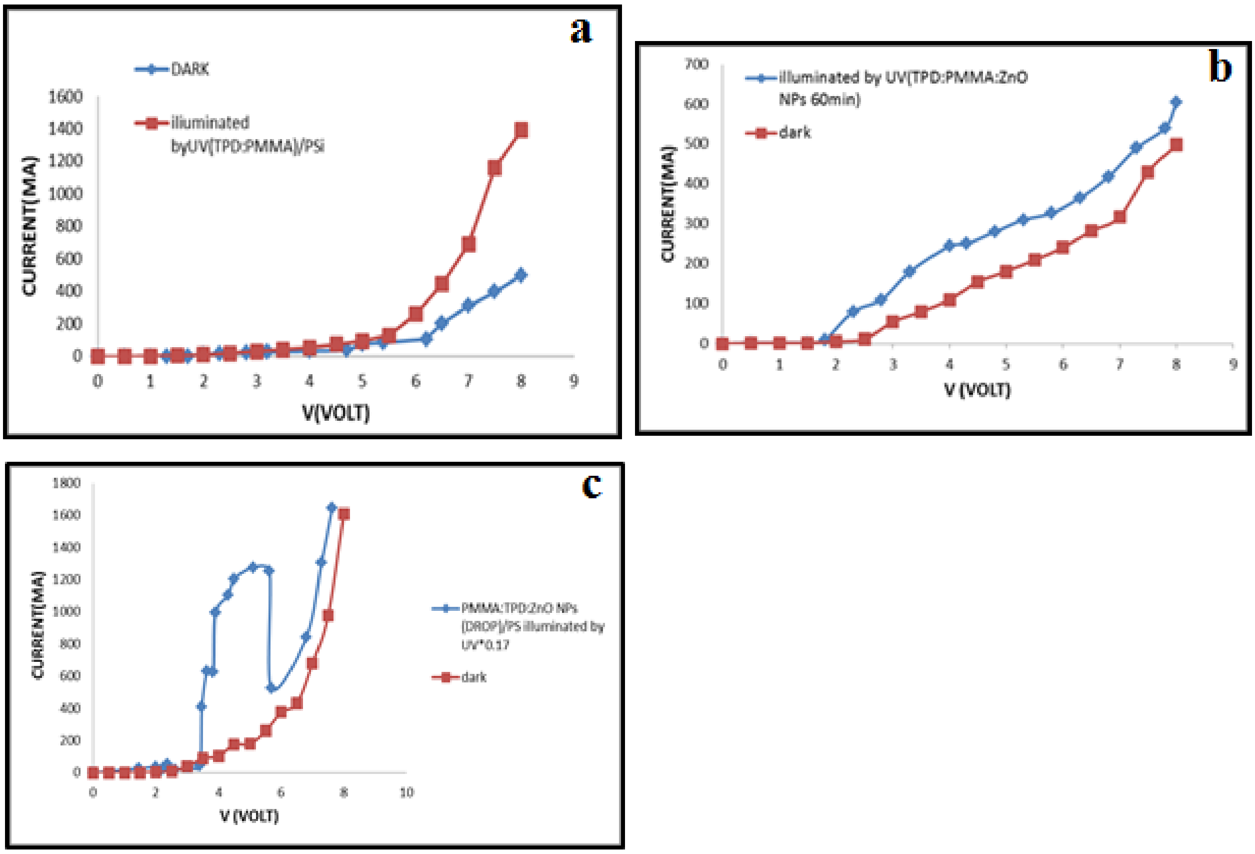

Fig5: Illustrate the I-V characteristics : (a,b) for ZnONPs:PMMA:TPD photoconductor based on PSi substrate by phase segregation method and (c): for ZnO:PMMA:TPD by drop casting method as a photovoltaic detector.

Here we can describe the photo detector as a photovoltaic devices analyzed using standard thermionic emission theory. According to this theory, the current in such a device could be expressed as[13]:

$$I = I_S\left[\exp\left(\frac{q(V - IR_S)}{nKBT}\right)\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where Is is the saturation current, Rs is the series resistance, kB is the Boltzmann constant, T is the absolute temperature, V is the applied voltage, and n is the ideality factor ,the value of ideality factor, tunneling factor and saturation current density can be calculated from intercepting the straight line with the current density at zero voltage bias, In Table 2 it is shown that the best value of the ideality factor is at the time of 60 min by drop casting method because of this method which made the film in a more homogeneous than the method of separation by spin coating.

Table 2:Values of ideality factor, saturation current density(Js) tunneling factor, for ZnO:TPD:PMMA/PS photoconductor device for reaction times(60 min) by phase segregation method and photovoltaic device by drop casting segregation method.

Photo detector	ideality factor n	Tunneling factor(At) (V^{-1})	Current density (nA/nm2)
TPD:PMMA	0.034	92	9.9 99
ZnO/TPD:PMMA/PSi 60 MIN	2.18	38	1 2

ZnO:TPD:PMMA/PSi 60 MIN(drop)	0.87	156	0.01
			0.099

The photocontrol gain (G) from the ratio of the PC/DC with the same bias voltage is G = τ / T, where τ is the charges carry life time, and T is the transient time between the detector electrodes. The temporal time is connected to the distance between the electrodes and to the mobility of the carriers; T = L^2/μ V_B, where L is the electrodes spacing. μ is the carrier mobility and VB is the bias voltage. Using the value of gain G and mobility for ZnO NPs as found from Hall measurement, l = 0.04 cm and V_B = 7 V. The carries life time (t) was found to be about 5.06×10^{-5}μs , 8.2×10^{-6}μs and 8.8×10^{-7}μs deposited on porous silicon for device as only polymers PMMA:TPD and ZnO NPs:PMMA:TPD by phase segregation method and drop casting method respectively.The specific detectivity (D*)which is sometimes called the normalized detectivity is the reciprocal of the noise equivalent power (NEP) normalized to the detector area of 0.07 cm^2 and a noise electrical band width Δf of 1 Hz can be written as:

D * = $\frac{R_\lambda (A\Delta f)^{\frac{1}{2}}}{I_n}$ ……………………………………………… (2)

Where the photoconductive detector is photo responsivity (A/W) in Rλ, the area of sensitivity of the detector is A / Watt, and noise current is I_n estimated by the following relation from the dark stream:

$I_n = (2eI_d\Delta f)^{\frac{1}{2}}$ ……………………………….(3)

where I_n represents the dark current and e represents the electronic charge The bandwidth of the sound Δf, which tends to lead to a current noise of approximately 1.13×10^{-21},3.003×10-22and1.47*10-23A, Δf =1 HZ The specific detection of manufactured devices as only polymers PMMA:TPD and ZnO NPs:PM MPA:TPD is shown to be value of photo responsivity Rλ =1.16×10-4, 3..6×10-6 and 8.4×10-6A /W.the specific detection of the fabricated devices as only polymers PMMA:TPD and ZnO NPs/PMMA:TPD by phase segregation method and drop casting method respectively, is found to be9.03×1012, 1.06*1014 and 5.08×1016 cm $Hz^{1/2}W^{-1}$. Additions to this device from the etching process and TPD polymer have increased the response time. This means that supplements are good for currency enhancement. In addition, it has also been found that the method of depositing the photodetector material has a better effect than the phase segregation method in which drop casts were produced as they did in the rest of the instruments. This is evident in Table 3.

Table 3: The figure of merit for ZnO photoconductive and photovoltaic devices.

photo detectors	T(μm)	$I_{n(AMP}$	R(AMP/Watt)	NEP(Watt)	D(Watt)-1	D*(Watt.Hz1/2.Cm)	Gain
PMMA:TPD	$5.06*10^{-5}$	$1.13*10^{-21}$	$1.16*10^{-4}$	$97*10^{-14}$	$1.03*10^{13}$	$9.03*10^{12}$	34
PMMA:TPD :ZnONPs (phase segregation method)	$8.2*10^{-6}$	$3.003*10^{-22}$	$3.6*10^{-6}$	$8.2*10^{-15}$	$1.219*10^{14}$	$1.06*10^{14}$	77
PMMA:TPD:ZnONPs (drop casting method)	$8.8*10^{-7}$	$1.47*10^{-23}$	$8.4*10^{-6}$	$1.7*10^{-16}$	$5.8*10^{16}$	$5.08*10^{16}$	88

5.Conclution

The photoconductive ZnO UV detector was prepared and deposited with a chemical method on porous silicone, By deposition of the devices by phase segregation and drop casting methods, the photoconductivity improved gain, then ZnO embedded in TPD:PMMA polymer highly improved the photoconductive gain from 34 to 77 by phase segregation method and to 88 by drop casting method , The responsivity was increased from to 3.6*10-6 by phase segregation to 8.4*10-6 by drop casting method and response time from 8.2*10-6 to 8.8*10-7 µs.

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