Correlation Study of Structural and Optical Properties of ZnO/PTAA Hybrid Heterojunction Layer

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Abstract. Zinc Oxide (ZnO) thin films have been deposited onto an ITO glass by RF sputtering method in a controlled condition followed by a layer of Poly(triarylamine) as an electron acceptor to form a hybrid heterojunction thin film. In this work, Poly(triarylamine) is deposited by using spin coating method at different spin rate ranging from 1000 RPM to 5000 RPM. The correlation between the structural and optical properties of this hybrid heterojunction were investigated. The crystallographic structure of ZnO and PTAA is analysed by obtaining its Full width half maximum and grain size value by using X-ray diffractometer. UV-Vis result strongly reveal that all the thin films exhibits high transparency (>80%) in visible region with wide band gap of 3.38 eV for ZnO and 3.1 eV for PTAA at 5000 RPM sintering. Surface morphology of the hybrid film is observed using an advance material microscope (HIROX) with 3 different lenses of low range, mid-range and high range. It is shown that, as the RPM speed is increasing the distribution of PTAA on the ZnO layer is smoother and uniform. The correlation value obtained for grain size and band gap is 0.9344 and 0.9136. Thus, concluded that grain size and bandgap of device is highly correlated.

Keywords: Zinc Oxide, Poly(triarylamine), RF Sputtering Method, hybrid-heterojunction, Morphology

1. Introduction
Nowadays, Zinc Oxide (ZnO) and Poly(triarylamine) (PTAA) had remarkably drawing worldwide attention due to its performance significantly recognized in the electronics and optoelectronics field. ZnO is an inorganic material and PTAA is polymer based organic material. They are widely used as a form of main material in various technology such as diode, solar cells, and laser. ZnO possess great characteristic such as wide band gap of 3.3 eV, low dielectric constant and large exciton binding energy approximately 60 meV [1][2]. Besides that, due to its crystallinity it led to greater stability, good piezoelectric and optical properties [1][3]. Poly[5bis(4-phenyl)(2,4,6-trimethylphenyl)amine] or shortly known as PTAA is a form of p-type amorphous polymer semiconductor with hole mobilities of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and air stability advantage [4]. Sudden interest in organic material such as PTAA is due to the factor of low fabrication cost, light in weight and mechanical stability at which this characteristic is not possible with crystalline silicon [5][6]. In this article, we thus investigate the structural form of heterojunction ZnO and PTAA with their optical properties and the effect of different RPM speed towards surface morphology of PTAA. For this purpose, ZnO is fabricated by RF magnetron followed by layering of PTAA by spin coating method.
2. Experimental

ZnO layer is deposited onto Indium Tin Oxide (ITO) glass by Radio Frequency Magnetron sputtering machine. The deposited time is constant for every sample which is 30 mins. Before deposition take place, ITO glass was soak in the Decon 90 solution overnight. The substrate then was cleaned ultrasonically with distilled water, methanol and acetone for 10 minutes each solution. After that, the substrate once again rinsed with distilled water to ensure zero contaminants on the substrate surface. The ITO glass is then blow with nitrogen gas in fume chamber for drying purposes. Deposition of ZnO is carried out in vacuum state of $1.0 \times 10^{-3}$ Torr in room temperature condition. Annealing procedure is carried out after the deposition process to obtain the best properties of ZnO. The samples are annealed at 400 °C for an hour in the furnace. The annealing process at 400 °C is carried out as ZnO form a better crystallinity structure quality compare to the room temperature [7][8]. For the second layer, PTAA powdered was dissolved in Chloroform and stirred at room temperature for more than 12 hours to form 0.5% wt solution. Spin coating method is applied to deposit the organic layer of PTAA. 1 mL of PTAA solution is dispensed and spread onto the ZnO layer with the sintering of 500 rpm for 5 seconds. The sintering process for every sample kept the same and act as constant variable. The sample was further spun with different speed of 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm and 5000 rpm.

In order to measure the structural properties of ZnO and PTAA, X-ray Diffractor Machine is being utilized for this purpose. This analytical technique is used to identify the crystallinity of both material and obtaining their Full Width Half Maxima (FWHM) value. For the optical properties, UV-vis spectrometer Lambda EZ210 has been used to obtain the transmittance and the band gap value of both materials. Lastly, surface morphology of interlayer material is taking into consideration and is been obtain using an advance material microscope (HIROX) to see the deposition of ZnO and the effect of different spin speed towards the deposition of PTAA.

3. Result

3.1 Structural Properties

The X ray diffraction pattern for ZnO and PTAA is clearly shown in Figure 2. X-ray is diffracted and scattered in many directions depending on its crystallite structure and orientation leading to distribution of bumps in a wide range of 2θ. In amorphous state, broad peak is form from low intensity X-ray that scattered individually passing through a smaller lattice plane of material. Broad diffraction peak of ZnO is observed at 34.09° with full width half maxima (FWHM) value of 0.8640. For PTAA film, broad peak is seen between the angle of 21° to 24° which agreed well with the research literature[9][10]. The FWHM value obtain for PTAA film are within 0.186 to 0.301 as the orientation of XRD pattern shows the amorphous state of PTAA as no obvious peak can be observed at the XRD
result. By obtaining the FWHM, crystallite size of PTAA and ZnO is determined using Scherrer’s formula in equation (1) and tabulated in Table 1 [11]

\[ G = \frac{0.9 \lambda}{\beta \cos \theta} \]  

Where \( G \) is the crystallite size of material, \( \lambda \) is the wavelength of X-Ray used (1.5406 Å), \( \beta \) is the value of FWHM in radian and \( \theta \) is the Bragg’s angle [11].

As tabulated in Table 1, fabricated ZnO thin film having a greater grain size of 16.3 nm after it been annealed at 400°C compare to room temperature. This indicate that, a better crystallite structure and greater film roughness. As for PTAA, the grain size varies with each RPM speed respectively. 5000 RPM speed rate show significant large grain size of 44.3 nm due to uniform distribution of PTAA polymer on to the ZnO layer as the thickness of the thin film decreases as the speed rate increases.

![XRD pattern of fabricated material](image1)

**Figure 2.** XRD pattern of fabricated material; (a) Zinc Oxide, ZnO (b) Poly(triarylamine), PTAA deposited at 5000 RPM.

**Table 1.** Full width half maxima (FWHM) and grain size of ZnO and PTAA thin film as deposited at 1000 RPM, 2000 RPM, 3000 RPM, 4000 RPM and 5000 RPM.

| Material | Parameter | FWHM | Grain size (nm) |
|----------|-----------|------|----------------|
| ZnO      | Room Temperature | 0.864 | 10.1 |
|          | Annealed 400°C   | 0.534 | 16.3 |
|          | 1000 RPM        | 0.301 | 28.1 |
|          | 2000 RPM        | 0.256 | 33.0 |
| PTAA     | 3000 RPM        | 0.236 | 35.6 |
|          | 4000 RPM        | 0.233 | 36.3 |

**3.2 Surface Morphology**

Surface morphology of thin films was studied using advance material microscope (HIROX). HIROX images of ZnO thin film and PTAA film deposited at 1000 RPM, 2000 RPM, 3000 RPM, 4000 RPM and 5000 RPM is shown in the Figure 3 respectively.
Figure 3. Surface morphology of fabricated thin film, ZnO and PTAA deposited at 5000 RPM observed by using HIROX advance material microscope; (a) Low range lens (b) Mid-range lens (c) High range lens (d) High range lens with magnification of 2000x.

As the speed rate of the spin costing increases the PTAA layer is deposited uniformly onto the ZnO layer. The centripetal force combine with the surface tension of the liquid PTAA pulls the coating into an even covering at the same time it evaporates leaving the desirable thin film onto the ZnO layer for a smoother surface.

3.3 Optical Properties

UV-Vis transmission spectra for ZnO and PTAA is shown in Figure 4. The transmittance spectra are obtained by using the UV-Vis spectrometer with the wavelength ranging from 200 to 850 nm.

Both the fabricated samples exhibit over 80% of transmittance where annealed ZnO shows slightly higher transmittance over the room temperature samples. As for PTAA, 4000 RPM and 5000 RPM shows a higher amount of transmittance value (>85%) when compare to the other speed rate.

Tauc Equation as in equation (2) is used to determine the optical band gap of ZnO and PTAA [8] [9][12].

$$ (a h v)^{1/2} = (h v - E_g) $$  \hspace{1cm} (2)

Where $a$ is the coefficient of absorption, and $hv$ is the quantum energy. In order to obtain the coefficient of absorption, equation (3) is utilized by calculating using the absorbance (Abs) and the thickness of the fabricated layer (t).

$$ a = \frac{2.303 \times \text{Abs}}{\text{t}} $$  \hspace{1cm} (3)
The estimation value of the band gap, $E_g$, is determined by extrapolating the straight line to the graph obtained from the equation $(\alpha h\nu)^{1/2} = 0$. The estimated value of optical band gap for ZnO thin film is 3.38 eV which fall in the range of corroborated value by the literature review [3][8][13] As for PTAA, the value of band gap is increasing with the increasing of spin rate. The value of bandgap obtained from 1000 RPM to 5000 RPM is 2.97 eV, 3.03 eV, 3.04 eV, 3.06 eV and 3.10 eV as reported by [14][15]. The correlation value between grain size and bandgap of PTAA is 0.9344 and 0.9163 approaching to 1 which indicates that a positive association relationship between grain size and bandgap value.

![Figure 4](image1.png)

**Figure 4.** Transmittance spectra of (a) PTAA at different rpm speed from 1000 RPM to 5000 RPM and (b) Estimated bandgap of ZnO thin film by using Tauc plot.

![Figure 5](image2.png)

**Figure 5.** The correlation value ($R^2$) between Grain size and band edge of PTAA thin film.

4. **Conclusion**

ZnO/PTAA hybrid heterojunction layer successfully fabricated using RF sputtering method and spin coating method. As for ZnO, the increase in temperature, result in a greater value of band edge from 3.20 eV at room temperature and 3.38 eV after been annealed at 400°C. Meanwhile for PTAA, As the speed of spin coating increase, it increases the value of band edge from 2.97 eV to 3.10 eV. The higher the grain size of thin film, the higher the band edge obtained as the value of correlation obtained are 0.9344 and 0.9163. Thus, represent the structural morphological of thin film whereby it is smooth and evenly distributed at the interface of the thin film.

5. **References**

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