Low Leakage Current by Solution Processed PTAA-ZnO Transparent Hybrid Hetero-Junction Device

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ORIGINAL ARTICLE - ELECTRONICS, MAGNETICS AND PHOTONICS

Low Leakage Current by Solution Processed PTAA-ZnO Transparent Hybrid Hetero-Junction Device

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Abstract

In this work solution processed novel poly-triarylamine (PTAA) organic p-type active layer on inorganic n-ZnO device transparency and electrical properties are investigated under illumination. Low cost organic–inorganic transparent hybrid hetero-junction (HHJ) is a promising candidate for next-generation photovoltaic applications. Greater band gap organic material window layer while inorganic material's higher thermal stability as HHJ is suitable for detection and photovoltaic applications. However, hetero-interface defects associated leakage current is the key issue of undermining large-area device electrical performance. Hetero-interface defect associated carriers optical absorption limits transparency whereas leakage current density is reliant on physical property and band barrier effect. It is demanded to investigate hetero-device physical stuff and band barrier effect on electrical properties. Novel PTAA is deposited on RF-sputtered inorganic n-ZnO/ITO/glass substrate by spin-coating method. 100 and 60 nm PTAA thin films are deposited with 1000 and 2000 revolution per minute (rpm) growth sequence, respectively. PTAA as a transparent p-emitter is shown to absorb incident light beyond visible band, thereby it has promoted excitonic effect. Device I–V characterization carried out at different annealing temperatures and applied voltage. Suitable annealing condition leakage current is shown to reduce nearly 10^{-4} A/cm^2 and at higher applied field the greater rectifying I(+)/I(−) ratio is realized. Grain size is shown to increase with annealing effect however; leakage current is remained almost independent of grain size.

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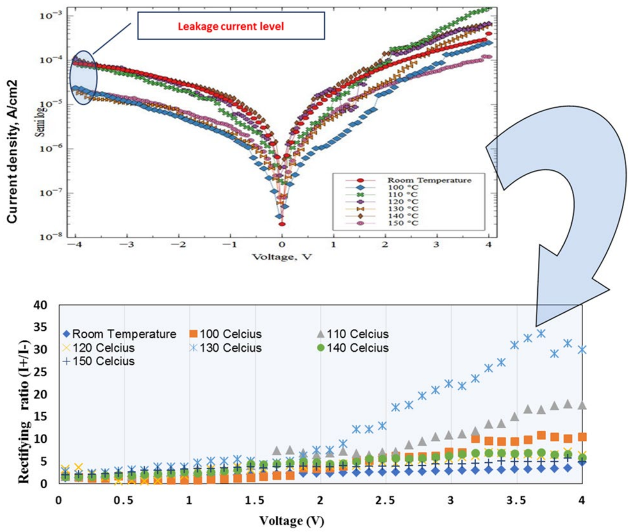
Graphic Abstract



Keywords ZnO · PTAA · Transparent · Annealing · Band barrier · Leakage current

1 Introduction

Cost-effective and transparent renewable energy technology is desirable along with Si wafer based mainstream technology to meet up the future solar photovoltaic (SPV) energy demands. Renewable energy is the most suitable alternative to conventional energy resources for households and buildings energy supply because those are consumed significant amounts of electricity. Necessities to pass sunlight through building windows, Si based non-transparent SPVs alternative is desirable. Therefore, researchers are trying to develop transparent PV cells to meet future energy demand [1, 2]. Materials selection for bottom and top as carrier transport layers must have to have high transparency for allowing visible band transmission. Efficient absorption of ultraviolet (UV) light is required for electrical energy. However, high processing temperature and complex design procedures are main limitation for the transparent device development. In this context, organic materials can overcome these challenges due to their low fabrication cost and beneficial to opto-electric conversion characteristics. Even though organic solar cell (OSC) was first developed long back but recently it has experienced significant advances to respond to the need for energy applications [3, 4]. Organic materials, however, exhibits high breakdown voltage due to it excitonic nature. In a recent study OSC as blended and bulk hetero-junction (BHJ) solar cell is exhibited greater open circuit voltage (Voc) and fill factor (FF) [5]. Low temperature processed organic carrier selective material is minimized interface defect that is reduced surface recombination velocity of solar photovoltaic [6]. Nevertheless, easy processing of organic carrier selective material has made it more demandable in opto-electronic fields. Similarly, inorganic ZnO possesses greater stability in the UV spectral region is preferable to usage in opto-electronic technologies [7]. For healthier electrical performance it is imperative to enhance carrier transport and hinders electrons towards p-emitter in inverted structure. In this purpose ZnO effect is vital for enhancement of PV performance [8]. ZnO large exciton binding energy of 60 meV paves the way for an intense near-band-edge excitonic emission at room and higher temperatures [9]. High radiation resistance and more flexibility of ZnO are reinforced to accommodate hetero-structure (HS) with minimum interface defects. Furthermore, greater flexibility of materials from II to VI groups is accommodated carrier with dissimilar materials upon light interactions. The inter-band transition is dominated by columbic interactions due to greater number of electrons in the conduction band leading to a higher binding effect that leads to less interface defects. Even higher growing temperature of ZnO improves crystalline property and in an active inverted device that is improved electrical property due to annealing effect [10]. Relatively thicker ZnO layer less transparency and thinner nanostructure greater defect density is prevalent. However, less thermal diffusion or leakage current is expected in relatively thicker ZnO-based devices [11].

Besides, ZnO based organic hetero-junction device; all inorganic photo device research is also progressed. All-inorganic transparent photo detectors [12] and solar photovoltaic devices [13] are studied recently and their fabrication and performance have been analyzed. Findings are demonstrated that the p-NiO/n-ZnO material interface electron barrier energy is greater than that of the hole barrier is turned them recombination prone. Relatively thick ZnO is subject to minimize the junction defects at high annealing temperatures. In past though p-conductivity was difficulty but at present organic materials p-type conduction problem is resolved by introduction of polymer hole transport materials (HTM). PTAA (poly-triarylamine) materials allows a barrier to electron thus it is being considered in emitter technology aimed at transparent opto-electronic devices. Novel PTAA polymer band edge and work function are greater than those measured for PEDOT:PSS [14]. Its higher conductivity and transmission window are also beneficial for next-generation photovoltaic applications. Emitter band barrier with n-ZnO can support as electrons reflector thus recombination effect is expected to be minimized. Therefore, in this study, typical PEDOT:PSS materials are replaced by highly conductive and thermally stable PTAA. ZnO of n-type conductivity has lowest resistivity [10–12] that can minimize contact loss. Hetero-junction aspects despite contact resistivity leakage current limitation are crucial. Those electronic properties are related to predicted energy states of novel PTAA-ZnO hetero interface as shown in Fig. 1. Fabrication process and annealing is influenced physical properties and it can improve interface with the aim of minimizing defects.

In this respect, highly stable PTAA material is anticipated to improve carrier conduction, and its valance band barrier with ZnO can limit leakage current. Thus, the photo-physical influence of novel PTAA-ZnO hybrid HJ potential is investigated in this work. Further analysis is conducted to find the optimal balance between optical transparency and excitonic energy conversion process, thus paving the way for future hybrid hetero-junction PV devices.

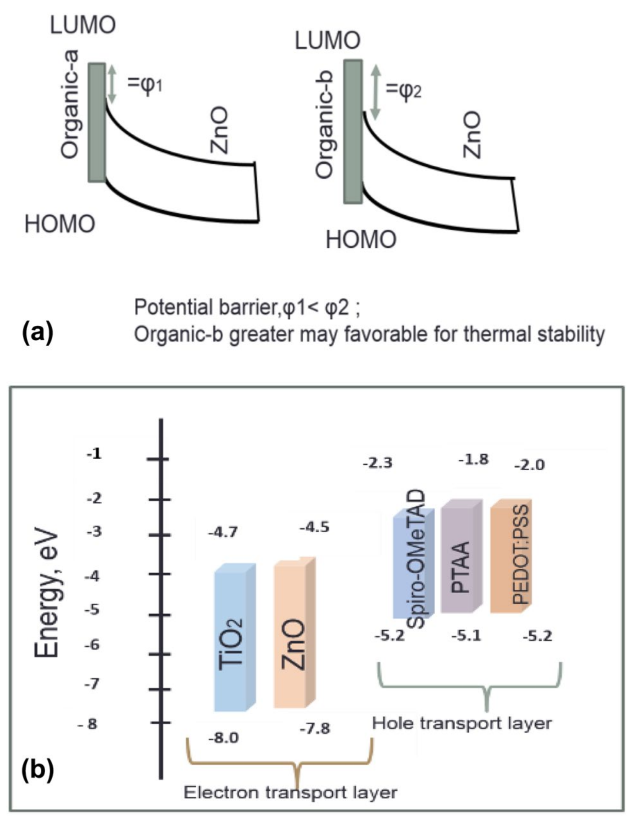


Fig. 1 Schematic hybrid PN junction (**a**); ZnO and PTAA energy level compare to others (**b**)

2 Experimental Details

2.1 Growth Process

In this work, RF-sputtered ZnO as a transparent base material is deposited on ITO electrode and its HJ with organic PTAA as emitter material has been developed by spin-coating method. The RF power was kept at 100 W while a mixture of argon (Ar) and nitrogen (N_2) gas flow rate is set to 8 sccm. At room temperature; these conditions yielded a ZnO film of ~ 300 nm thickness after 40-min deposition. Aiming to improve ZnO structure, it is annealed at 400 °C for 60 min after it has been loaded into an organic chamber for PTAA deposition. PTAA (Lumtec) is initially dissolved and soaked in chloroform for 12 h to obtain 1% wt polymer mixture. It is deposited on the sputtered ZnO layer at a spin-coating speed of 1000 and 2000 rpm, which yielded ~ 100 nm and ~ 60 nm thick PTAA layer, respectively. Finally, the device is annealed at range of 100–150 °C temperature. The full-fledged set-up, sequence and the resulting sample layout are shown in Fig. 2. RF sputtering stoichiometry and growth rate of the spin-coating method introduced some difficulties during the fabrication process.

2.2 Characterizations

Thermal annealing, optical and interface (current density–voltage, I–V) analysis was performed by conducting measurements at different temperatures to explore the energy conversion potential of the device under study. XRD measurements were conducted to determine grain size (by applying the Scherer Equation) and its relationship with leakage current and barrier height (numerically calculated). The general-purpose photovoltaic device model (GPVDM) software is implemented for HS typical design and interface assessment.

$$I = Is\ exp[(q(V - IRs)/nkT) - 1] \quad (1)$$

$$I_S = AA^*T^2 \exp(-\varphi_B/KT) \quad (2)$$

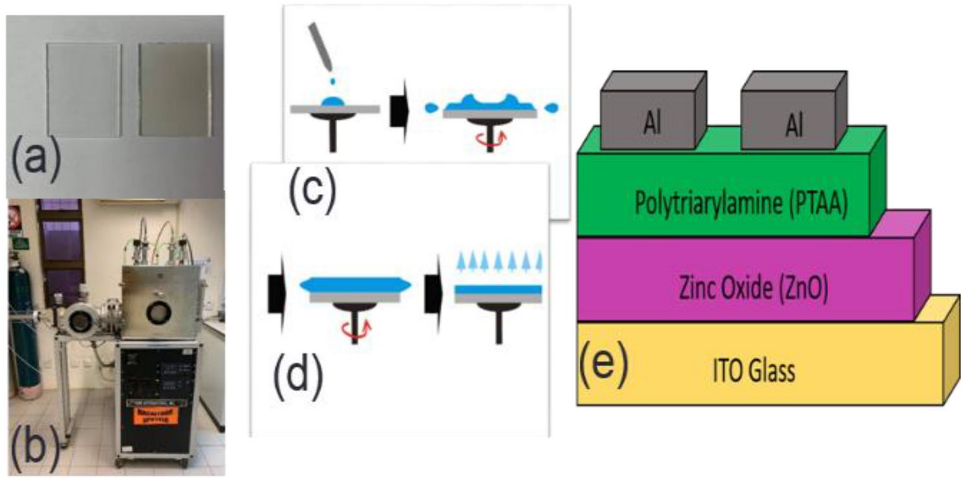


Fig. 2 Substrate (glass and ITO) (**a**), RF sputtering set up (**b**), PTAA deposition (**c**), annealing (**d**) and schematic design (**e**)

Thermionic model leakage current, *Is*, and barrier height, φ_B is numerically calculated by Eq. (2). It is diverse from all inorganic or metal-inorganic devices due to diverse binding energy effect.

3 Results and Discussion

3.1 Optical Properties

The dissimilar materials photon energy absorption and localized energy level variance has been displayed. The GPVDM software model is shown in Fig. 3a, b.

The photo-physical properties and barrier-related energy distribution in PTAA-ZnO hybrid HJ is demonstrated. ITO and ZnO layers, along with PTAA emitter material photo energy absorption at different depths and hetero-interface energy level variation is esteemed. The result is further specified the image of photon density distribution within the HS, as shown in Fig. 3b, and is typical for organic solar cells model [15]. In addition, transparency of base-layer materials is confirmed by UV–VIS transmittance measurements, as shown in Fig. 3c, while the Fig. 3d shows different-temperature annealed ITO transmittance spectrum. Both software and optical characterization-based data are revealed that the device exhibits generous transmittance properties over the visible band of the electromagnetic spectrum.

3.2 Electrical Properties

Electrical output of hybrid device is crucially depending on interface properties. Transparency influences on electrical transport mechanism at the interface. Low density of carrier determines lower optical absorption at the hetero interface thus, higher optical transparency is desired. Optoelectronic device purpose spin coated materials deposition and subsequent annealing is anticipated. This process is supported to re-crystallizing the materials in which interface states and their effect on device electrical performance analysis is vital. Device interface defect is highly dependent on leakage current density. Depending on annealing condition device electrical performance, especially the leakage current density measurement is potential. Thus, considering the PTAA melting temperature, annealing temperature was set below 150 °C and after annealing the samples positive and negative bias voltage was applied. The leakage current density variations were measured and plotted for diverse annealing temperature samples under illumination. These I–V characterizations by positive and negative voltages application, the eventual current density is shown in Fig. 4.

Contact material transparency and low sheet resistance is also essential for enhancing electrical properties. Annealing temperature effect on leakage current density is obtained from the semi-log (current) versus voltage analysis in the applied voltage in the range of − 4 to + 4 V. Leakage current density $< 10^{-4}$ A/cm^2 was measured for PTAA of 100 nm thickness, which is below previously published data for related technology [12, 16]. PEDOT:PSS greater barrier with respect to n-Si is supposed to reflect back electrons in PEDOT:PSS/nSi HJ [16].However, in this study, greater nZnO/PTAA barrier and ZnO columbic interaction may reduce carrier recombination. Investigating the annealing temperature effect on current density, it is evident that high-temperature annealing yields grain properties superior to those obtained at room temperature. The normal and log scale I–V characterizations data have been shown in Fig. 4a, c and Fig. 4b, d which may have influence on the PTAA physical properties at different annealing temperatures. Annealing of the active layer can potentially improve interface property thus higher field reduces carrier recombination or leakage current. It can be precisely observed in ratifying ratio analysis. The attribute of rectifying ratio for 2000 and 1000 rpm growth rate of PTAA on ZnO/ITO can be seen below in Fig. 5a, b. The variation of I(+)/I(−) ratio at diverse

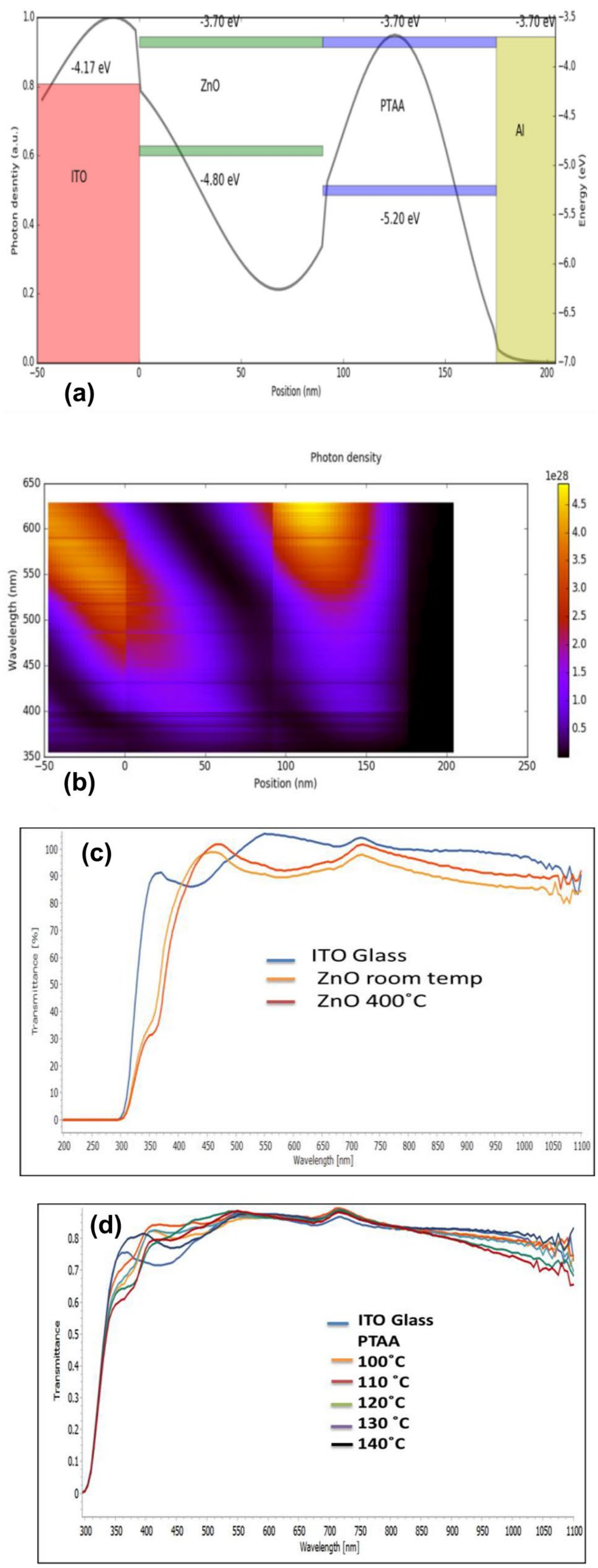


Fig. 3 Carrier accumulation due to abrupt interface band barrier (**a**), carrier density profile (**b**) (simulation data) and transmittance of base layers materials (**c**), temperature dependent PTAA transmittance (**d**)

annealing temperature and voltage of fields are shown. Data is been taken from Fig. 4a, c; however, some anomalies are found for diverse annealing conduction though it reason isn't clear.

3.3 Photo-Physical Properties

Variation of barrier height with grain size at different annealing temperatures for 1000 and 2000 rpm growth rate of PTAA on ZnO/ITO is shown below in Fig. 6.

Almost linear trend is achieved; however, anomalies observed higher temperature are possibly due to the thermal effect. For PTAA deposited at 2000 rpm, variations of barrier height in relation to grain size are very precise over the entire annealing temperature range. Compared to 1000 rpm growth, thinner and more consistent film is obtained at 2000 rpm. It is generally known that smaller-grained thin film has a greater defect density and could potentially maximize the interface defects. Greater grain size helps reduce grain boundaries or defects, leading to greater barrier height.

However, it is difficult to deduce carrier properties of hybrid hetero-structure from the grain size-barrier height relationship. Barrier height seems to be related to photo-physical status of active materials in which hetero-interface is significant. Interface barrier is shown to be overly dependent on grain size and annealing condition. Thus, leakage current relationship with barrier height for different growth rates was finally investigated. Figure 7 shows the relationship between grain size and leakage current.

The barrier height is quantum level energy barrier related to material's excitonic interaction along with growth parameters and it is marked variation with annealing temperature. Uniform variation of grain size with annealing temperature is observed for both 1000 rpm and 2000 rpm PTAA growth, as shown in Figs. 6 and 7. For 2000 rpm growth sequence may reduce growth rate and thus yield better linearity. The leakage current is obtained for 1000 and 2000 rpm PTAA growth rate that exhibits very similar trend as a function of grain size variation. At low temperature and low grain size, leakage current is remained steady as the annealing temperature and grain size is increased. Though grain size plays an important role to improve barrier height but no marked effect is shown for leakage current lessening. The increasing of grain size is due to the annealing temperature that supplies enough amount of energy for the polymer molecule to vibrate and reconstruct its molecular structure. This phenomenon, the PTAA polymer makes proper bondage onto ZnO thin film. Therefore, temperature indirectly affecting the grain size thus also gives effects towards the barrier height. It is observed that, grain size of PTAA thin film at 1000 RPM is greater compare to the 2000 rpm as the thickness of PTAA layer is different. In sum, barrier height and grain size can be modified by annealing process

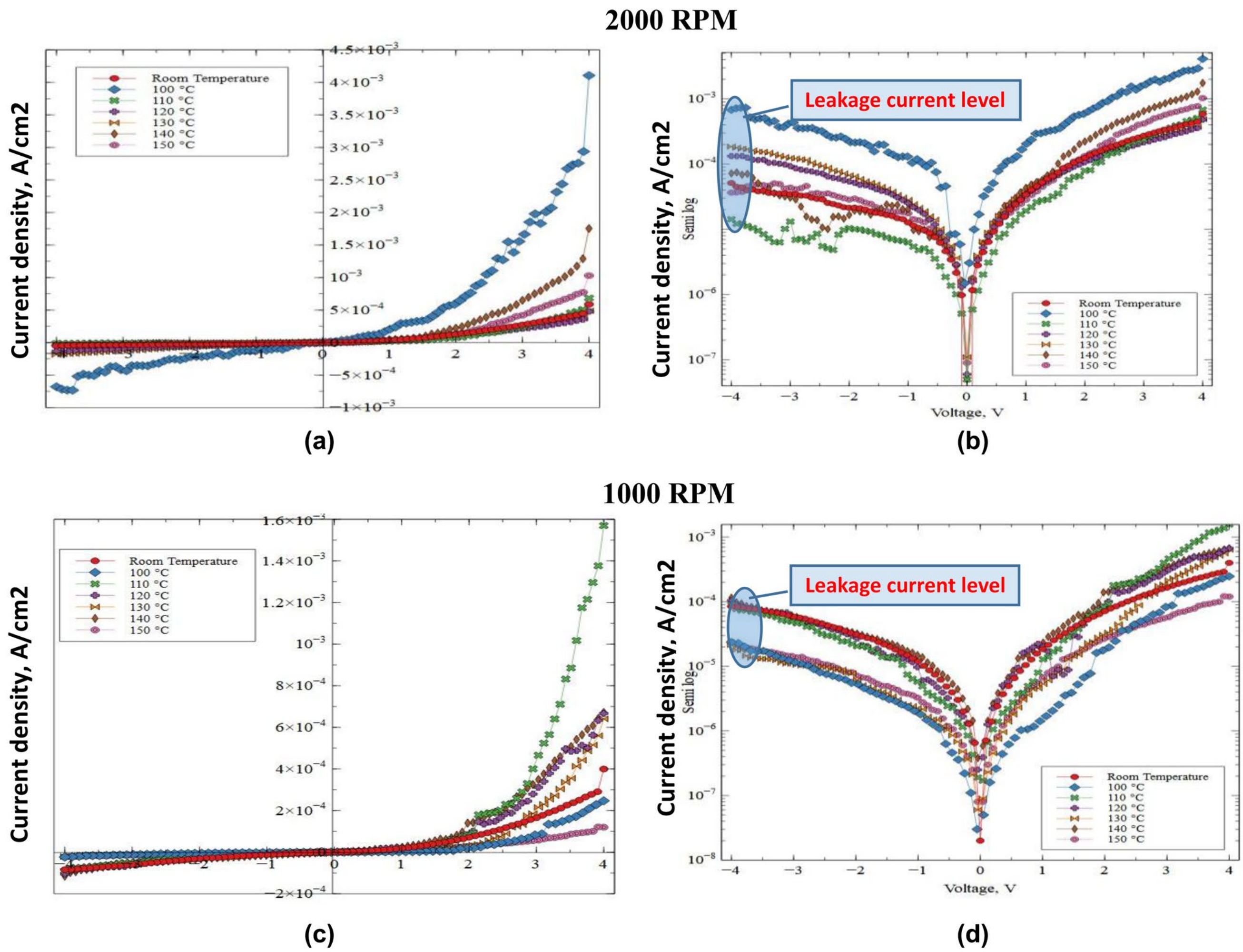


Fig. 4 Thermal annealing effect on active layer current density by I–V analysis (**a**) and (**c**) under illumination. Log scale leakage current (**b**) and (**d**) for 2000 and 1000 rpm respectively

however; leakage current is mostly influenced by field effect along with minimum effect of annealing process. This can be concluded that, the PTAA thin film is depicted high resistance result in low rectifying ratio. Current density and leakage current variation under different growth and annealing conditions of novel PTAA emitter is demonstrated to be suitable for next generation transparent renewable photovoltaic devices. However, lower photo current is possibly due to Schottky nature of the p-layer contract that is naturally vastly series resistive.

3.4 Correlation with XRD Data and Analysis

X-ray diffraction and scattering is depending on the structure and orientation of the crystal, thus leading to the distribution of bumps in a wide range of 2θ. In amorphous state, the broad peak is formed from low intensity X-rays that scatter individually while passing through a smaller lattice plane of a crystal. A broad diffraction peak of ZnO is observed at 34.46° with FWHM value of 2.60. Thus, showing that annealing of thin films leads to increasing grain size of ZnO from 7.844 to 9.764 nm. Meanwhile, the PTAA film depicts a broad peak between the angles of 23°–24° which agrees well with the research literature [17, 18]. The FWHM values obtain for PTAA film are within the range of 0.139–0.346, as the orientation of XRD pattern show amorphous phase of PTAA with grain size of 4.39 nm to 21.83 nm. The temperature gives effects towards the arrangement of the atomic molecules in the inorganic and organic semiconductor materials [19]. By annealing, the particle reassembles and attaching themselves towards each other producing a higher grain size [20]. Overall results of XRD spectroscopy are tabulated in Table 1.

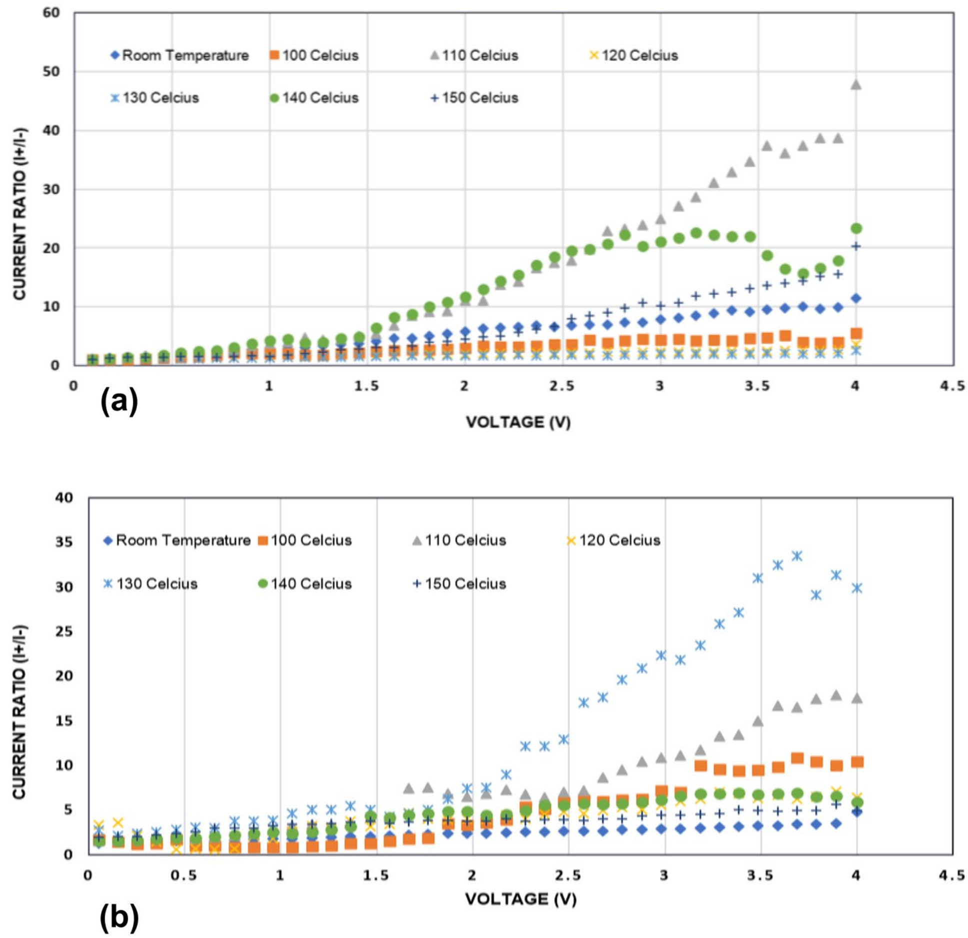


Fig. 5 The attribute of rectifying I(+)/I(−) ratio for 2000 and 1000 rpm growth rate of PTAA on ZnO/ITO

4 Conclusion

In this work, fundamental study of novel p-type PTAA/n-type ZnO hybrid HJ is accomplished. Good transparency in the visible band and its electrical performance at diverse annealing temperature and applied field (voltage) settings are analyzed. Low density of interface carrier determines lower optical absorption at the hetero interface thus, higher optical transparency is perceived. Different growth strategies, annealing temperatures and field effects on electrical properties are exposed. Suitable annealing condition leakage current is shown to reduce nearly to 10^{-4} A/cm^2 and at higher potential or field greater rectifying I(+)/I(−) ratio is realized. Grain size is shown to increase with annealing effect however; leakage current is bare to almost independent to grain size of PTAA on ZnO/ITO/glass substrate. Greater band barrier between PTAA and n-ZnO is shown to improve rectifying ratio, RR = I (v+)/I (v−) that is influenced by higher applied voltage or field effect. Though greater rectifying ratio is prevalent in dark analysis but in our study one of the key interests was to investigate the transparency of the device. Thus, it has been conducted under illumination because normally organic materials lower electrical permittivity induces higher binding energy that may not affect significantly by either temperature or illumination. One of the limitations of ratio enhancement may due to greater contact or series resistance for higher work function Al metal contact. It could possibly lessened by engaging lower work function Ag or Au materials instead of Al that can also be markedly increase photo current density. It will be a topic of future investigations of PTAA-ZnO hybrid HJ.

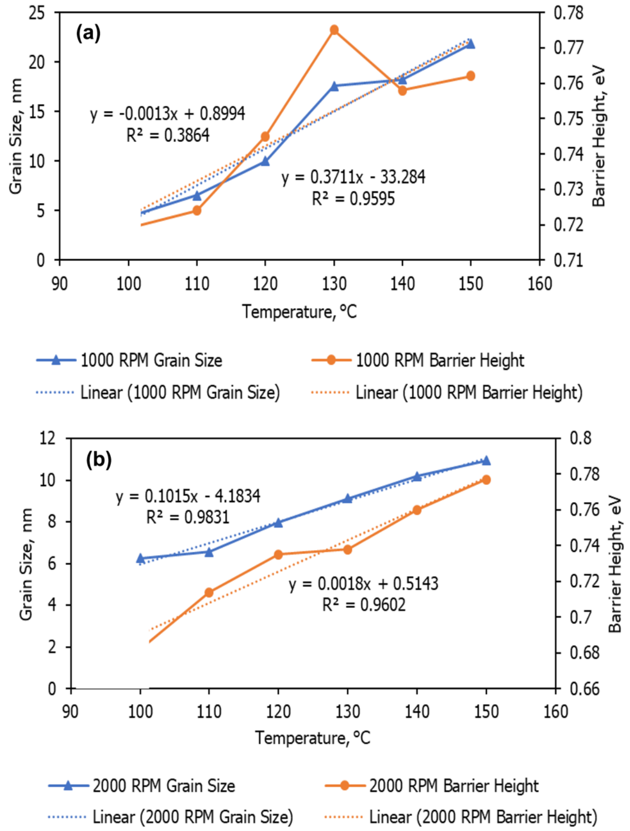


Fig. 6 Interface barrier height variation with annealing temperature for 1000 rpm (**a**) and 2000 rpm (**b**) growth

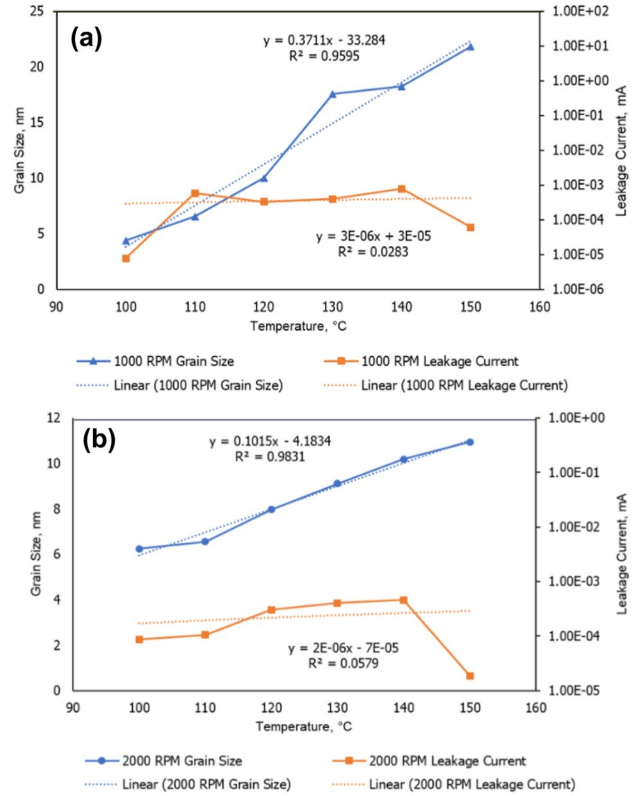


Fig. 7 Variation of leakage current with grain size at 1000 rpm (**a**) and 2000 rpm (**b**) growth rate of PTAA

Table 1 XRD Results of ZnO-PTAA diode

Thin film layer	Temperature (°C)	Diffraction peak (°)	Interlayer spacing (Å)	Grain size (nm)
Zinc oxide, ZnO	Room temperature	34.09	2.627	7.844
	400	34.46	2.600	9.764
Polytriarylamine, PTAA; 1000 RPM	100	24.31	0.346	4.390
	110	23.33	0.230	6.556
	120	24.77	0.152	10.010
	130	24.07	0.086	17.584
	140	23.01	0.082	18.260
	150	24.07	0.069	21.831
Polytriarylamine, PTAA; 2000 RPM	100	23.01	0.240	6.253
	110	23.33	0.230	6.556
	120	24.07	0.190	7.968
	130	24.33	0.166	9.118
	140	23.55	0.148	10.189
	150	23.45	0.139	10.949

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