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# Fabrication of zinc oxide/ polyaniline (ZnO/PANI) heterojunction and its characterisation at room temperature

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ABSTRACT

We report the formation of a diode like ZnO/PANI heterojunction structure by RF sputtering technique with a high rectification ratio in the laboratory. The diode parameters obtained from the I-V data using the established methods of Cheung and Norde's function, based on the thermionic emission model of diode, agrees with each other. The current mechanism in the diode was ohmic at lower voltages (at voltages less than 2.8 V) where as space charge limited current (SCLC) dominates at higher voltage (above 3.5 V). The measured I-V characteristics remain the same under bending conditions also. This indicates that this heterojunction could be exploited positively in flexible electronics.

## 1. Introduction

Recent trends of extensive research on ZnO attributes to its distinct properties such as wide band gap (~3.37 eV) at 300 K temperature, easy preparation at nanoscales, biocompatibility, high chemical stability, highly resistive to high-energy radiation with its applicability in varied fields such as optoelectronic devices, near-UV lasers, photovoltaics, sensors and transparent electronics [1–8]. This is because of the uniqueness of ZnO that exhibit simultaneously the semiconducting, piezoelectric, pyroelectric and optical properties as well as electrical, catalytic and electronic properties [9–11]. The tunability in the properties of ZnO films has a significant dependence on the substrate onto which they were grown [12]. Several articles in literature are solely devoted to the fabrication of ZnO based heterojunctions, and their possible applications in high performance devices such as gas sensors, Light-emitting diodes (LED), solar cells etc. [13–16]. A lot of attention has been paid for the development of heterojunctions of ZnO using p-type conductive oxides so as to avoid the difficulty of growing p-type ZnO for its possible applications in various fields [16]. Polyaniline (PANI), a p-type semiconducting polymer, stands out amongst the conducting polymers due to its simpler synthesis process, physical and chemical stability, unique conduction mechanism, eco-friendly, light weight, flexibility, facile fabrication and low cost [17–21]. Because of these distinct characteristics, the heterojunctions of ZnO/PANI have been investigated by several researchers [22–25].

In this communication, we report the formation of a ZnO/PANI heterojunction by RF sputtering technique which exhibits a diode like $I-V$ characteristics at room temperature under dark conditions. The characteristics remain significantly the same under bending state indicating a vital potential of its applications in flexible electronics. The electrical parameters of the diode so fabricated are obtained from the $I-V$ measurements using the Cheung's method and Norde's functions.

## 2. Experimental details

Firstly, the p-type polyaniline (PANI) film is deposited by electrochemical polymerization, potentiostatically for 600 s on the Au coated flexible PET working electrode. The n-type ZnO film is deposited by RF sputtering technique, by carrying out deposition for 15 min. The electrochemical polymerization is performed potentiostatically in a classic three-electrode cell, in which 100 nm thick, Au thermally evaporated on flexible PET is used as the working electrode. In this a Pt wire served as the counter electrode, and a standard Ag/AgCl functioned as the reference electrode. Aniline (Sigma) was purified by distillation and stored at 4 °C in dark. HCl (Sigma) was used as received. Double distilled water was used for the preparation of all the above solutions. The experiment was carried out at 5 °C, using an

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ice bath. Au coated PET substrates (2×1 cm) were vertically immersed in solution of aniline (0.1 M) dissolved in HCl (1 M) and maintained at 0–5 °C. A constant potential of 0.75 V was applied, for 600 s. RF magnetron Sputtering unit was used for the deposition of the ZnO on predeposited PANI films. A ZnO target (99.99% pure) of 2-inch diameter and 2 mm thickness was used. Vacuum chamber was first evacuated upto $5.5\times10^{-6}$ mbar using diffusion pump with liquid $N_2$ trap so as to avoid air contamination. Argon gas (99.999% pure) was used for the plasma creation. After the optimization of the gas pressure, argon pressure was fixed at 0.3 mbar. Thin layer (~100 nm) of Au is deposited on top of the ZnO by RF sputtering technique for the contact pad. The $I-V$ measurement on the heterojunction was performed using Keithley Digital 2450 sourcemeter interface with a computer.

## 3. Results and discussion

### 3.1. UV–visible studies

For the PANI film, UV–visible spectroscopy was done to assure the conducting form (emeraldine salt). One can observe, three peaks at nearly $E_1$=3.35 eV, $E_2$=2.84 eV and $E_3$=1.47 eV, respectively in the spectrum of the PANI film (Fig. 1). These three peaks are the characteristic peaks assigned to PANI thin films. The peak at $E_1$ is the first electronic transitions occurring from the upper defect band to the conduction band (π-π* transitions). The peak centered at $E_2$ is direct optical transition from the second highest occupied molecular energy level in the valence band to the polaron band and the last peak at $E_3$ is direct optical transitions between the highest occupied energy levels of the valence band to the polaron band.

The band-edge absorption due to the transition of electrons from the valence band to the conduction band is observed clearly for ZnO films from the UV–visible absorption studies carried out on films. Fig. 2(a) shows the results obtained for the band-edge transition. Fig. 2(b) shows the band-gap energies of the films determined from Tauc's relation i.e. plot (hν) vs $(\alpha h\nu)^2$, where hν represents energy and α signifies the absorption co-efficient. Band-gap energy obtained was found to be 3.156 eV. The UV–visible studies on PANI and ZnO films confirm the formation of conducting form of PANI and pure ZnO.

### 3.2. I-V characteristics and the diode parameters

The $I-V$ characteristic of Au/ZnO/PANI/Au heterojunction measured at 300 K in dark is shown in Fig. 3. The same characteristic was observed under bending conditions (45° and 90°) also. The heterojunction so formed shows a rectifying behaviour with a current rectification ratio of~ 600 at ±5 volts, a signature of forming a diode like structure between ZnO and PANI. The semilog forward and reverse bias $I-V$ curve of Fig. 4 shows that in the low forward bias voltage region, the $I-V$ characteristics is linear; it becomes exponential for a small region and then follows a linear line again.

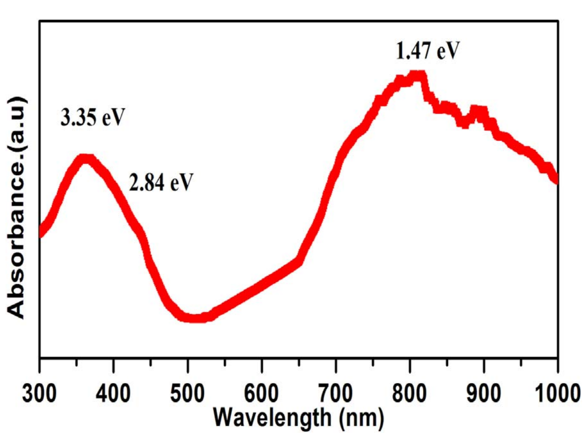


**Fig. 1.** UV–vis spectra of PANI films.

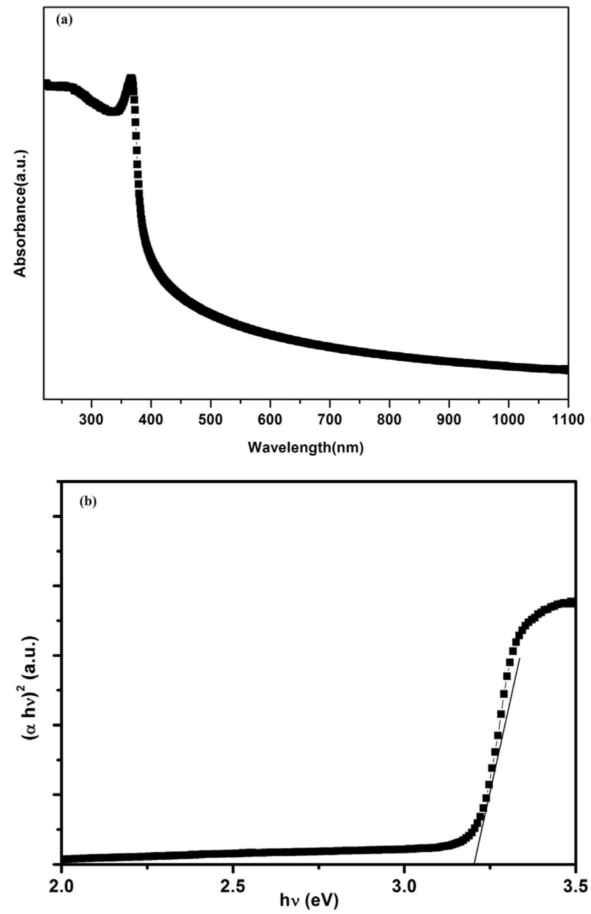


**Fig. 2.** (a) UV–visible absorption spectra of ZnO film (b) determination of band-gap energy.

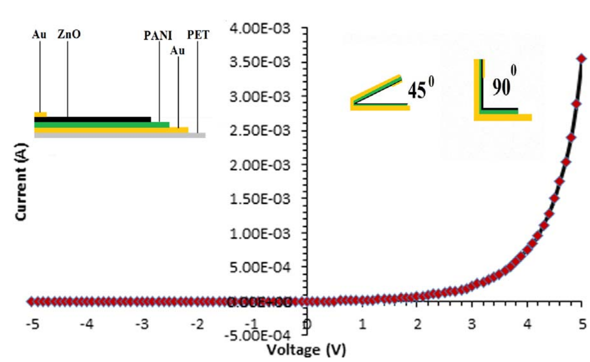


**Fig. 3.** Dark $I-V$ characteristics of ZnO/PANI heterojunction measured at 300 K, in flat and bending condition at an angle of 45° and 90°. Inset shows the schematic of the diode.

Following the framework of thermionic emission theory, the $I-V$ equation of this heterojunction is written as [1]:

$$I = I_0\left(e^{\frac{V-IR_s}{nV_{th}}} - 1\right) \tag{1}$$

$$I_0 = AA^*T^2e^{\frac{-\varphi_b}{V_{th}}} \tag{2}$$

where $R_s$,$n$, $A$, $A^*$,$\varphi_b$, $V_{th}$ are series resistance, ideality factor, area of the diode, effective Richardson constant, barrier height and the thermal voltage ($V_{th}$= $k_BT/q$, $k_B$ is the Boltzmann constant, $T$ is temperature in Kelvin and $q$ is the electronic charge) respectively. The value of $A^*$ for