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CONDENSED MATTER

Schottky Diodes Based on Polyaniline/Multi-Walled Carbon Nanotube Composites

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Abstract Polyaniline/multi-walled carbon nanotube composites (PANI/MWCNT), with various concentration of multi-walled carbon nanotube, were synthesized. Several Schottky diodes were fabricated, where PANI or PANI/MWCNT composites, aluminum, and gold were used as semiconductor, Schottky contact, and ohmic contact, respectively. Then current–voltage characteristics of the fabricated diodes were measured at room temperature and within the bias range of −5 to + 5 V. The measurements were repeated three times for each sample to verify repeatability of experiment. The obtained results show that by increasing the MWCNT concentration, the current intensity increases. Furthermore, I-V characteristics of pure polyaniline Schottky diode follows the thermionic emission mechanism while the I-V characteristics of Schottky diodes based on PANI/MWCNT composites show two distinct power law regions. At lower voltages, the mechanism follows Ohm's Law, whereas at higher voltages, the mechanism is compatible with space charge limited conduction emission mechanism. The parameters of Schottky diodes were determined, and it was observed that critical voltage decreased when the concentration of MWCNT in the composite increased.

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1 Introduction

In the recent decades, semiconducting polymers due to their unique electrical and optical properties have attracted noticeable attention in academy and industry for the fabrication of microelectronic and photonic devices. These polymers include polyaniline (PANI) [1], polypyrrole (PPy) [2], and other conjugated polymers [3]. Several devices are made from these polymers, including field effect transistor (FET) [4], Schottky diodes [5, 6], light emitting diodes (LEDs) [7], etc. Several different research groups have illustrated fabrication of Schottky diodes using vacuum deposition [8], solvent casting [9], electro polymerization [10], and pellets [11] of polyaniline. It has been demonstrated that the addition of carbon nanotubes (CNTs) to conducting polymers improves the mechanical and thermal stability and increases the electrical conductivity of devices made with such materials [12]. It has been found that composites of polymers containing low weight percentage of CNTs have good mechanical properties and enhanced DC conductivity [13].

2 Experimental Details

2.1 Materials

Aniline was supplied from Merck and was distilled twice prior to synthesis. Hydrochloric acid (HCl), potassium per sulfate (KPS), and *N*-methyl-2-pyrrolidinone (NMP), purchased from Merck, were used as received. Multi-walled carbon nanotube from Neutrino was used as received.

2.2 Synthesis of PANI and PANI/MWCNT Composites

Aniline was polymerized in an aqueous acidic solution. In a typical procedure, 20 mmol of KPS was dissolved in 100 mL of distilled water, and then the solution was added drop-wise to a solution of 2 mL aniline dissolved in 160 mL of HCl (0.5 M) aqueous solution, while the reaction mixture was stirred at 0–2 °C for 12 h. The greenish precipitate was collected and washed repeatedly with HCl (0.5 M) solution to remove unreacted oxidant and monomer until the under washing solution became colorless. Then, the remained polymer on the filter paper was washed several times with distilled water to get pH 7 for washing solution and dried to get the polyaniline, similar to ref. [14]. PANI/MWCNT composites have been synthesized by "in situ" polymerization process. The weight percent of multi-walled carbon nanotube (MWCNT) was varied from 0.5, 1, 2, and 5 (wt %) relative PANI/MWCNT nanocomposite. Appropriate amount of MWCNTs was dispersed in 118 mL HCl (0.5 M) and sonicated for 1 h in order to obtain a reasonable dispersion of MWCN T. Then, 1.5 mL of aniline was added to the mixture and sonication was continued for 1 h. Then, potassium persulfate (4.32 g in 86 mL water) was added drop-wise under stirring. The reaction was continued at 0–2 °C for 12 h. The dark green product was dried after filtering and washing, similar to ref. [12].

2.3 Fabrication of Schottky Diodes

PANI and PANI/MWCNT composites solutions with 0.5, 1, 2, and 5 (wt%) of MWCNT were prepared at room temperature by adding 0.1 g of composite powder in 20 mL NMP, sonication was continued for 2 h, and then solution was stirred for 6 h. For ease, the samples were referenced as S-1, S-2, S-3, S-4, and S-5 which correspond to 0, 0.5, 1, 2, and 5 wt% of MWCNT in PANI/MWCNT composite, respectively.

In this work, gold was chosen as the ohmic contact of the diodes because of its relatively high work function (Φ= 5.1 eV) and aluminum was chosen as the Schottky contact because of its relatively low work function (Φ=3.9 eV) in comparison with p-type polyaniline (Φ=4.1–4.45 eV) [15, 16]. For fabrication of Schottky diodes, first, a thin layer of gold was coated on a circular test glass by thermal-resistance evaporation technique and then a thin film layer of prepared composite solution was spin coated on gold. Finally, a layer of aluminum was deposited on the surface of polymer film by vacuum evaporation technique under ~10^{-5} Torr. Schottky contacts to the front side of the polymer films were formed using a shadow mask to form square shapes with approximate thickness of 1 μm and a length of 3 mm. A schematic representation of this device structure is shown in Fig. 1.

3 Results and Discussion

Uniform behaviors of a nanocomposite, consisting of a conducting polymer and CNTs, depend on suitable distribution of nanotubes within the polymer matrix. Scanning electron microscopy is a good instrument for investigation of nanotube distribution in a polymer matrix. The SEM image of the edge of a torn sample of a PANI/MWCNT composite pellet is shown in Fig. 2. It is observed that MWCNTs were protruded from the edge of the composite film. This image indicates that the MWCNTs are acceptably dispersed within the PANI matrix.

Current vs. voltage (I-V) measurements of fabricated diodes were performed at room temperature. The currents were measured within the bias range −5 V, +5 V. The measurements were repeated three times for each sample to verify repeatability of experiment. I-V characteristics of the Al-PANI/MWCNT-Au Schottky diodes with various concentration of MWCNT were shown in Fig. 3. It is known that an asymmetric flow of electrons through a system is called rectifier of electrical current. The curves shown in Fig. 3 are asymmetric and non-linear indicating a rectifying behavior of the PANI-Al and PANI/MWCNT-Al hetero junctions. Furthermore, I-V characteristics indicate that with the addition of MWCNTs and increasing of their concentrations, the current intensity in these diodes increases. This is in accordance with the fact that as the MWCNT concentration increases, the conductivity of the composite increases. This procedure in the I-V characteristics is in agreement with the results reported by other investigators regarding in situ polymerized and solution processed composites [17, 18].

Saxena and Santhanam have proposed that the non-linear current–voltage characteristics of the metal/polymer junction could be due to the thermionic emission, space charge limited conduction (SCLC), or Poole–Frenkel emission [19]. According to the thermionic emission model, I-V relationship for the Schottky barrier devices is given as [6, 15]

$$J = J_0 \ \exp(\mathrm{eV/nkT}), \tag{1}$$

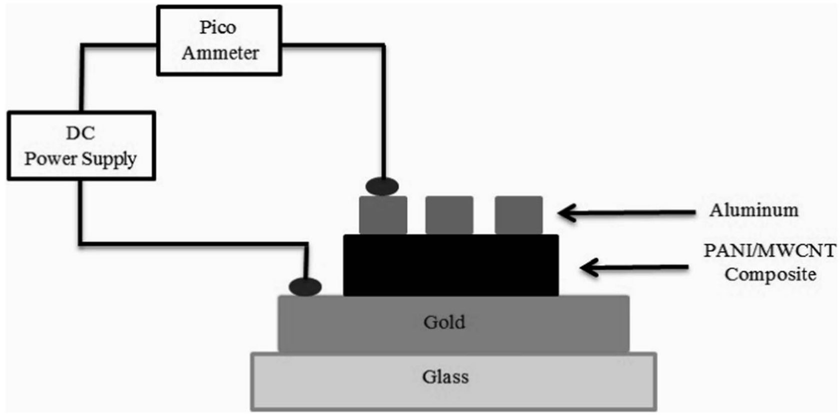
where, e is the electric charge, n is the ideality factor, k is the Boltzmann constant, T is absolute temperature, and $J_0=I_0/A$ is the reverse saturation current density, in which A is the effective area of diode. From J_0, the barrier height (φ_b) can be calculated using the Richardson equation [6, 15],

$$J_0 = A^* \ T^2 \ \exp(-e\varphi_b/kT), \tag{2}$$

where A^* is Richardson constant (120 A/cm^2 K^2 for free electron). The value of ideality factor (n) can be obtained from the following equation [20]:

$$n = \frac{e/kT}{(d \ \ln \ J/dV)}. \tag{3}$$

Fig. 1 Schematic of PANI/MWCNT Schottky diode structure



The Poole- Frenkel emission depends on the material bulk barriers (acceptor and donor sites, traps, or electrons in the valence band) [21]. The current density for Poole–Frenkel emission can be expressed by the following equation:

$$J/V = (J_0/V_0)\ \exp\left[\ \beta(V/d)^{1/2}/nkT\right], \tag{4}$$

where d is the thickness of the coated polymer and $\beta=(e^3/\pi\varepsilon\varepsilon_0)^{1/2}$, in which ε is the dielectric constant of the polymer and ε_0, is the free-space permittivity.

The SCLC mechanism depends on the traps at the interfacial region between metal and polymer [15]. The current density for SCLC mechanism is given by the following equation:

$$J = \left[\left(8\varepsilon\varepsilon_0\mu V^2\right)/\left(9d^3\right)\right] \propto\ V^2. \tag{5}$$

where μ is the carrier mobility.

In thermionic emission mechanism, the plot of *log* (*I*) vs. *V* is linear; in Poole–Frenkel emission, the plot of *log* (*I*/*V*) vs. $V^{1/2}$ should be straight line. However, when the plot of *log* (*I*) vs. *log* (*V*) is linear, system will follow the SCLC mechanism.

In sample S-1 (pure PANI), the nonlinear *log* (*I*) vs. *log* (*V*) curve (Fig. 4) eliminates the possibility of SCLC process; also, *log* (*I*/*V*) vs. $V^{1/2}$ plot is nonlinear (Fig. 5) which eliminates the possibility of Poole–Frenkel process. These results suggest that the thermionic emission theory can be applied to evaluate junction parameters for Au-PANI-Al Schottky diode. The plots of *log* (*I*) vs. *V* were given in Fig. 6. Experimentally, J_0 is obtained by extrapolating the linear part of *log* (*J*) vs. *V* and taking the intercept with J-axis. This extrapolated value of current density at zero voltage is the saturation current J_0. The ideality factor can be obtained from Eq. (3). The calculated values of parameters J_0, φ_b, and n for sample S-1 are 0.6 ($\mu A/cm^2$), 0.79 (eV), and 3.7, respectively.

I-V curves of S-2, S-3, S-4, and S-5, shown in Fig. 3, indicate a deviation from the Schottky behavior that has been observed in the case of pure PANI diode. This deviation could be a result of the increase in conductivity due to existence of MWCNT in composite, which may produce materials with high conductance and thus have such a high effective doping concentration. These results signify that further current transport mechanisms dominate in the PANI/MWCNT composite devices. The characteristics obtained by plotting I-V curves in logarithmic scale (Fig. 7) reveal two separable linear regions, with a slow transition between the two regions. The two

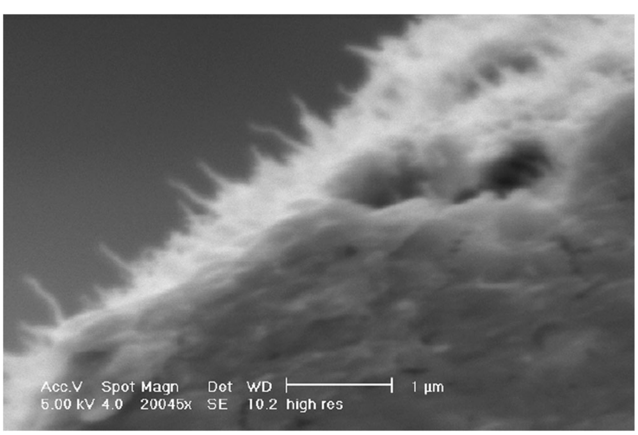


Fig. 2 SEM image of the edge of a PANI/MWCNT pellet

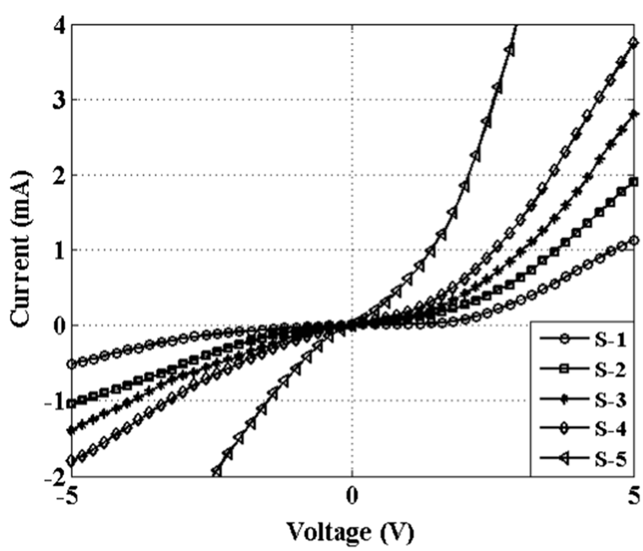


Fig. 3 I-V Characteristics of Al-PANI/MWCNT-Au Schottky diodes with various concentrations of MWCNT

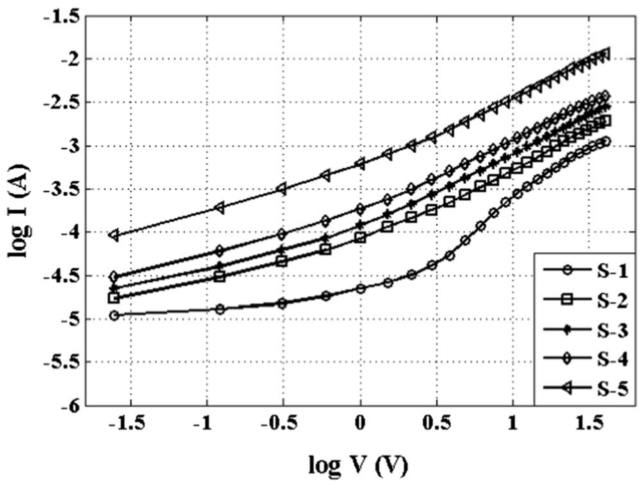


Fig. 4 log (I)–log (V) plots of diodes

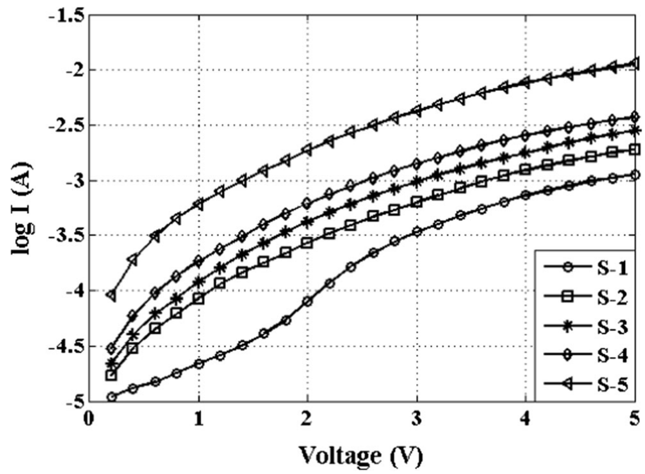


Fig. 6 log (I)–V plots of diodes

separate linear regions on the plot can be fitted to power law equations with different exponents. The general power law equation can be represented as follows:

$$I = K\ \ V^m, \tag{6}$$

where K is a constant and m is the exponent, which is determined from the slope of the *log* (*I*)–*log* (*V*) curve. At lower voltages, the exponent, m_1, for S-2, S-3, S-4, and S-5 are determined to be 1.04, 1.03, 1.02, and 0.99, respectively. These values imply that the currents vary linearly with voltage and hence the current flow mechanism is governed by Ohm's law. At higher voltages, the exponent, m_2, for S-2, S-3, S-4, and S-5 are 2.02, 1.94, 1.92, and 1.4, respectively, and hence the current flow mechanism is governed by SCLC mechanism. At lower voltages, the density of thermally generated free carriers in the composite diodes is dominant, thus the injected carriers from the contacts are neutralized by the thermally generated carriers. Therefore, Ohm's law dominates in this low-voltage region. When the density of the injected carriers from the contacts becomes comparable with the density of the thermally generated free carriers, the space charge limited conduction mechanism begins. The applied voltage in which this transition occurs is called the critical voltage, *Vc*, and it is defined by the following equation [22]:

$$V_C = \frac{8}{9}\frac{qp_0d^2}{\varepsilon_0\varepsilon_r\theta}, \tag{7}$$

where d is the thickness of the film, p_0 is the density of the thermally generated free carriers, ε_0 is the free-space permittivity, ε_r is the dielectric constant of the composite film, and θ is the trap factor given by

$$\theta = \frac{p}{p+p_t}, \tag{8}$$

where p is the density of free carriers and p_t is the density of trapped carriers.

From Fig. 7, it is observed that V_C for S-2, S-3, S-4, and S-5 are 1.22, 0.97, 0.94, and 0.75 V respectively.

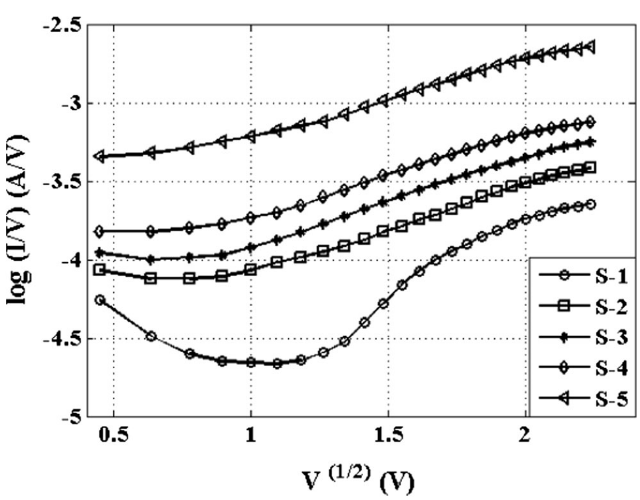


Fig. 5 log (I/V)–$V^{1/2}$ plots of diodes

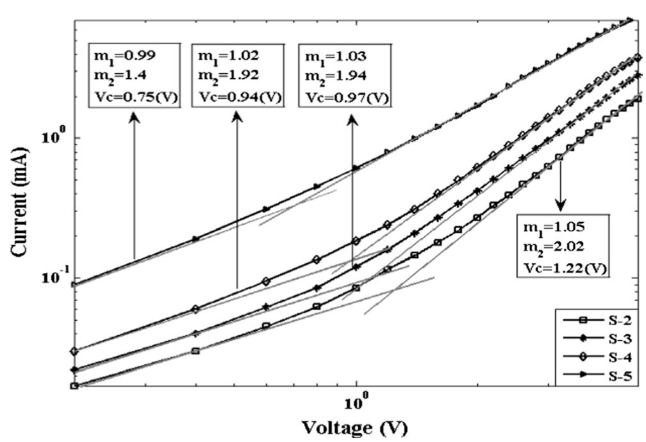


Fig. 7 I-V plots of composite diodes in logarithmic scale with power law fit parameters

From the results, it is observed that as the MWCNT concentration in the composite increases from S-2 to S-5, the critical voltage, V_C, decreases. This can be related to the increase in conductivity of the PANI/MWCNT composites with increasing of MWCNT concentration, which may be a result of an increase in the density of free carriers, p, in the composites. These additional free carriers can be imported by the MWCNTs that form conducting networks within the PANI matrix, and therefore cause an increase in current. From Eq. (8), it is observed that with an increase in the density of free carriers, p, the trap parameter, θ, effectively increases. Therefore, from Eq. (7), it is comprehended that with an increase in θ, the critical voltage, V_C, decreases.

4 Conclusions

PANI and PANI/MWCNT composites with various concentrations of MWCNT were synthesized. Schottky diodes were fabricated using Al as Schottky contact, Au as ohmic contact, and PANI or PANI/MWCNT composites as semiconductor. I-V characteristics of diodes were measured. It was observed that when the concentration of MWCNT increases, the current intensity in the diodes increases. Furthermore, I-V characteristics showed that Schottky diode based on pure PANI follows the thermionic emission mechanism. However, when PANI/MWCNT composites were used, I-V characteristics showed two distinct power law regions. It was seen that at lower voltages, the mechanism follows Ohm's Law, whereas at higher voltages, the mechanism is compatible with SCLC mechanism. The parameters of Schottky diodes for each mechanism have been calculated and observed that the critical voltage, Vc, decreases with increase in the concentration of MWCNTs in the composite.

It was shown that MWCNTs play an important role in current–voltage characteristics of diode. However, further investigation will be required to determine optimal concentration of MWCNT in composition.

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