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Study the Electrical Properties of Carbon Nanotubes /Polyaniline Nanocomposites

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Abstract Several schottky diodes were fabricated from polyaniline/ Carbon nanotube (single and multi-walled) composites. These composites were synthesized with different concentration and two carbon nanotubes types, Single and Multi-Walled Carbon Nanotubes (SWCNT & MWCNT). Aluminum and silver paste were chosen as schottky and ohmic contact respectively. physical and electrical were used to studied these composite by using Atomic Force Microscopy (AFM) and electrical measurements. The Root Mean Square RMS surface roughness of the composite samples was found to be around 4nm. The current-voltage characteristic were measurements for all samples in the bias range $\pm 15V$ at room temperature. The results shows the increasing in carbon nanotubes concentrations increase the current intensity, and the single walled gave higher current intensity than multi walled carbon nanotubes . The current –voltage characteristics for the composite devices shows the current at lower voltages obeys ohm's contact while at higher voltages child's law is dominated.

Keywords—*Polyaniline, CNT, electrical properties.*

I. Introduction

Since the discovery of Ijiman et. al.[1] the carbon nanotubes (CNT) takes a great attention from researchers and scientist due to their excellent electrical properties. It have a wide range of application such as supercapacitance, devices, Schottky contact, solar cell, gas sensor [2-7]. CNT /polymer composite result a nanocomposite with high electrical conductivity [8,9]. Polyaniline (PANI) is the most conductive polymer used because it's easy synthesis and good electrical properties so it can use as electronic material[10]. PANI distinguishes with three forms which can be divided into fully oxidized pernigraniline, half-oxidized emeraldine base (EB) and fully reduced leucoemeraldine base (LB). The most stable and conductive (when doped) form of PANI is Emeraldine or what is called (emeraldine salt) [11] . There are many ways to fabricate Schottky diodes from semiconducting polymers including electropolymerization[12], solvent casting[13], vacuum deposition[14] and pullets[15]. In this paper, polyaniline was synthesized chemically, the I-V characteristics were measured for the fabricated Schottky diodes AL-PANI/CNT-Ag.

2. Experimental

A. Material

The two types of CNT (purity =95%) were supplied by Neutrino factory, India. The diameters of them were in the range of (1-2)nm and (10-20)nm respectively with length 30 μ m for both. Hopkin and William Germany was supplied the aniline with purity 99.99%. Hydrochloric acid (HCl) was obtained from Samchun Pure Chemical (Korea) and ammonium persulfate (NH₄)₂S₂O₈ (99.95%) was supplied Himedia Laboratories PVT.LTD (India).



B. Instrument

Atomic Force Microscopy images were obtained using SPM, Model AA 3000, angstrom. The RMS surface roughness of the composite was evaluated based on data obtained over the entire sample. The I-V characteristic was measured By Keithly digital electrometer 616

C. Synthesis of PANI

Fig.(1) illustrate the polymerization of aniline .The base preparation of PANI was done by oxidation of 0.2M aniline hydrochloride with 0.25M ammonium persulfate in acidic medium. Then the two solutions dissolved in 1M HCl aqueous solution separately. By using a rounder, both were mixed and stirring to polymerize. After polymerization ending, the mixture left at rest for 24h, then the precipitate of PANI was collected by a filter and washed with of 0.2M HCl. PANI hydrochloride emeraldine powder was dried in air for short time.

D. PANI/CNT Composite

The composites of polyaniline with CNT was synthesis via in situ polymerization. Two weight percentages were chosen for both CNT types (0.1 and 0.8) wt% to dissolved in 1M HCL solution and sonicated for 2h, then transferred into a 250 three-neck flask with ice-bath. The aniline monomer was also dissolved in 1M HCL solution then added to the CNT. A 2.5 ammonium persulfate (APS) was slowly dropwise into the suspension with constant stirring at reaction temperature 25°C for 12h. the resulting mixture was collected by filter papers and washed several time with distilled water and acetone. Then left to dry in vacuum at 80° for 4h [16].

E. Fabrication of Schottky Diodes

Polyaniline is a p-type semiconductor ($\phi = 4.1-4.5\text{eV}$), the work function value is essential to choose the ohmic contact and schottky junction, for ohmic contact the silver paste was chosen because its high work function ($\phi = 4.67\text{eV}$) comparable with PANI, while Al has lower work function ($\phi = 3.9\text{eV}$) and chosen as schottky diode.

The fabrication of Schottky diode was done by coating a thin layer of silver paste of the sample by thermal evaporation technique under $\sim 10^{-6}$ Torr by using a shadow circular mask. Then on the other surface of sample a layer of aluminum was deposited.

3. Results and Discussion

Figure (2) shows measurements of current vs. voltage for fabricated schottky diode within the bias range $\pm 15\text{V}$ at room temperature. It shows the expected behavior of Schottky diode, the curve asymmetric and non-linear for all samples which indicating a rectifier behavior. The effect of addition of CNT was shown and increasing concentration leads to increase the current and conductivity, this results agrees with many researchers[17-18].

The thermoionic emission model expressed the I-V relationship for Schottky diode

$$J = J_0 e^{\frac{eV}{nKT}} \quad (1)$$

Where n is the ideality factor, e is the electric charge, T is absolute temperature, k is Boltzmann constant and $J_0 = I_0/A$ is the reverse saturation current density, A is the effective area and I_0 is the reverse saturation current of the diode. For calculation the barrier height (ϕ_b) depending on J_0 , the Richardson equation can be used[20-22]

$$J = A^* T^2 e^{-\frac{\phi_b}{KT}} \quad (2)$$

Where A^* is the Richardson constant ($120 \text{ A/cm}^2 \text{ K}^2$ for free electron).

The plot of $\log(I)$ vs. V is linear in the thermionic mechanism, fig. (3), while in the thermionic emission, the plot of $\log(I/V)$ vs. $V^{1/2}$, fig. (4), is a straight line, here the system will follow SCLC mechanism.

Depending on the non-linearity behavior of pure PANI shown in fig. (4&5) the SCLC mechanism and Poole-Frenkel process were eliminated.

By plotting the logarithm scale of IV reveals two linear regions with different slopes, which can be fitted to the power law between voltage and current, this formula (general power law) can be expressed as $I=KV^m$ (3)

Where K is constant and m is an expression determined from fig. (5). At low voltage, the exponent $m=4.27, 4.26, 4.35, 4.43$ for PANI/SWCNT (0.1 & 0.8)%wt and PANI/MWCNT (0.1 & 0.8)%wt respectively, shows the current flow mechanism in this region follows Ohm's law, this can be explained by the dominance of thermally generated free carriers from localized defect states. These injected carriers are neutralized from the contacts by thermally generated carriers. For this Ohm's law dominated here.

At high voltage, the exponent $m= 1.62, 1.44, 1.58, 1.4$ for PANI/SWCNT (0.1 & 0.8)%wt and PANI/MWCNT (0.1 & 0.8)%wt respectively, here the SCLC mechanism is dominant. The SCLC mechanism begins when there is a comparability between the density of the injected carriers from the contacts with the density of the thermally generated free carriers; these results were in good agreement with [18, 19, 20].

Fig.(6) shows the AFM image of two chosen samples in addition to the pure PANI, the RMS surface roughness for the composite films were about 4nm, almost the same for pure PANI.

4. Conclusion

PANI and PANI/CNT composites with various concentrations and types of CNT were chemically synthesized. Schottky diodes were fabricated by using Al as Schottky contact, silver paste as ohmic contact and PANI as semiconductor, the I-V characteristics were studied. It shows the current intensity increases with increasing CNT concentration and SWCNT has higher current intensity than MWCNT because of the nature of SWCNT which has only a single surface. It shows the Schottky diode made from PANI follows the thermionic emission mechanism. The IV characteristic of the PANI/CNT composites distinguishes two power law regions. Where at lower voltages the mechanisms follow Ohm's law, but at higher voltages the mechanisms follow SCLC mechanism.

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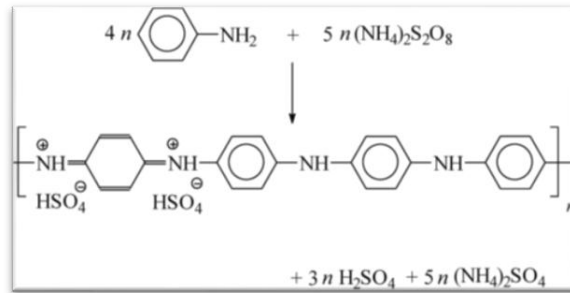


Figure 1: polymerization process of aniline [15].

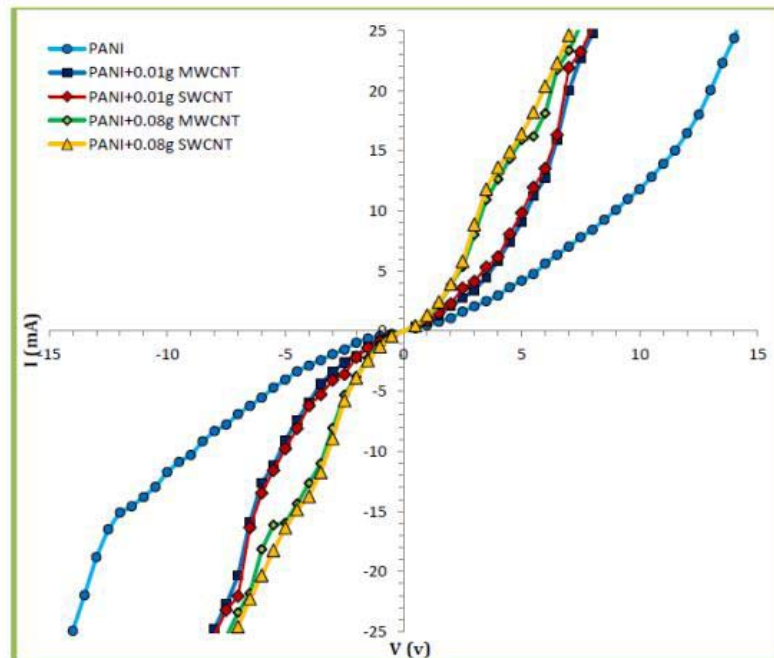


Figure.2: I-V Characteristics of pure PANI and PANI/CNT Schottky diodes

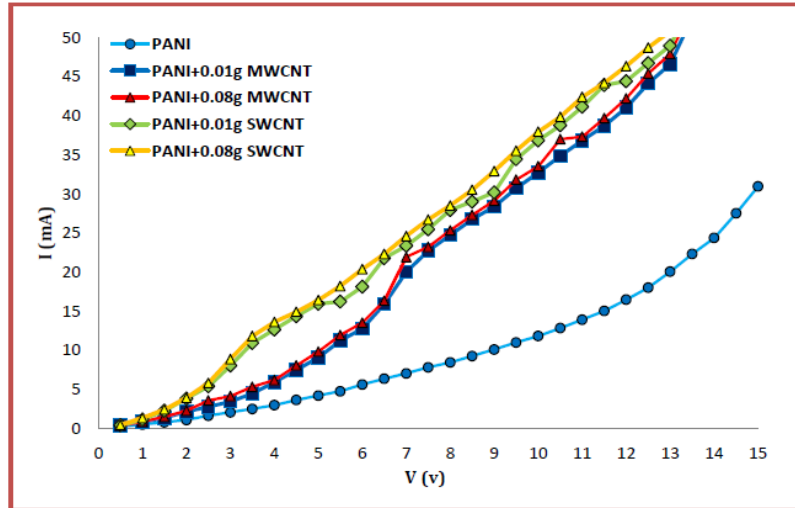


Figure 3: IV plots of Schottky diodes

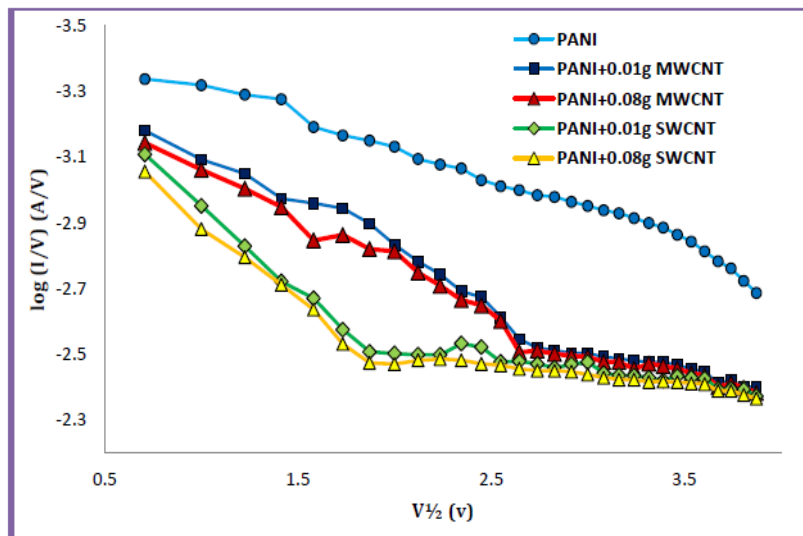


Figure 4: $\log(I/V)$ vs. $V^{1/2}$ plots of Schottky diodes

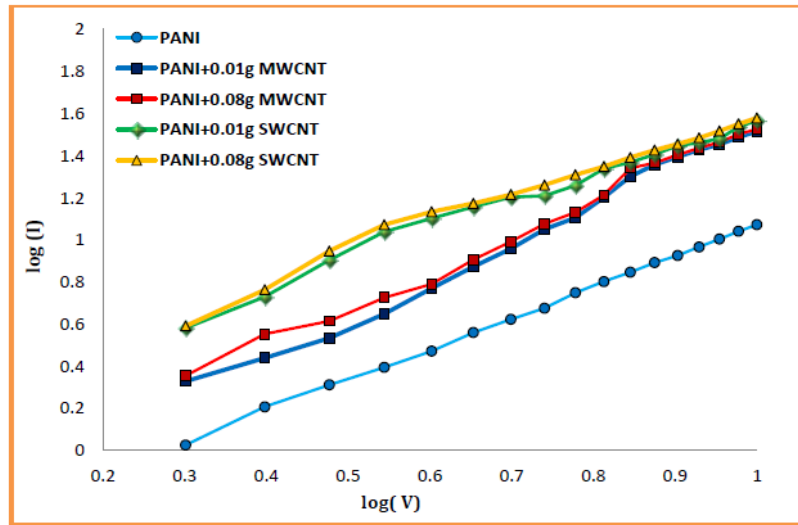


Figure 5: log(I) vs. log(V) plots of diodes

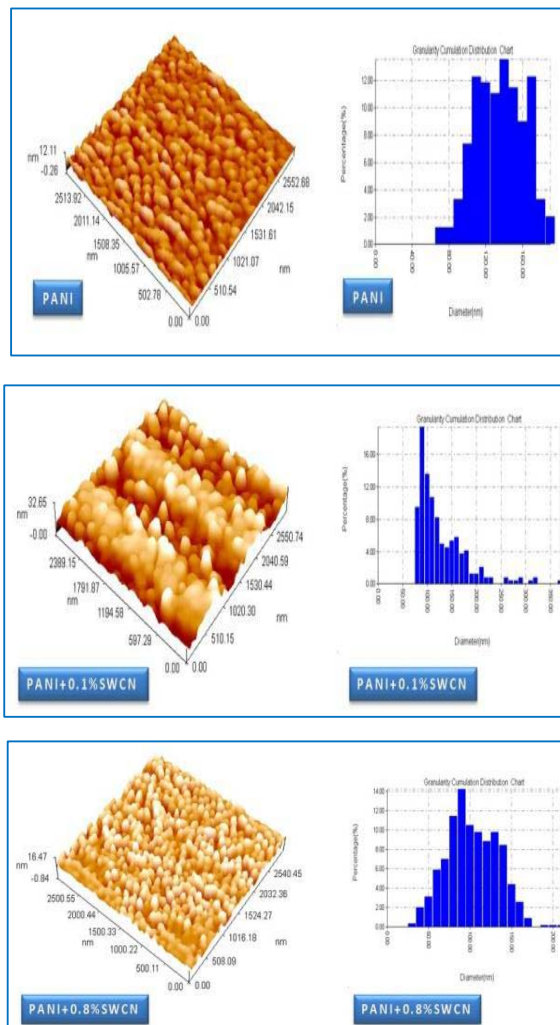


Figure 6: AFM image of pure PANI, 0.8% PANI/SWCNT and CNT/MWCNT respectively.