



PIEZORESISTIVITY OF CARBON NANOTUBES STRAIN SENSORS

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ABSTRACT

Carbon nanotubes are highly sensitive to strain even at macro and nanoscale. The high strain sensitivity is due to its piezoresistive behaviour. The piezoresistivity of CNT and their polymer composites are derive from three main components i.e. contact resistance between CNTs, tunneling resistance between neighbouring CNTs and CNT piezoresistivity. The contact resistance of CNT network depends on the region of contact and it lies in the range between few hundred to thousand kΩs. While the tunneling resistance of CNT network depends on the distance between its neighbouring CNTs. As the distance d between CNTs increases within 1nm due to its applied strain the tunneling resistance increases exponentially. The tunneling effect is more dominant when the concentration of CNT filler in composite is close to percolation threshold. The piezoresistivity of CNT/polymer composites are also dependent on environmental conditions such as temperature, pressure etc. It changes with the change in temperature due to infiltration of polymer into CNT networks.

Keywords: piezoresistivity, percolation threshold, tunneling effect.

1. INTRODUCTION

Carbon nanotubes occur in powdered form, which is black in colour. Each powder particle of CNT comprises of carbon atoms in hexagonal lattice forming a layer of graphitic sheet, which is rolled up in the form of seamless hollow cylinder. The diameter of this cylinder is in nanometers and length is in micrometers or even in millimeters. Carbon nanotubes are classified as single walled (SWCNTs), double walled (DWCNTs) and multi walled (MWCNTs) depending on the number of graphitic concentric layers one inside another. Each graphitic layer has carbon bond with sp^2 hybridisation and there exist weak vanderwall forces between the graphitic layers. Due to its unique cylindrical structure with sp^2 hybridised carbon bond, it is the strongest and stiffest material discovered so far [1].

CNTs possess a very high tensile strength (~100GPa), young's modulus (~1TPa), electrical conductivity ($10^9 A/cm^2$), thermal conductivity (3500W/MK) and also exhibit piezoresistive behaviour i.e. their electrical properties changes with the change in mechanical deformation. The strain sensing performance of CNT is mainly due to its piezoresistive behaviour [2].

The piezoresistivity of the CNT and their polymer composite networks derive from three main components; contact resistance between CNTs, tunneling resistance between neighbouring CNTs and CNTs piezoresistivity [3]. These three components are dependent on various parameters such as; quality of CNT used quality of polymer used, percolation threshold of composite, tunneling distance and environmental conditions. This paper focuses on the piezoresistivity of CNT and CNT/polymer nanocomposite strain sensors. This article is organized into four different sections. Section 1 gives an overview of piezoresistivity of CNT networks. Section 2 theoretically analyses the effect of tunneling distance on piezoresistivity of CNT networks by

using numerical simulations. Section 3 numerically simulated the effect of percolation threshold on piezoresistivity of CNT networks and Section 4 give the performance analyses of CNT based strain sensors at different temperatures.

2. PIEZORESISTIVITY OF CNT NETWORKS

When the CNT material is subjected to strain, the conductive network of carbon nanotube changes which result into an increase in their resistivity. With the change in resistivity their resistance also changes. In any conductive material, the electrical resistance R can be expressed by the following equation

$$R = \rho \frac{L}{A} \quad (1)$$

Where ρ is the intrinsic electrical resistivity, L is the length and A is the crosssectional area of the material [4]. The resistance of carbon nanotube is divided into two types: intrinsic resistance and intertube resistance strain sensing phenomenon in a carbon nanotube network is attributed to two types of resistances. The first is the intrinsic resistance, R^{CNT} , and the second is the intertube resistances. The intrinsic resistance of multi walled CNT lie in the range of 0.2 to 0.4 kΩ/μm and it increases exponentially with respect to applied strain. The intertube resistance is quite higher as compared to intrinsic resistance. It is further divided into two types: the contact resistance, R^C (resistance between tubes that are physically in contact) and the tunneling resistance R_{tunnel} (resistance between tubes that are separated by small gap) as shown in Figure-1 [5][6].

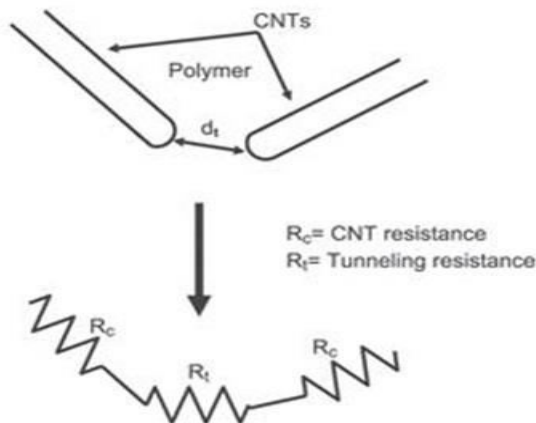


Figure-1. Tunneling effect in CNT [7].

The contact resistance depends on the contact region and it lies in the range between few hundred to thousand kΩs. Based on Simmon's theory [7], tunneling resistance between CNTs can be estimated by

$$R_{\text{tunnel}} = \frac{V}{AJ} = \frac{h^2 d}{A e^2 \sqrt{2m\lambda}} \exp\left(\frac{4\pi d}{h} \sqrt{2m\lambda}\right) \quad (2)$$

Where J is tunneling current density, V the electrical potential difference, e the quantum of electricity, m the mass of electron, h Planck's constant, d the distance between CNTs, λ the height of barrier (for polymer, 0.5 eV~2.5 eV), and A the cross sectional area of tunnel. The conduction of electrons within the CNT network occurs due to tunneling effect when the gap between CNTs is within 1.0 nm. As the distance d between CNTs increases due to applied strain tunneling resistance R_{tunnel} increases nonlinearly in exponential manner as shown in Figure-2.

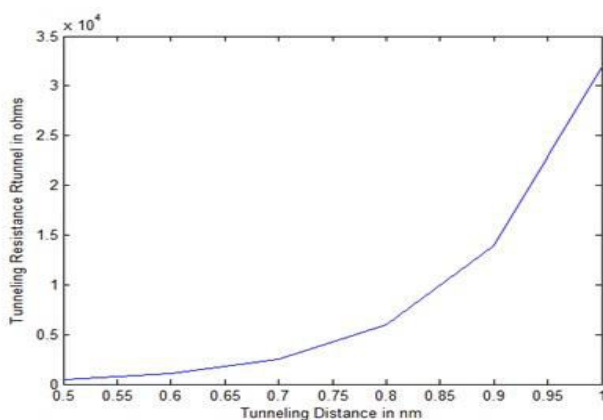


Figure-2. Tunneling resistance of CNT in ohms with respect to intertube distance in nm, considering diameter = 50nm and $\lambda = 0.5$ eV.

The total resistance of CNT film changes with the applied strain and it is the result of change in intrinsic and intertube resistance. The change in intrinsic resistance under strain is due to the variation of band gap of individual, which depends on the chirality of the tube and it varies exponentially with strain. Under strain, intertube

resistance also changes due to the change in inter-tube distances between neighbouring CNTs. When the concentration of CNTs in composite is close to percolation threshold then the change of intertube resistances is more dominant than intrinsic resistance. At percolation threshold, the total resistance of CNT networks changes nonlinearly and this effect of non-linearity is due to tunneling effect. The working mechanism in piezoresistive CNT strain sensors is mainly attributed to: a) variation of chiral angle of tube, changes intrinsic resistance nonlinearly; b) variation in contact region among CNTs, affecting contact resistance R^C and c) increase in distance between neighboring CNTs, increases R_{tunnel} nonlinearly [8][9].

3. PERCOLATION THRESHOLD IN CNT NETWORKS

In recent years, numerous studies has been done to fabricate various nanocomposites with the use of CNTs as conducting fillers in insulating polymer materials to harness the exceptional electrical properties of CNTs. With gradually increasing the conducting filler content, composites undergo a percolation transition where the electrical conductivity of the composite increases remarkably following a percolation power law. The volume fraction of filler particles at which its nature changes from an insulator to a conductor is called as the percolation threshold. Above percolation threshold, further addition of CNT filler particles into the polymer matrix result into a gradual increase in the electrical conductivity of CNT until it achieves a constant level as shown in Figure-3. In general, a given scaling law can describe the electrical conductivity of heterogeneous systems above the percolation threshold [10].

$$\sigma = \sigma_0 (\theta - \theta_c)^t \quad (3)$$

Where θ is weight fraction of the conducting filler, θ_c corresponds to the percolation threshold and t refers to the critical exponent i.e. t lies in the range between 2 to 4.

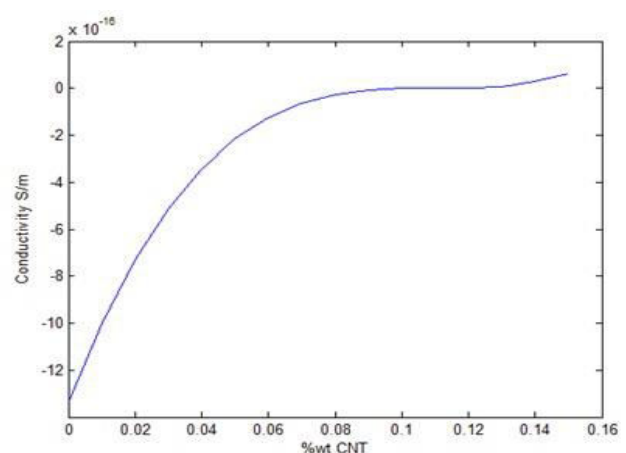


Figure-3. Percolation threshold in CNT networks for $\theta = 0$ to 0.15%wt, $\theta_c = 0.1$ and $t = 3$ [24].



Numerous studies have shown that the percolation threshold and conductivity depend strongly on the polymer type, fabrication parameters, aspect ratio of CNTs, disentanglement of CNT agglomerates, uniform spatial distribution of individual CNTs and degree of alignment. Therefore, percolation thresholds ranging from less than 0.5 wt % to over 10.0 wt % of CNTs loading have been observed experimentally. Experimental studies shows that the higher the aspect ratio of filler particles in composite lower is the percolation threshold of composite for e.g. percolation threshold of CNT reinforced polymer nanocomposites is much lower than the conventional fillers, such as metallic particles, carbon fibers and carbon black, due to their extremely high aspect ratios. Higher aggregates of CNTs as well as perfect dispersion state of CNTs in composites result into higher percolation threshold. So for obtaining the low percolation threshold of composite, a proper dispersion process is required. Alignment of CNTs in composite also plays a crucial role in obtaining the percolation threshold of composite. Aligned CNTs in composite have lower percolation threshold than randomly distributed CNTs. At low CNT concentrations (0.1 wt%–0.5 wt%), the conductivity of the aligned composite can be up to five orders of magnitude higher than that of randomly distributed CNTs [11].

4. EFFECT OF TEMPERATURE ON PIEZORESISTIVITY OF CNT/POLYMER COMPOSITE STRAIN SENSORS

In CNT/polymer composite film, the total resistance R_{total} is combination of individual carbon nano tube resistance R_{cnt} and the nanotube-nanotube tunneling resistance R_{tunnel} , i.e.

$$R_{total} = R_{cnt} + R_{tunnel} \quad (4)$$

Among these two, tunneling resistance plays dominant role in determining the overall resistance of MWCNT/Polymer composite film. When the temperature increases or decreases, the difference in thermal expansion coefficient between nanotubes and polymer significantly changes the tunneling distance as the polymer phase expand or contract respectively. Due to the change in tunneling distance with the change in temperature, tunneling resistance of composite sample also changes. The total electrical resistance of MWCNT/Polymer composite film as a function of temperature is expressed as

$$R_{total}(T) = R_{cnt}T^{-\alpha} + R_{tunnel}T \quad (5)$$

Where α is a constant with a value between 0.36-0.95 for MWCNT and T is the operating temperature apart from ambient temperature [12][13]. The relation between total resistances in CNT with respect to temperature T , considering $R_{cnt} = 1K\Omega$, $R_{tunnel} \ll R_{cnt}$, $\alpha = 0.38$ and T is in the range between 250 to 300 Kelvin as shown in Figure-4.

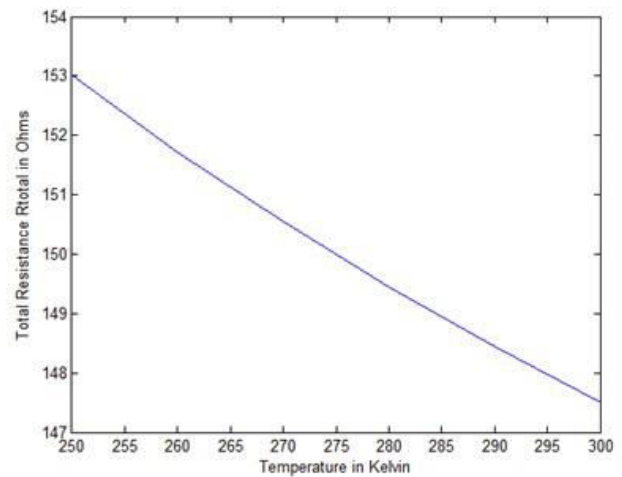


Figure-4. Resistance of CNT with respect to temperature.

In CNT/polymer composite film, there is significant infiltration of polymer into CNT networks, which makes the resistivity-temperature characteristics of the film nonlinear and nonreversible in nature [14].

5. CONCLUSIONS

In summary, numerous numerical simulations have been conducted to understand the effect of various parameters on piezoresistivity of CNT networks as strain sensors. Under small strain, the change in contact resistance of pure CNT strain sensor dominates instead of change in tunneling resistance and the piezoresistivity curve is found to be approximately linear. The nonlinear piezoresistivity is numerically found in CNT/polymer nanocomposites for the case of low CNT loading, which can be explained by tunneling effect. The effect of tunneling in nanocomposites is more predominant when the CNT loading is below percolation threshold than above percolation threshold. Piezoresistivity of CNT/polymer strain sensors also vary with the change in temperature. Further work is required to control the effect of temperature on piezoresistivity of CNT/polymer strain sensors.

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