Effects of single-walled carbon nanotube defects and alignment angles on percolation conductivity in carbon nanotubes thin film

M. Berahman1,2,†, M. Taheri1,2,‡, M. H. Sheikhi1,2,* A. Zarifkar1,∗
1School of Electrical and Computer Eng., Shiraz University, Shiraz, Iran
2Nanotechnology Research Institute, Shiraz University, Shiraz, Iran
†berahman@shirazu.ac.ir, ‡mtaheri@shirazu.ac.ir, *msheikhi@shirazu.ac.ir, ′zarifkar@shirazu.ac.ir

Abstract: thin film carbon nanotubes have shown interesting potential for practical application such as sensors and transparent conductive films. However, lack of theoretical background on thin films and their dependency on CNTs properties prevent the progression of the technology in electronic. In this paper, based on the Monte-Carlo approach, we study the effects of nanotubes orientations and double vacancy on the percolation conductivity. We show that defects can decrease the film conductance. However, CNTs which are highly orientated will increase the conduction, significantly. CNTs alignment in specific direction may cause the film to reach the percolation threshold at higher values. Furthermore, we represent that, these values vary for different angles and orientations. These results can be implemented in practice, in order to provide the optimal conductance for single-walled carbon nanotube films.

Keywords: Monte-Carlo simulation, defect, alignment, percolation, thin film carbon nanotubes

1. Introduction

Single-wall carbon nanotube (SWNT) structures started a new era, due to their exceptional electrical properties, high mobilities and ballistic transport [1, 2].

According to their applications in thin film transistors [3], optoelectronic devices [4] and sensors, SWNTs are dispersed in macroscopic carbon nanotube networks. In these configurations they can act as a random resistor network trying to find a current pathway across a film.

Network conductivity can be expressed by percolation theory, and calculated in various algorithms. R. Fogelholm, in the 1980’s, developed an efficient algorithm for large networks which was applied to system near the percolation threshold [5]. Other studies were using iterative solvers [6] and matrix transformations [7] to determine whole current distribution. In 2011, a faster algorithm, which was known as Node Elimination method, was performed through MATLAB Monte Carlo simulation [8]. The Transfer-Matrix and Node-Elimination methods have the same principle, but Transfer-Matrix accords to one specific order of elimination of the nodes, while the other one can be accomplished in any order [9].

In this model CNTs film assumed to be completely random network and its investigation needs many samples, therefore high speed simulation is required. As a result of that, Node Elimination algorithm is an appropriate method for calculating conductivity. Each carbon nanotube considered as a 1-dimensional conductive stick with specific resistance.

According to the fact that, CNTs are not perfect and they may have defects, we have investigated the effects of carbon nanotubes defects on percolation conductivity. By performing alternating electrical field, CNTs may align in specific angles. We have studied the effects of nanotube alignment angles on pathway conductance. It has been presented that these parameters, affect the network conductivity, considerably, which can be adjusted in order to offer optimal electrical performance in future applications in sensors and flexible microelectronics.
2. Method

Thin CNTs film as channel between source and drain has been simulated through Monte-Carlo approach. In this process, the film is assumed to be 2-Dimensional square. Carbon nanotubes are generated randomly, according to their one end position and orientation.

Experimental results have shown that, in presence of alternating electrical field, SWNTs are aligned in some specific directions. As a result, some selected angles, ranging from $\Theta = 0^\circ$ to $\Theta = 90^\circ$ have been chosen, with respect to horizontal axis, as our samples. Generated CNTs are then aligned in these directions, during each time processing the simulation. Percolation pathways between two electrodes (source/drain) are formed by CNTs which meet each other at the intersection points. X-coordinate of the intersection point for tube i and j is obtained from:

$$x = (b_j - b_i) / (m_i - m_j)$$ (1)

$m_i$ is each tube slope and $b_i$ is it's intercept. Tube i is compared against all other SWNTs by equation (1). In order to find the appropriate connected tube, $x$ must fit the both tubes limitations. Due to intersection matrix Tubes with just one contact with the network are omitted and the remaining creates percolation pathways. The pathway can be seen for $\Theta = 60^\circ$ in Fig. 1.

In order to consider CNTs defects in this random structure, SWNTs with single and double vacancies are simulated in Trans Siesta, and their resistances are calculated individually. By using these in Landauer conductance formula, which is added by tube-tube Junction resistance, the whole resistance for nanotube segment with defect is expressed by

$$R = R_b (1 + L / l_c) + 2 R_j$$ (2)

$L_c$ is the tube length, $R_b$ is the quantum contact resistance, for the pure CNT is approximately 6.5 kΩ, for CNT with single vacancy is 9.54 kΩ and for double vacancy is 8.34 kΩ, which are achieved from Trans Siesta. $l_c$ is critical length, assumed to be 0.2 um.

The effective conductance between two electrodes is calculated from Node-Elimination algorithm, which is based on Kirchhoff's current law. In this procedure, nodes are specifying in two categories, internal and external nodes. Internal nodes voltages, nodes between source and drain, are defined by their neighbours. Without changing network properties, they can be removed and compensation resistances are added to the neighbours. By continuing the process, the remaining nodes, would be source and drain with an effective conductance between them.

In our simulation, CNTs with single vacancy are distributed with 0.5 % probability, while CNTs with double vacancy defects are ranging from 0% to 80%. The reason can be explained by the fact that, single vacancy is not stable and tends to convert to double vacancy, therefore its probability is so less than double vacancy.

We repeat the simulation for nanotubes alignment, according to different number of processed CNTs. Start from 1100, increasing by 100 each time, and finally reach the 1800, which seems to be suitable, due to the numbers of created pathways, among 232 samples. The film is $25\mu m \times 25\mu m$ square as a test system, which is a close approximation to the experimental results, as the interval between each two electrodes is near to $25\mu m$.

Experimental figures from Atomic force microscopy (AFM) in thin films, which are based on randomly orientated CNTs, show that it would be possible to consider CNTs lengths much longer than their diameters. Each simulation process takes almost an hour long; however, it might be doubled as the CNTs density increase.

Fig. 2: plot of films conductance vs. nanotube alignment angles, which range from 0 degree to near the 90 degree. The red line depicts a 4th degree polynomial fit curve.

Fig. 3: plot of films conductance vs. double vacancy defects, ranging from 0% to almost 80%, for three different paths, namely path1=1115$\mu m$, path2=1117$\mu m$, path3=1138$\mu m$. red line represents a linear model for path3.

Their results and effects on percolation conductance are discussed as below.
3. Result and Discussion

Figure 2 illustrates how the film conductance is changing due to the nanotubes orientations, ranging from 0 degree to 90 degree.

At low angles, from 0 to 20 degree, conductance rises gradually; however, it increases sharply after the angles near to $\Theta=30$ degree. Between almost $\Theta=30^\circ$ and $\Theta=60^\circ$, the conductance trend is almost linear. When CNTs are orientated at low angles, which are almost parallel to the electrodes, they seldom intersect each other, therefore the conductance decreases. As the angles rise, intersections may highly occur. It might be expected that film with CNTs completely aligned in electrode direction, has the Maximum conductance, but Fig. 2, shows that it reaches the peak near to the $\Theta=80^\circ$.

Figure 3 shows the plot of conductance versus double vacancy defect for three different paths, namely path1=1115$\mu$m, path2=1117$\mu$m, path3=1138$\mu$m. In This simulation, paths represent 270 samples. In all three paths the conductance is declining slightly, while the double vacancy probability is rising from 0% to 80%. Moreover, the conductance decrease seems to be linear for all paths. By 80 percent changes in double vacancy, conductance may fall to almost 10% of its initial value. These effects on network conduction agree the practical results [10].

Figure 4 shows the normalized conductance versus generated random CNTs, from 1100 to 1800, for five different nanotubes alignment angles. In low CNTs density, normalized conductance is near to zero, which means that hardly ever the pathways (known as percolation threshold) have been created. By increasing nanotubes density, the conductance rises, for almost all angles. However, there is a sharp rise for $\Theta=60^\circ$ in comparison to the lower angles. It is obtained from the Fig. 4 that for the same CNTs density, films with greater nanotubes angles, cause to the higher normalized conductance. This can be explained by the fact that, CNTs which are orientated in high angles form the conduction paths with more junctions. As a result, more nanotubes segments appear in the pathways, lead to the high conductance value. The red line in Fig. 4 represents the cubic polynomial fit curve for $\Theta=60^\circ$ orientation. These results are based on 232 samples for each specific orientation.

Figure 5 shows the effects of both nanotubes alignment and defects on film conductance behaviour. CNTs orientation are changing from $\Theta=0^\circ$ to $\Theta=80^\circ$, while their defects rising from 10% to 30%. It is evident from Fig. 5, that effects of CNTs alignment are much greater than that of defects. In this process, 216 samples have been examined. According to the fact that by generating films, based on random CNTs with special orientations during each time sampling, the path between two electrodes is going to change. As a result in presence of nanotubes alignment, defects are going to show themselves, in higher number of sampling.

Our results demonstrate that, in order to compensate the adverse effects of defects on CNTs film's conductance, it would be possible to use proper orientation. However, aligning CNTs in specific direction would shift percolation threshold to higher values which is equal to more CNTs density in experimental samples [11].

4. Conclusion

Monte Carlo simulation has performed on CNTs thin film, which is based on random generated carbon nanotubes. Film conductance is calculated through Node-
Elimination algorithm, which is considerably faster than other methods. Effects of nanotubes alignment on path conductance have been studied. It is obtained that maximum conductivity occurs for angles near to 80 degree, but not 90 degree. We also, have considered CNTs with defects. By increasing defects probability, conductance has decreased almost linearly.

We have demonstrated that percolation threshold is dependent to the nanotubes orientation, with respect to horizontal axis, as higher angles lead to the higher probability for making paths between the two electrodes. A good agreement is found between our simulation and experimental results, due to the defects and nanotubes alignment effects on path conductance, individually.

Finally, it can be figured out that nanotubes orientation and their defects are two vital parameters in percolative conductivity between source and drain.

References

[11] These experimental investigations will be reported elsewhere.