Igor Sikorsky Kyiv Polytechnic Institute

2017 IEEE 37th International Conference on ELECTRONICS AND NANOTECHNOLOGY (ELNANO)

CONFERENCE PROCEEDINGS

April 18-20, 2017
Kyiv, Ukraine

2017 IEEE 37th International Conference on Electronics and Nanotechnology (ELNANO)

Copyright and Reprint Permission

IEEE Catalog Number: CFP1705U-USB
ISBN: 978-1-5386-1700-7

Organizing Committee of IEEE **ELNANO-2017**
Work phone: +38 (044) 204-99-09
E-mail: elnano@ieee.org.ua

Faculty of Electronics,
Igor Sikorsky Kyiv Polytechnic Institute
Polytekhnichna Str. 16/9, Block #12, off. 423,
03056, Kyiv, Ukraine

2017 IEEE 37th International Conference on Electronics and Nanotechnology (ELNANO)

Simulation of the Tunelling Conductivity in Nanotube/Dielectric Composite

Andriy Stelmashchuk, Ivan Karbovnyk
Electronics and Computer Technologies Dpt.
Ivan Franko National University of Lviv
Lviv, Ukraine
steelandriy@gmail.com
ivan_karbovnyck@yahoo.com

Halyna Klym
Specialized Computer System Dpt.
Lviv Polytechnic National University
Lviv, Ukraine
klymha@yahoo.com;
halyna.i.klym@lpnu.ua

Dmytro Lukashevych, Dmytro Chalyy
Lviv State University of Life Safety
Lviv, Ukraine
cnsmn@mail.ru; tactic.lviv@gmail.com

***Abstract* — An approach to calculating integral conductivity of a model nanotube/dielectric composite system is discussed. Conductivity of random nanotube network formed in the dielectric medium is simulated considering tunneling conductivity between individual nanotubes being in close proximity and taking into account intrinsic conductivity of nanotubes.**

Keywords — nanocomposite; nanotube; tunelling conductivity; computer simulation;

I. Introduction

Nanocomposites that are obtained by introducing different nanofillers into insulating matrices have been proven to exhibit outstanding mechanical and electrical properties and therefore attracts much attention of the researchers [1-11]. Nanotubes randomly dispersed in dielectric medium (typically polymer) can form conductive network that defines electrical properties of such a composite system. Usually, very low concentration of nanofiller is needed to make such system conductive as the aspect ratio for nanotubes is very high. When percolation threshold is reached, conductive paths that appear inside the insulating host matrix allow electrons transfer along the nanotubes that form the network. Individual nanotubes are known to have remarkable current-carry capacity with orders of magnitude higher that conventional metals. After summing up the aforementioned information one can conclude that many opportunities to exploit features of nanotube based composites in electronic applications arise [5].

Apart from the intrinsic conductivity of the filling elements (nanotubes) there are two principal mechanisms to be considered [12]. The first item of interest is a direct contact between two adjacent nanotubes. The second one is related to the tunneling effect. This quantum phenomenon comes into play when distance between adjacent nanotubes is smaller than the tunneling gap for carries (electrons).

Considering the number of elements in the conductive network and complex nature of involved effects, reliable model description of nanocomposite with tunneling conductivity is a challenging task. Here we present an attempt to explore how tunneling effect influence the integral conductivity of nanocomposite system that is defined as a dielectric matrix filled randomly with carbon nanotubes (CNTs).

II. Nanocomposite cunductivity simulation method

A. Model of nanotube dielectric composite

Nanotube/dielectric composite can be described as 3D volume box also known as representative volume element (RVE) [12] filled with randomly dispersed conductive carbon nanotubes. Electrodes attached to the two opposite sides of RVE act as the entry points of the external electric circuit. In the simplest model CNTs can penetrate each other. In our case we are using “hard core” model in which CNTs can’t overlap by its volumes. In the “hard core” model an electric contact between nanotubes is provided by tunneling effect which usually exists among nanoscale objects. In papers [13, 14] it is mentioned that tunneling conductivity has more significant impact on the resulting conductivity of the RVE than the resistance of the nanotubes themselves. So, it is crucial that the effect of tunneling conductivity is not neglected when computer simulations of nanotube composite are performed.

B. Simulation model

In our model, CNT is represented as a cylinder with spherical faces. The axis of this cylinder starts at point *A* with coordinates (x_1, y_1, z_1) and ends at point *B* (x_2, y_2, z_2). The process of generating and placing nanotube in RVE consists of several phases. First of all, the coordinates of starting point are calculated as [15]:

$$x_1 = rand \times L_x \tag{1}$$

$$y_1 = rand \times L_y \tag{2}$$

$$z_1 = rand \times L_z \tag{3}$$

where $rand$ is a random floating point value from [0,1] range. Then the random direction in space is described by two angles α and β:

$$\alpha = 2\pi \times rand_1 \tag{4}$$

$$\beta = 2\pi \times rand_2 \tag{5}$$

Using this direction, the position of the end point *B* is defined as:

978-1-5386-1701-4/17/$31.00 ©2017 IEEE

$$x_2 = x_1 + length \times cos(\alpha) cos(\beta) \quad (6)$$

$$y_2 = y_1 + length \times \sin(\alpha) cos(\beta) \quad (7)$$

$$z_2 = z_1 + length \times \sin(\beta) \quad (8)$$

If the obtained by aforementioned procedure point *B* is located outside of the boundaries of RVE then the exceeding part of the newly generated CNT is cut off, so we are sure that our CNT lies within RVE.

In the "hard core" model we have to guarantee that there are no collisions between nanotubes after adding new CNTs to the system. In order to achieve this, we check the distances between the newly generated nanotube and all the other nanotubes already placed inside RVE. If the shortest distance between the axes of the pair of the tubes being checked is less than CNT diameter *d* it means that tubes are penetrating each other. In this case the newly generated tube is rejected and not placed into the RVE. The process continues up to the point the desired volume fraction of CNTs inside RVE is reached. This evaluation process requires additional computational costs since a significant amount of the nanotubes is thrown away, especially at high volume fraction ratios.

Electrical connection between CNTs is assumed to exist if the shortest distance *D* between them is smaller than the tunneling cut-off distance.

In order to find conducting (or percolative) cluster between electrodes we have implemented the weighted union find algorithm with the pass compression. This cluster consists of all the nanotubes which have conductive path to both electrodes. It is important to take into account that there can be several parallel conductive clusters.

C. *Resistor network formation*

We use random resistor network approach described in [16] to simulate the equivalent conductivity of the CNTs system. In order to convert the set of connected nanotubes into a such type of representative resistor network, locations of all connections between CNTs must be found. To illustrate the technique we utilize, the example of possible connection pattern is shown on Fig 1. Each contact place between two CNTs is represented as a pair of "junction" points: one on the axis of the first CNT and the other one on the axis of the second CNT. At the same time a pair of "junction" points located at the same nanotube defines the part of this nanotube as the segment with length l_s (see Fig 1), which the electric current will be run through.

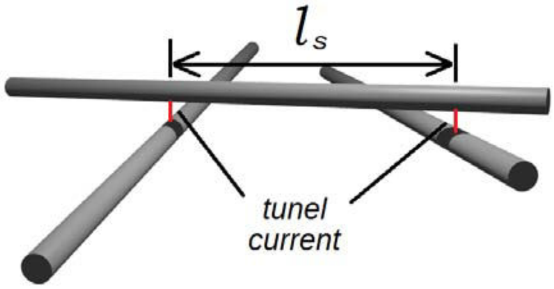

Fig. 1. Possible connection pattern between CNTs.

Let's describe the process which allows us to find both the shortest distance between CNTs and the actual coordinates of these "junction" points. The coordinates of the point on the CNT axis can be described by the following expression:

$$p + \alpha \cdot \vec{d}, \quad (9)$$

where p is the point of the start of the CNT, $\vec{d}$ is the directional vector of the CNT and α is a variable coefficient ($\alpha \in [0,1]$), whose concrete values define the points located on the CNT axis.

Let $p_1 + \alpha \cdot \vec{d}_1$ and $p_2 + \beta \cdot \vec{d}_2$ be the arbitrary points on the first and second CNTs respectively, and the distance between these segments is to be found. Then $(p_1 + \alpha \cdot \vec{d}_1) - (p_2 + \beta \cdot \vec{d}_2)$ is the vector, which connects these two points. The minimal distance between CNTs can be obtained as the norm of this aforementioned vector:

$$D = \| (p_1 + \alpha \cdot \vec{d}_1) - (p_2 + \beta \cdot \vec{d}_2) \|^2 . \quad (10)$$

Taking into account the property of scalar product $(\vec{a}, \vec{a}) = \| \vec{a} \|^2$ we can conclude that for finding the values of the coefficients α and β we have to find the values, which provide the minimal scalar product of the vector with itself. So, after some transformations we obtain the following expressions for finding coefficients α and β.

Auxiliary notations:

$$\begin{aligned} &A_1 = (\vec{d}_1, \vec{d}_1),\ A_2 = (\vec{d}_1, \vec{d}_2), \\ &B_1 = (\vec{d}_2, \vec{d}_1),\ B_2 = (\vec{d}_2, \vec{d}_2), \\ &C_1 = (\overrightarrow{p_2 - p_1}, \vec{d}_1), \\ &C_1 = (\overrightarrow{p_2 - p_1}, \vec{d}_2), \\ &D = (A_1 \cdot B_2 - B_1 \cdot A_2). \end{aligned} \quad (10)$$

The values of the unknown coefficients:

$$\begin{aligned} \alpha &= \frac{(C_1 \cdot B_2 - B_1 \cdot C_2)}{D}, \\ \beta &= \frac{(C_2 \cdot A_1 - C_1 \cdot A_2)}{D}. \end{aligned} \quad (11)$$

If the found values of the coefficients α and β do not belong to the interval [0,1] then their values should be adjusted to nearest admissible values.

D. *CNT and contact conductivities*

In our model, we are considering two types of conductivity: tunneling conductivity between CNTs and CNT intrinsic conductivity. Two CNTs are treated as the connected ones, when the shortest distance between them is shorter than some preset value of the cut-off distance d_{cutoff} .

Let us define a part of CNT by a pair of points located on its axis. Suppose, the length of this segment is l_s (see Fig 1).

Then the intrinsic resistance of this part of CNT can be calculated according to the formula[14, 15]:

$$R_{intrinsic} = \frac{4l_s}{\pi \sigma_{CNT} d^2}, \quad (12)$$

where σ_{CNT} is the intrinsic electrical conductivity of the CNT and d is the diameter of the CNT.

The contact resistance between a pair of nanotubes is caused by a tunneling effect at the "junction" points. Suppose, the shortest distance between a pair of nanotubes is d_{kp}, where d_{kp} is shorter than d_{cutoff}. Then the contact resistance can be estimated using Landauer-Büttiker formalism as [17-21]:

$$R_{contact} = \frac{h}{2e^2} \frac{1}{NP}, \quad (13)$$

$$P = \begin{cases} \exp(-\frac{d_{vdw}}{d_{tunnel}}) & for\ 0 \le d_{kp} \le d + d_{vdw} \\ \exp(-\frac{d_{kp} - d}{d_{tunnel}}) & for\ d + d_{vdw} \le d_{kp} \le d + d_{cutoff} \end{cases}, \quad (14)$$

$$d_{tunnel} = \frac{h}{2\pi} \frac{1}{\sqrt{2m_e \Delta E}}, \quad (15)$$

where h is Planck`s constant; P is the transmission probability for the electron to tunneling between CNTs; N is the number of conduction channels, which is dimensionless and related to diameter of a CNT [22]; e is the charge of an electron; d_{vdw} is the van der Waals separation distance [23, 24], which limits the minimum distance between a pair of CNTs; d_{tunnel} is the tunneling characteristic length; m_e is the mass of an electron; ΔE is the height of energy barrier [25].

In our simulations, a random resistor network is represented as the matrix of conductivities between all "junction" points. After applying Kirchhoff`s current law the system of linear equations is created. Since a "junction" point has only few connections to the other points the resulting matrix is sparse. That's why we use a specific sparse solver to achieve good simulation performance. SuperLU [26-28] library is used to solve this system of linear algebraic equations and obtain the values of electric potential at all the "junction" points. After that the equivalent conductivity of random resistance network is calculated.

III. Results and Discussions

We have developed software for simulation of nanotube-dielectric composite conductivity using described in previous chapter "hard core" model. The main role of simulations was to explore how tunneling effect influencing the total conductivity of nanocomposite described by CNTs hard core model. For the purpose of comparison, "soft core" model was also implemented.

The very first challenge we encounter is, obviously, to compare our computer simulation results with experimental measurements, which are available, for example, in [15]. To accomplish this goal, we set up the parameters of the system under simulation as follows in Table 1.

TABLE I. Parameters of Simulated Composite

Parameter name	Value
RVE size	1000 *nm* 1000 *nm* 100 *nm*
CNT length	200 *nm*
CNT diameter	2 *nm*
CNT aspect ratio	100
CNT intrinsic conductivity	10^4 *S/m*
Tunnel cut off distance	1.9 *nm*

The results of the simulations for various CNTs volume fractions are shown on Fig 2.

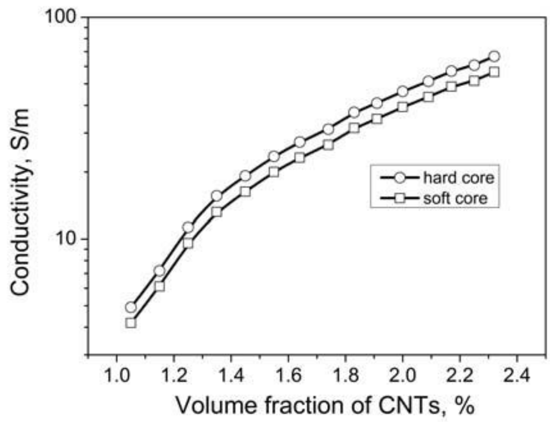

Fig. 2. Composite conductivity both for soft core and hard core models.

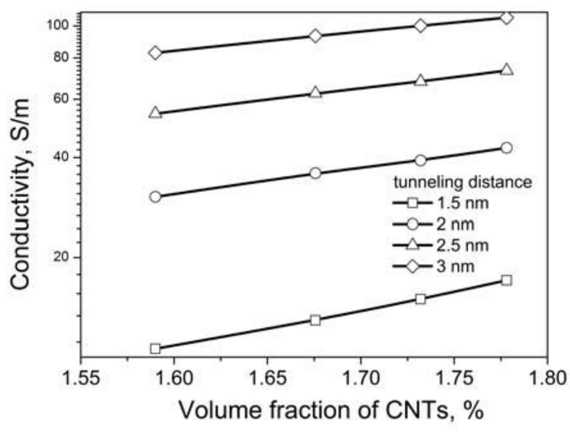

Fig. 3. Dependency of composite conductivity on tunneling cut-of distance.

The data shown on "hard core" part of Fig. 2 coincides with experimental results [15] both qualitatively and quantitatively. Also, one can notice the difference in actual values of the simulation results between “soft core” and “hard core” models, but the behavior of both models develops in the same way as volume fraction changes.

Looking at the Fig. 3 we can conclude that tunneling cut-off distance does not affect significantly the character of the system`s behavior depending on volume fraction changes. On the other hand, the tunneling cut-off distance does influence on the actual values of the electric conductivity of the system.

IV. Conclusion

3D model of a dielectric volume filled randomly with conductive nanotubes (nanotube/dielectric composite) is presented. Computer simulations performed in the frame of this model allowed us to calculate the total conductivity of such composite. The influence of tunneling distance parameter of the system conductivity was investigated. The results of the simulations coincide with experimental data obtained by other researchers and also indicate the difference for the cases of overlapping nanotubes (“soft core” model) and non-overlapping nanotubes (“hard core” model). The comparison with measured results shows that "hard core" model can be effectivelly used for predicting the parameters of fabricated composite being an important step towards the creation of the material with desired properties.

Acknowledgment

Halyna Klym and Dmytro Chalyy thank to Ministry of Education and Science of Ukraine for support (Project for young researchers No. 0116U004411).

References

[1] I. Karbovnyk, I. Bolesta, I. Rovetskii, S. Velgosh, and H. Klym, “Studies of CdI2-Bi3 microstructures with optical methods, atomic force microscopy and positron annihilation spectroscopy”, Materials Science-Poland, 2014, vol. 32, no. 3, pp. 391-395.

[2] H. Klym, I. Hadzaman, A. Ingram, O. Shpotyuk, “Multilayer thick-film structures based on spinel ceramics”, Canadian Journal of Physics, 2014, vol. 92, no. 7/8, pp. 822-826.

[3] H. Klym, I. Hadzaman, O. Shpotyuk, M. Brunner, “Integrated thick-film nanostructures based on spinel ceramics”, Nanoscale research letters, 2014, vol. 9:149-1-6.

[4] M. Vakiv, I. Hadzaman, H. Klym, O. Shpotyuk, M. Brunner, “Multifunctional thick-film structures based on spinel ceramics for environment sensors,” Journal of Physics: Conf. Ser., 2011, vol. 289: 012011.

[5] I. Karbovnyk, I. Olenych, O. Aksimentyeva, H. Klym, O. Dzendzelyuk, Y. Olenych, O. Hrushetska “Effect of Radiation on the Electrical Properties of PEDOT-Based Nanocomposites”, Nanoscale Research Letters, 2016, vol.11:84.1-84.5.

[6] A. Stelmashchuk, I. Karbovnyk, H. Klym, “Computer simulations of nanotube networks in dielectric matrix”, Proc. of the XIIIth Int. Conf. “Modern problems of radio engineering, telecommunications, and computer science TCSET’2016” Lviv-Slavsko, Ukraine, 2016, p. 415-417.

[7] I. Karbovnyk, J. Collins, I. Bolesta, A. Stelmashchuk, A. Kolkevych, S. Velupillai, H. Klym, O. Fedyshyn, S. Tymoshuk, I. Kolych, “Random nanostructured metallic films for environmental monitoring and optical sensing: experimental and computational studies”, Nanoscale Research Letters, 2015, vol. 10: 151.1-151.5.

[8] Stelmashchuk A. Percolation in a Random Network of Conducting Nanotubes: a Computer Simulation Study / A. Stelmashchuk, I. Karbovnyk, I. Bolesta // Proceedings of the 11-th International Conference" Modern Problems of Radio Engineering, Telecommunications and Computer Science" (TCSET 2012). – Lviv-Slavske, Ukraine, 21-24 February 2012. – P. 240.

[9] I.B. Olenych, O.I. Aksimentyeva, I.D. Karbovnyk, Yu.I. Olenych, L.I. Yarytska, “Preparation and properties of hybrid poly(3,4-ethylenedioxythiophene)–carbon nanotubes composites”, Proc. of the Int. Conf. “Nanomaterials: Applications and Properties”, 2014, vol. 3, no. 2: 02NNSA13-1 13-3.

[10] G.D. Seidel, D.C. Lagoudas, “A micromechanics model for the electrical conductivity of nanotube-polymer nanocomposites”, Journal of Composite Materials, 2009, vol. 43, no. 9, pp. 917-941.

[11] M.S. Fuhrer et al., “Crossed Nanotube Junctions”, Science, 2000, vol. 288, no. 494, pp. 494-497.

[12] W.S. Bao, S.A. Meguid, Z.H. Zhu, M.J. Meguid, “Modeling electrical conductivities of nanocomposites with aligned carbon nanotubes”, Nanotechnology, 2011, vol.22, no. 48: 485704.

[13] Y. Yu, G. Song, L. Sun, “Determinant role of tunneling resistance in electrical conductivity of polymer composites reinforced by well dispersed carbon nanotubes”, J. Appl. Phys., 2010, vol. 108: 084319.

[14] W.S. Bao, S.A. Meguid, Z.H. Zhu, G.J. Weng, “Tunneling resistance and its effect on the electrical conductivity of carbon nanotube nanocomposites”, J. Appl. Phys., 2012, vol. 111: 093726.

[15] N. Hu, Z. Masuda, C. Yan, G. Yamamoto, “The electrical properties of polymer nanocomposites with carbon nanotube fillers”, Nanotechnology, 2008, vol.19, no. 21: 215701.

[16] W. Fang, H.J. Jang, S.N. Leung, “Evaluation and modelling of electrically conductive polymer nanocomposites with carbon nanotube networks”, Composites Part B, 2015, vol. 83, pp. 184-193.

[17] M. Büttiker, Y. Imry, R. Landauer, S. Pinhas, “Generalized many-channel conductance formula with application to small rings”, Phys Rev B, 1985, vol. 31:6207-15.

[18] R. Tamura, M. Tsukada, “Electronic transport in carbon nanotube junctions”, Solid State Commun, 1997, vol. 101, no.8: 601-5.

[19] R. Saito, G. Dresselhaus, M. S. Dresselhaus, “Physical properties of carbon nanotubes. Volume 3”, London: Imperial College Press, 1998.

[20] Y. Imry, R. Landauer, “Conductance viewed as transmission”, Rev. Mod. Phys., 1999, vol. 71, no. 2: 306-12.

[21] A. Buldum, J.P. Lu, “Contact resistance between carbon nanotubes”, Phys. Rev. B, 2001, vol. 63: 161403-6.

[22] A. Naeemi, J.D. Meindl, “Performance modeling for carbon nanotube interconnects”, In: Carbon nanotube electronics, New-York: Springer, 2009, pp. 163-190.

[23] T. Hertel, R.E. Walkup, P. Avouris, “Deformation of carbon nanotubes by surface van der Waals forces”, Phys. Rev. B, 1998, vol. 58: 13870-3.

[24] L.A. Girifalco, M. Hodak, R.S. Lee, “Carbon nanotubes, buckyballs, ropes and a universal graphitic potential”, Phys. Rev. B, 2000, vol. 62: 13104.

[25] J.G. Simmons, “Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film”, J. Appl. Phys., 1963, vol. 34, no. 6: 1793-803.

[26] X. S. Li, “An overview of SuperLU: algorithms, implementation, and user interface”, toms, 2005, vol. 31, no. 3, pp. 302-325.

[27] X.S. Li, J.W. Demmel, J.R. Gilbert , L. Grigori, M. Shao, I. Yamazaki, “SuperLU users` guide”, Lawrence Berkeley National Laboratory, 1999.

[28] J.W. Demmel, S.C. Eisenstat, J.R. Gilbert, X.S. Li, J.W.H. Liu, “A supernodal approach to sparse matrix pivoting”, SIAM J. Matrix Analysis and Applications, 1999, vol. 20, no. 3, pp. 720-755.