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Investigation of Physical Properties of CNT-Se bi-layer system Mixed by 70 MeV Ni^{7+} ions and by Pulsed Laser Irradiation

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ABSTRACT

Thin films of multi-walled carbon nanotubes (MWCNTs) were grown on glass substrate by spin coating technique from dispersed solution contains 0.05 mg of carbon nanotubes in 5 ml DMF solution. Thin films of selenium has been deposited by thermal evaporation technique above the MWCNTs layer. The investigated thin films of CNT-Se bi-layer system were irradiated by 70 MeV Ni^{7+} ions and by pulsed laser irradiation for mixing the bi-layer system. The surface morphological analysis was carried out by FESEM which clearly shows covering of selenium nanoparticles above carbon nanotubes. The surface morphology also shows selenium layer is embedded into the MWCNTs layer after irradiation. Raman analysis displays the presence of characteristic bands in the CNT-Se bi-layer system before and after irradiation. Electrical analysis shows an enhancement of electrical conductivity and reduction of an activation energy after irradiation. The electrical conductivity of the irradiated thin films of CNT-Se bi-layer system lies in between the conductivity's of thin films of isolated Selenium and MWCNT's.

Keywords: Thin films; Laser-irradiation; Swift Heavy Ion Irradiation; Electrical Properties.

I.INTRODUCTION

Compound semiconductors have potential applications in optoelectronic fields such as displays, sensors, microwave communication, solar cells, optical communication and radiation detector [1-4] etc. They provide a wide variety of energy gaps and mobility's, so that materials are available with properties that meet specific requirements, which is the major advantage of the compound semiconductors over elemental semiconductors like silicon and germanium. Selenium based compound semiconductors have been extensively studied over the past decades because they are the promising materials receiving attention in view of the fabrication of various solid state devices. This study describes the physical properties of CNT-Se bi-layer system (compound semiconductor) mixed by irradiation techniques for property modification. Because (multi-walled carbon nanotubes) MWCNTs have the features like tunable band gap, high absorption coefficient, and high intrinsic charge carrier mobility [5]. Recently, there has been an intriguing interest in studying the interaction of radiations with compound semiconductor thin films. The radiation effects in Nano-science provide immense opportunities and effective means to engineer the compound semiconductor materials properties for various potential application. Material modifications include ion beam mixing in which atoms of one layer mingled with the atoms of other layers with the help of energy deposited by the incident ions. The influence of swift heavy ions in materials can be explained on the basis of special models: Coulomb Explosion [6] and Thermal Spike model [7]. These models are used for explaining the ion-matter interaction in detail. The major concerning parameter of all these models is the electronic energy loss. Several studies are reported regarding the study of ion beam mixing of bi-layer systems [8-10]. Likewise, in laser irradiation of materials, only the absorbed part of the energy can induce a structural transformation leading to the processes like heating and melting. However, in semiconductors, the absorbed photons can generate electron-hole pairs with a definite amount of kinetic energy. The creation of plasma can take place when these "hot" carriers thermalize between each other. Once the common carrier temperature is reached, these carriers transfer their kinetic energy to the lattice through recombination and phonon generation, which leading to lattice heating and melting. In the present case, the mixing of bilayer CNT-Se system will take place under the influence of energy deposition by laser pulses.

II.EXPERIMENTAL STUDIES

The bulk sample of amorphous selenium has been prepared by thermal quenching technique from fine powder of pure Selenium (having purity 99.999%). This selenium powder was put into quartz ampoule which was sealed under a vacuum of 10^{-6} Torr. After sealing, the ampoule was placed in a Microprocessor-Controlled Programmable Muffle Furnace, where the temperature was increased at a constant heating rate of 4 ℃/min up to 900℃ and the material within the ampoules is allowed to melt at 900℃ for 15 h. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. After rocking for about 15 hours, the obtained melt of Selenium was rapidly quenched in ice-cooled water. After quenching, ingot has been removed by breaking the ampoule and grinded into a fine powder with the help of pastel and mortol. Multi-walled carbon nanotubes with the diameter in the range of 20-40 nm and several micrometers in length was used. To make dispersed solution, 0.05 mg of carbon nanotubes were dispersed in 5 ml DMF using ultrasonicator for 8 hours. Thin layer of ~ 300 nm of multi-walled CNT was deposited on cleaned glass substrate by spin coating technique (with 2000 rpm). The glass substrates were cleaned ultrasonically first by water and then by acetone. After this, thin layer of ~ 300 nm of selenium was deposited by thermal evaporation technique above the CNT layer through molybdenum boat under a vacuum of 10^{-5} Torr.

2.1 Irradiation details

The investigated thin films of CNT-Se were irradiated by 70 MeV Ni^{6+} ions in the fluence range of 1×10^{12} ions/cm^2 to 5×10^{13}ions/cm^2 [defined as: 1×10^{12} ions/cm^2= CNT-Se (SHI_1), 5×10^{12} ions/cm^2= CNT-Se (SHI_2),1×10^{13} ions/cm^2= CNT-Se (SHI_3), 5×10^{13} ions/cm^2= CNT-Se (SHI_4)] using 15UD Pelletron Accelerator facility at IUAC, New Delhi, India. The ion beam was scanned over an area of 1 cm^2 and beam current was 1 pnA (particles nanoampare).The estimated electronic loss (S_e) 7.536×10^4 eV/nm, nuclear energy loss (S_n) 20.70eV/nm15.92 um which is the feasible range for ions to traverse the entire film thickness. Also the investigated thin films were irradiated by TEA N_2pulsed laser having wavelength 337.1 nm,

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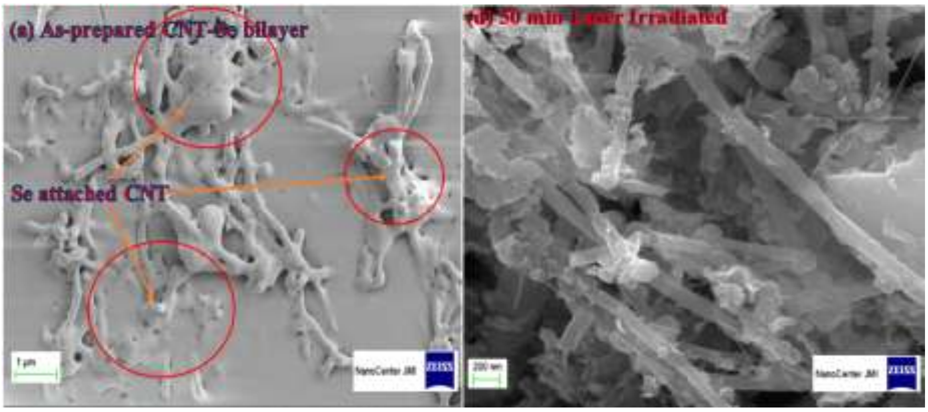
Power 100 kW and Pulse width 1 ns, for different time durations 10, 20, 30, 40 and 50 min [defined as: 10 min.= CNT-Se (L_1), 20 min.= CNT-Se (L_2), 30 min.= CNT-Se (L_3),40 min.= CNT-Se (L_4),50 min.= CNT-Se (L_5)].

2.2Characterization details

Surface morphological effects of the investigated thin films has been analyzed by using Field Emission Scanning Electron Microscope (FESEM) (Model:Σigma by Carl Zeiss employed with Gemini Column (Patented technology of Corl Zeiss).The phonon mode study was carried out with the help of Renishaw inVia Raman Microscope, which consisting of the Ar ion laser with 514.5 nm wavelength and 50 mW power. For electrical measurements, electrodes with 1 mm gap was made by using the silver paste on the investigated thin films. Dark dc conductivity and measurements were carried out in the temperature range of 310-390 Kat constant voltage of 1.5 V by mounting the thin films in a specially designed metallic sample holder.

III.EDX AND FESEM ANALYSIS

Energy Dispersive X-ray (EDX) analysis is a versatile technique used for elemental composition in sample. EDX makes use of the X-ray spectrum obtained by a solid sample when bombarded with a focused beam of electrons in order to obtain a localized chemical analysis. The elemental composition of investigated thin films of CNT-Se bilayer system has been verified by EDX analysis which confirms the presence of both CNT and Se in the prepared bi-layer thin film. Furthermore the surface effects occurred due to irradiation has been analyzed by FESEM, the obtained micrographs are shown in Fig.1. This technique probes the surface structure of samples using a focused beam of high energy electrons. The recorded SEM images of the investigated thin films shows the selenium coating above the MWCNTs covering the surface of CNTs. The irradiated thin films displayed the selenium layer is embedded into the MWCNTs layer and hence two layers are mixed.



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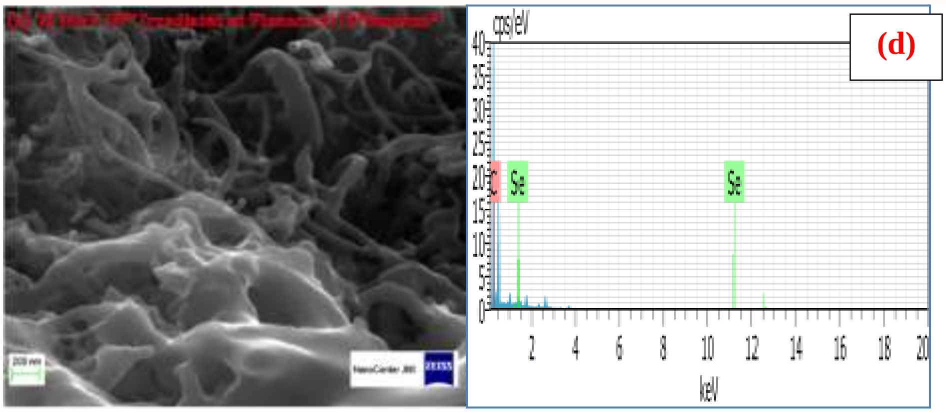


Figure 1. Scanning electron micrograph images of (a) as-prepared and (b) 50 minute laser irradiated (c) 70 MeV Ni^{7+} ions irradiated thin films of CNT-Se bi-layer system. (d) EDX spectra of as-prepared CNT-Se bi-layer system.

IV.RAMAN STUDY

Fig.2 shows the recorded Raman spectra of the as-prepared and irradiated thin films. Raman spectra of as-prepared selenium (AP_Se) film exhibit a band at 252.22 cm^{-1} which is a characteristic peak of pristine Selenium, which reciprocates the longitudinal optical (LO) phonon modes in the chain-structured Se molecule [11]. This study also shows presence of characteristic bands in the Raman spectrum of as-prepared MWCNT (AP_CNT) thin film as well as CNT-Se thin film bilayer system before and after irradiation. The D-band around ~ 1358.42 cm^{-1} , G-band at ~ 1576.69cm^{-1} and $G^{/}$ - band at ~ 2632.43cm^{-1} confirms the presence of MWCNTs, the position of these band are found to be slightly red shifted in CNT-Se bilayer system due to presence of Se. The D band which is a characteristic mode present in the Raman spectra of MWCNTs is a longitudinal optical (LO) phonon mode and is known as the disordered or defect mode because a defect is required to elastically scatter in order for the process to conserve momentum [12]. This mode is usually located between 1330 $cm^{-1}$and 1360 cm^{-1}[12]. The D band is present in all carbon allotropes, including sp^2 and sp^3 amorphous carbon. In CNTs, this band is activated from the first-order scattering process of sp^2 carbons by the presence of in-plane substitution hetero-atoms, vacancies, grain boundaries, or other defects, and by finite-size effects [12]. The presence of D-band in MWCNT basically points out the presence of disorder and defects in it. The G-band originates from the graphitic nature of samples that is the cystallinity, pristine arrays of atoms in the sample. The G band is a tangential shear mode of carbon atoms that corresponds to the stretching mode in the graphite plane [12]. The G'-band is another characteristic mode found in Raman spectrum of CNTs. The G'-band frequency is close to twice that of the D-band and is found from 2500 $cm^{-1}$to 2900 cm^{-1}. This is a second-order process from two zone boundary LO phonons. The G' band is an intrinsic property of the nanotube and graphite, and present even in defect-free nanotubes for which the D band is completely absent [12]. The existence of all these modes in the Raman spectra confirms the presence of MWCNT in pure MWCNT thin film and in the CNT-Se bilayer system. Also, one can observe from Raman analysis that the peak intensity of CNT-Se bilayer system increases after irradiation (both by laser as well as by SHI).

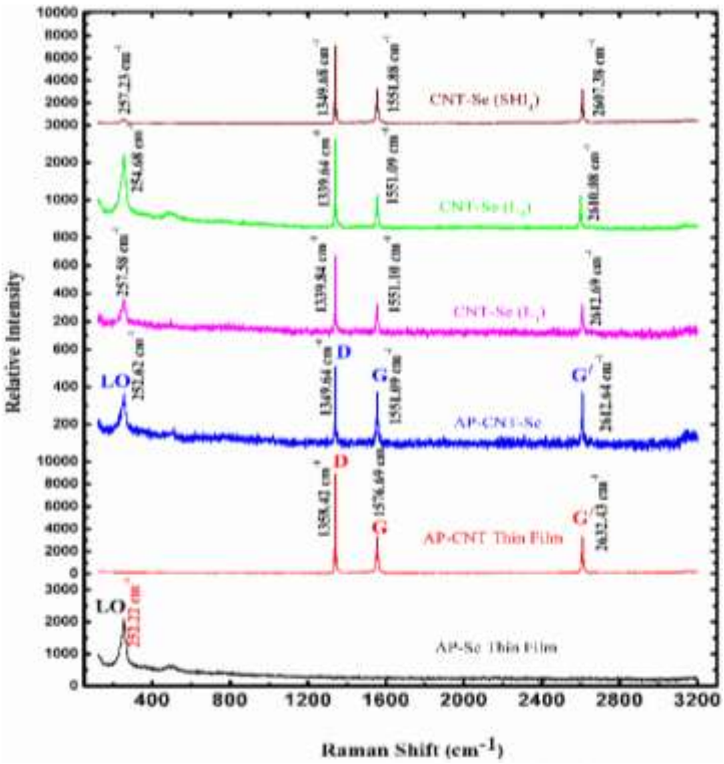


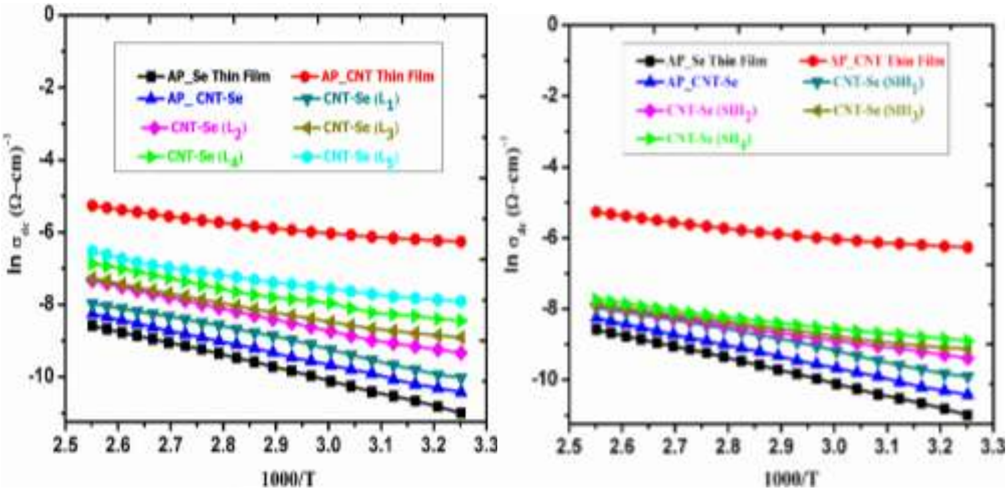
Figure 2. Raman spectra of thin films of Se, MWCNTs, as-prepared and irradiated CNT-Se bi-layer system.

V.ELECTRICAL STUDIES

In order to study the electrical transport in the as-prepared and laser/Swift heavy ion (SHI) irradiated CNT-Se bilayer system dc conductivity measurements were carried out. The dc conductivity measurements were performed in temperature range (310 K- 390 K). Fig.3 shows the plots of ln σ_{dc} versus 1000/T are found to be straight lines and indicate the semiconducting nature of all the films [13]. For semiconductors, dc conductivity can be expressed by Arrhenius relation [13] as:

$$\boldsymbol{\sigma_{dc} = \sigma_0 \exp[-\Delta E_{dc}/KT]} \qquad \textbf{(1)}$$

Where $\boldsymbol{\sigma_0}$ is pre-exponential factor related to the material, $\Delta\mathbf{E}$ is activation energy, K is the Boltzmann constant and T is the temperature. Activation energy $\Delta\mathbf{E}$ is calculated by the slopeof ln $\boldsymbol{\sigma_{dc}}$ versus 1000/T and using equation (1). Slope of the curve is estimated by using linear fit [13]. Values of activation energy $\Delta\mathbf{E}$, dc conductivity $\boldsymbol{\sigma_{dc}}$ and pre-exponential factor ($\boldsymbol{\sigma_0}$) are given in Table1.The dc conductivity (σ_{dc}) of selenium as-deposited film is calculated to be $6.00\times10^{-5}\ \Omega^{-1}cm^{-1}$, which is in good agreement with the values reported by other researchers [14, 15]. In present work, the conductivity of as-deposited MWCNT film is also calculated and is $2.77\times10^{-3}\ \Omega^{-1}cm^{-1}$, which is also in consensus to the values of conductivities of MWCNT reported by other researchers [16]. Further, the conductivity of as-prepared and laser and swift heavy ion (SHI) irradiated CNT-Se bilayer system is also calculated, and it is noticed that the conductivity of the system increases when subjected to laser and Swift heavy ion(SHI) irradiation, also the conductivity of the system is found to increase with the irradiation time. The conductivity of as-prepared CNT-Se bilayer system increases on irradiation with laser (or SHI) which is due the increase in the number of conduction electrons in the system as a result of thermal activation caused the by the high intesity of laser, moreover it is seen, on increasing the irradiation time the conductivity further increases (same in the case of SHI irradiation). Similar effect of increase in conductivity in CNT-Se network is reported [17] when the system is subjected to heat. According to Davis and Mott the pre exponential factor for conduction in localized states should be two or three orders smaller than the conduction in extended states. For conduction in extended states the pre exponential factor σ_0 is reported to be of order $10^4\ \Omega^{-1}$ cm^{-1}. The value of pre exponential factor σ_0 in the present system is of order $10^{-1}\ \Omega^{-1}\ cm^{-1}$ (nonirradiated) and of order $10^2\ \Omega^{-1}\ cm^{-1}$ (laser/SHI irradiated). From this we can conclude that the conduction in the non-irradiated CNT-Se bilayer system is mainly due to hopping of charge carriers in localized states but after irradiation of the sample it shift to extended states.



Irradiation details	$\sigma_{dc}(\Omega^{-1}cm^{-1})$	$\sigma_0(\Omega^{-1}cm^{-1})$	ΔE_{dc}(eV)
AP_Se Thin Film	6.00×10^{-5}	1.24×10^{0}	0.296
AP_CNT Thin Film	2.77×10^{-3}	1.78×10^{-1}	0.124
AP_CNT-Se	8.88×10^{-5}	7.45×10^{-1}	0.269
CNT-Se (L_1)	1.40×10^{-4}	8.44×10^{-1}	0.259
CNT-Se (L_2)	2.23×10^{-4}	1.05×10^{1}	0.252
CNT-Se (L_3)	3.83×10^{-4}	4.14×10^{-1}	0.208
CNT-Se (L_4)	4.08×10^{-4}	3.12×10^{-1}	0.198
CNT-Se (L_5)	6.16×10^{-4}	1.68×10^{-1}	0.167

CNT-Se (SHI_1)	1.46×10^{-4}	5.86×10^{-1}	0.247
CNT-Se (SHI_2)	1.71×10^{-4}	8.57×10^{-2}	0.185
CNT-Se (SHI_3)	1.95×10^{-4}	4.31×10^{-2}	0.161
CNT-Se (SHI_4)	2.89×10^{-4}	2.56×10^{-2}	0.141

(a) **(b)**

Figure 3. Variation of dark d. c. conductivity (σ_{dc}) with 1000/T of Se, MWCNTs and CNT-Se bilayer mixing by (a) laser irradiation (b) SHI irradiation.

Table.1. Electrical parameters at a temperature of 345 K of as-prepared thin films of Se, MWCNTs and CNT-Se bilayer mixing by laser irradiation and SHI irradiation.

VI.CONCLUSION

In this study, the results of the CNT-Se bilayer system deposited on glass substrate, mixed by laser and swift heavy ion irradiation techniques. Surface morphology of the investigated thin films show selenium coating above MWCNTs. Electrical analysis shows the enhancement of dc conductivity after irradiation. It was found that the value of activation energy decreases after irradiation. Therefore such a material may be feasible for solar cell fabrication, photoconductor and other optoelectronic applications because of high values of absorption coefficient and large conductivity.

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REFERENCES

[1] T. Surek, Crystal Growth, Crystal Growth and Materials Research in Photovoltaics: Progress and Challenges, 2005, 275, 292-304.

[2] Benjamin J. Eggleton, Barry Luther-Davies & Kathleen Richardson, Chalcogenide Photonics, Nature Photonics, 2011, 5, 141–148

[3] K. Onabe, Calculation of Miscibility Gap in Quaternary InGaPAs with Strictly Regular Solution Approximation, Jpn. J. Appl. Phys. 1982, 21, 797.

[4] M. Cuzin, Some New Developments in the Field of High Atomic Number Materials, Nucl. Instrum. Methods A, 1987, 253, 407-417.

[5] C. Silva, C, Organic Photovoltaics: Some Like it Hot, Nature, Materials, 2013, 12, 5–6.

[6] R. L. Fleischer, P. B. Price, R. M. Walker, Nuclear Tracks in Solids. Berkeley: Univ. of California Press, (1975).

[7] L. T. Chadderton, and M. I. Torrens, Fission Damage in Crystals (Methuen & Co. Ltd. Paris, 1969) pp. 113 and 190.

[8] S. Gupta, D. C. Agarwal, J. Prakash, S. A. Khan, S. K. Tripathi, A. Tripathi, S. Neeleshwar, S. K. Srivastava, B. K. Panigrahi, R. Chandra, D. K. Avasthi, PbTe Formation by Swift Heavy Ion Beam Induced Interface Mixing of Te/PbO Bilayer, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2012, 289, 22–27.

[9] T. Diana, D. C. Agarwal, P. K. Kulriya, S. K. Tripathi, H. Nandakumar Sarma, Interfacial Mixing in Te/Bi Thin Film System, Advanced Materials Letters, 2014, 5 (4), 223-228.

[10] R. Sreekumar, P. M. Ratheesh Kumar, C. Sudha Kartha, K. P. Vijaya kumar, D. Kabiraj, S. A. Khan, D. K. Avasthi, Y. Kashiwaba, T. Abe, Swift Heavy Ion-induced Interface Mixing in In/Sb Semiconductor Science Technology, 2006, 21, 382–386.

[11] E. C. Oliveira, E. Deflon, K. D. Machado, T. G. Silva, A. S. Mangrich, Structural, Vibrational and Optical Studies on an Amorphous $Se_{90}P_{10}$ Alloy Produced by Mechanical Alloying, J. Phys.: Condens. Matter, 2012, 24, 115802 (6pp).

[12] www.deltanu.com, DeltaNu Application Note, Characterization of Carbon Nanotubes with Raman Spectroscopy.

[13] N. F. Mott, E. A. Davis, Electronics Processes in Non-Crystalline Materials, Chapter 9, Chalcogenides and Other Glasses, Clarendon Press, Oxford, 1979, Second Edition, 452-457.

[14] R. Roy, V. S. Choudhary, M. K. Patra, A. Pandya, Effect of Annealing Temperature on the Electrical and Optical Properties of Nano-crystalline Selenium Thin Films, Journal of Optoelectronics and Advanced Materials, 2006, 8 (4), 1352 – 1355.

[15] A. Singh, L. Song, R. A. Lessard, Structural, Morphological, and Optical Recording Characterization of Selenium Films, Optical Engineering, 1987, 26 (9), 944-948.

[16] N. K. Njuguan, M. Y. C. Bell John, K. Y. Prassad, Temperature Dependent Electrical Resistivity in Expoxy: Multiwalled Carbon Nanotube Nanocomposite, 2011, 5^{th} World Congress on Engineering Asset Management (WCEAM-2010), ISBN: 9780857293015.

[17] O. V. Kharissova , G. A. Rangel Cárdenas , B. I. Kharisov , M. J. Yacamán U. O. Méndez, Synthesis and Characterization of a Composite Based on Carbon Nanotubes and Selenium, International Journal of Green Nanotechnology: Materials Science & Engineering, 2009, 1, M34–M42.