Int. J. Nanoelectronics and Materials **8** (2015) 83-90

Opto-electronic properties of carbon nanotube doped ITO electrode using ArF excimer laser annealing.

H. Salar Amoli[1,*] , H. Amanidaz[2], S. A. Mozaffari[1], M. R. Moharamzadeh[1], A. Abdous[2]

[1]*Thin Layer and Nanocoating Lab, Iranian Research Organization for Science and Technology, No 71, Forsat St, Englab Ave, Tehran. I. R. Iran.*
[2]*Amirkabir University of Technology, Dept of Chemistry, Tehran, I. R. Iran.*

Received 27 June 2013; Revised 25 May 2014; Accepted 16 Nov. 2014

Abstract

Transparent conductive nanocomposite thin films of indium tin oxide (ITO) and carbon nanotubes (CNTs) in various concentrations are prepared on flexible polyethyleneterephtalate (PET) substrate using spin coating process. CNTs distributed homogeneously into ITO solution by sonication technique. The annealing of the substrate was performed by excimer laser annealing. The sheet resistance was found to drop by 50 % compared to pure ITO film, while transparency remained with no significant changes when using up to 0.08 % CNT. The uniformity was studied by scanning electron microscopy and the rms roughness of 12 nm was obtained by atomic force microscopy (AFM). The addition of the carbon nanotubes to ITO solutions could effectively increase the mechanical strength of the CNT/ITO thin films.

Keywords: Optical properties of thin film; Annealing; Excimer laser.
PACS: 78.66.Bz; 81.40.Ef; 79.20.Eb.

1. Introduction

Transparent conducting metal oxide films have a number of applications in electronic lighting devices, display technology (including touch panels) and thin film solar cells [1-4]. ITO also has singular optical and electrical properties in crystal serving flat display, thin film transistor and solar cells [5-8]. However, most scientist and engineers are concern about lack of robustness of ITO films in mechanical flexibility and thermal stability [9, 10]. To achieve greater conductivity, transparency and multi-functionality, electrode modification with another material is sometimes used in opto-electronics [11]. For example Ti, Au [12] and ZnO modified ITO electrodes are commonly used [13-18]. In this regards

[*]) For corresponding: Email: salar@irost.ir.
* For correspondence Tel; (98) 21-226 15 119, Fax; (98)21-83532158 E-mail; salar@irost.org.

with ITO. Carbon nanotubes, due to its unique graphene structure provide extraordinary electrical conductivity, optical properties and mechanical strength and smoother surface morphology. Also CNTs doped ITO, provide greater environmental stability and better wet ability and charge injection uniformity.

The CNTs doped ITO films are fabricated by solution processing and are mechanically flexible and used as anodes for organic light –emitting diodes (OLED) [22, 23] and organic photovoltaic's (OPVs) [24, 25]. Although it is possible to form a coating layer with uniform thickness of CNT: ITO on polymer substrate using spin coating process, this method suffering high resistivity even after annealing by heating (up to 180^0C). So, pulse laser technique which is used for the wide range of materials include dielectric to metal ceramics, semiconductors, polymer and biological tissues was used to overcome this problem.

The objective of this research are to incorporating CNTs into the ITO and investigate the feasibility of the performances in mechanical flexibility, conductivity and transparency on a flexible polymer and find the effect of excimer annealing method. PET has been used as substrate due to its low density and softness. In addition the experiment of this work aimed to develop a series of functional electrodes with a range of CNTs concentrations in the anode films. Finally, a standard bending test was carried out on the CNTs/ITO films. The changes in the sheet surface roughness were investigated to find the effect of CNTs on mechanical strength.

2. Experimental

The polymer (PET) was cut into pieces of 50 x 50 mm in size to serve as substrate on which the CNTs/ITO films were to be deposited. The substrates were `cleaned ultrasonically in an acetone and alcohol solution to remove all organic contaminations and then by distilled water, detergent, ethanol and diluted acid accordingly. These processes causes to remove micro scale adsorbed particles, grease and impurity on the surface of the substrate.

High purity reagents and materials obtained commercially (Sigma-Aldrich Pte Ltd.) and ethanol (Merck 99.9%) was used as a dispersion medium.

The composite material of CNTs/ITO was prepared by mixing ITO paste with 2-n-butxyethyl acetate to form a dilute solution which then mixed with various concentrations (0.002 to 0.014 %) of CNTs to achieve the different composites. The composites were subjected to a sonication process for 45 minutes for distribution in the solutions. The solutions were spin coated on the PET substrates. The optimum spin rate and duration was found to be 1500 rpm for 50 s. The substrate then subjected to baked in an oven at 180^0C for 60 min in atmosphere. After which, the substrates were treated by ArF excimer laser treatment at 40 mJ/cm^2 with 2 Hz frequency for 5 shots. The sheet resistance of the CNTs: ITO films coated on PET substrate were measured by four-point probe (Jandel RM3000). All values of film thickness and the electrical characteristics are average data from measuring different position on the coated substrate. The surface morphologies were characterized by optical microscope model; ZEISS-Axisokop 2-Mat and Scanning Electron Microscope (SEM), KYKY-EM3200.

Layer thickness was determined with a cross section of the SEM image.

(i) The optical transmittance of the films was measured with a UV-VIS Perkin – Elmer scanning spectrometer in a wavelength range of 300-800 nm.

(ii) The graphs of the transmittance versus CNTs concentrations were obtained in order to study the effect of the CNTs on the optical properties of the thin films.

(iii) The surface roughness of the CNTs/ITO films was measured with AFM equipment "Veeco-autoprobe-CP research".

3. Results and Discussion

In the fabrication of CNTs /ITO composite, the most critical point is homogeny distribution of carbon nanotubes. In this work homogeneous CNTs solutions were formed by adding 0.002 to 0.01 percent of CNT to ITO solutions and subjected to sonication process for 45 min. In order to evaluate the homogeneity of the final solution, the thin films was spin coated onto a PET substrate at a speed of 1500 rpm, baked in an oven at 180 ^{0}C for 60 min and examined under the scanning electron microscopy while the final thickness was about 2 micron. Prior to SEM analysis a low temperature growth technique and excimer treatment was employed. Both continuous wave and pulse excimer laser can be used for treatment of CNTs/ITO on PET substrates. But excimer mode was preferable due to higher cooling rates and a reduce heat affected. Fig 1 (A and B) shows thin films of ITO and CNTs/ITO electrode annealed by excimer laser. It reveals uniform distribution and dispersion over the substrate surface and it shows, CNTs influence on crystal structure of thin films.

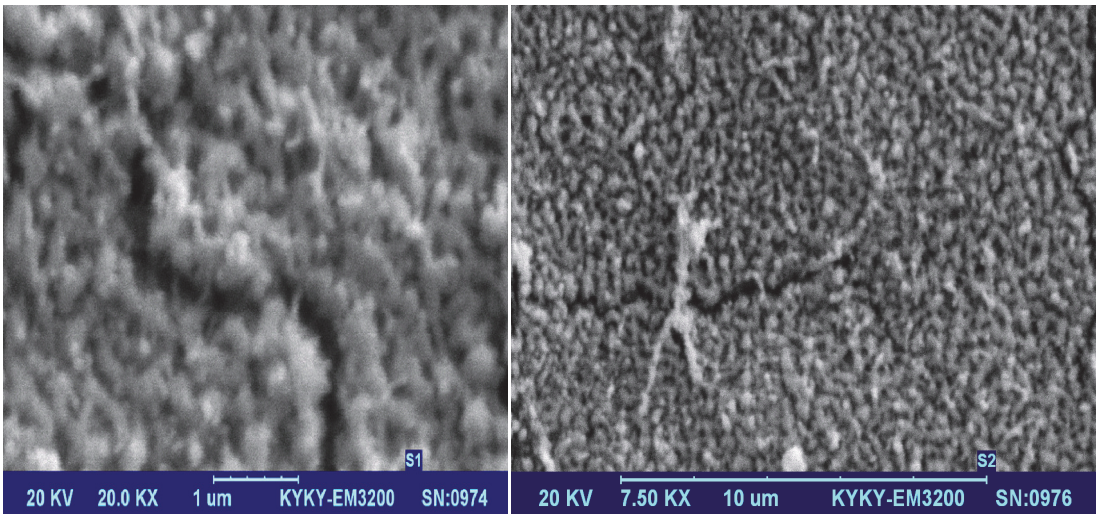
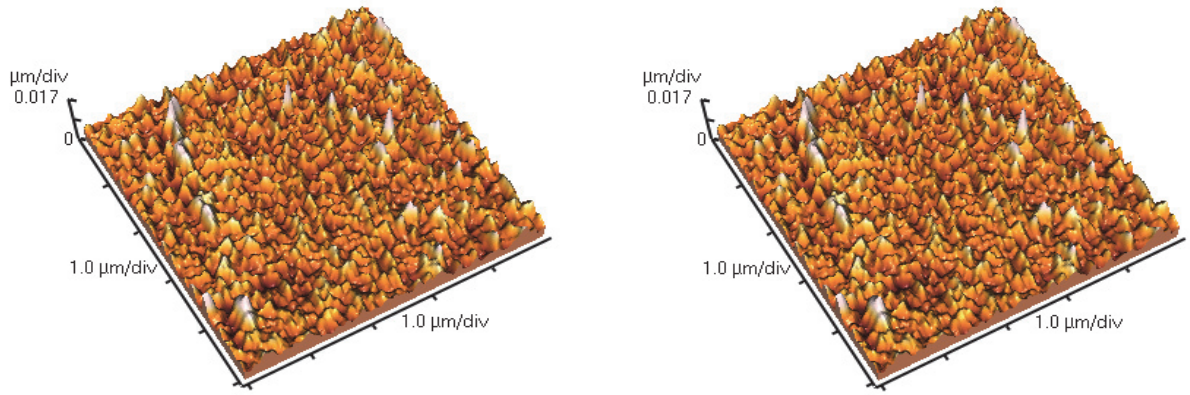


Fig.1: SEM images of CNTs/ITO films, A and B) annealed with excimer laser and indicate CNT act as bridge between the cracks causes by treatment.

As in Fig 1, A, indicates with the increasing number of shots, cracking in the films increased and reduced the conductivity significantly. In this method UV photons from the laser are efficiently absorbed by ITO layer. Also, ArF Excimer laser treatment reduces grain boundary and increases particle sizes. Fig 1, b, shows that CNT transfer electrons along the film surface and acts as bridge between the cracks causes by treatment.

Fig. 2 shows the contact mode of AFM images. The rms roughness is about 12 nm for CNT/ITO and 8 nm for ITO films. The surface roughness of the CNT – enhanced ITO represent a jump when using 0.006 % CNT: ITO composite. So, it can be concluded that addition of CNT up to 0.006 % provided extra mechanical resilience. The rms roughness's of ITO modified CNT surface increase with increasing the concentration of CNTs. But

when the amount of CNT in composite increased to about 0.01% it had affected on optical transmittance and reduces the transparency dramatically.



A B

Fig. 2: AFM images of A; ITO and B; ITO modified by 0.006 % CNT

The results of sheet resistance measurements are shown in Fig 3. The graph shows that there is an inverse relationship between the sheet resistance and the CNT concentrations. By increasing the amount of CNT the sheet resistance declined rapidly. It was noted that by increasing more than 0.008 % CNTs the rate of this reduction stops and for CNT concentration more than 0.014 % has reverse affect. It means that increasing of the CNTs has an important limitation. This limitation is due to glomeration of CNT at high concentration. This result is in agreement with the work of Lin et.al, [26].

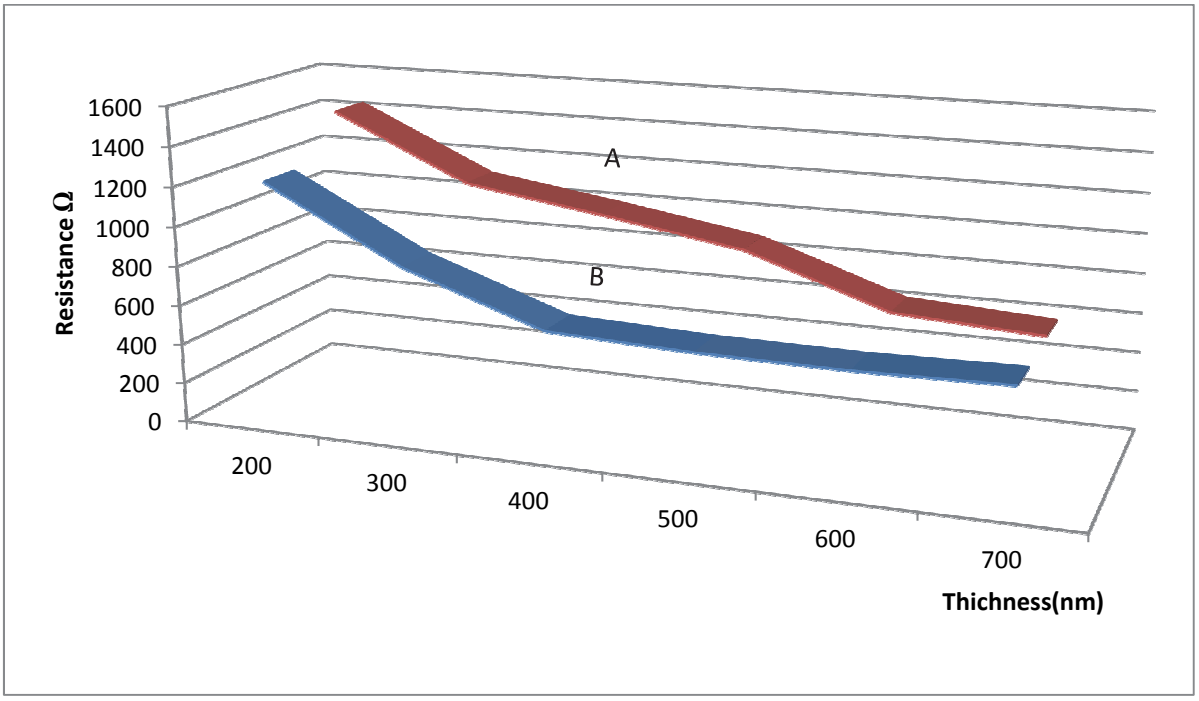


Fig. 3: Graph of sheet resistance versus percentage of CNTs for CNTs/ITO films. ó A)Thermal annealed B) excimer laser annealed.

Fig. 4 shows optical transmittance spectra of CNTs/ITO from 300 to 800 nm which is visible range in various CNTs concentrations. The transmission percentages were calculated from the measured percentage transmission of the corresponding bare substrate.

The maximum transmittance can reach 84% in the wavelength of 550 nm. Based on this information it is concluded that the transmittance of ITO film is higher at the full range of the wavelength, comparing to a PET substrate coated with CNT/ITO.

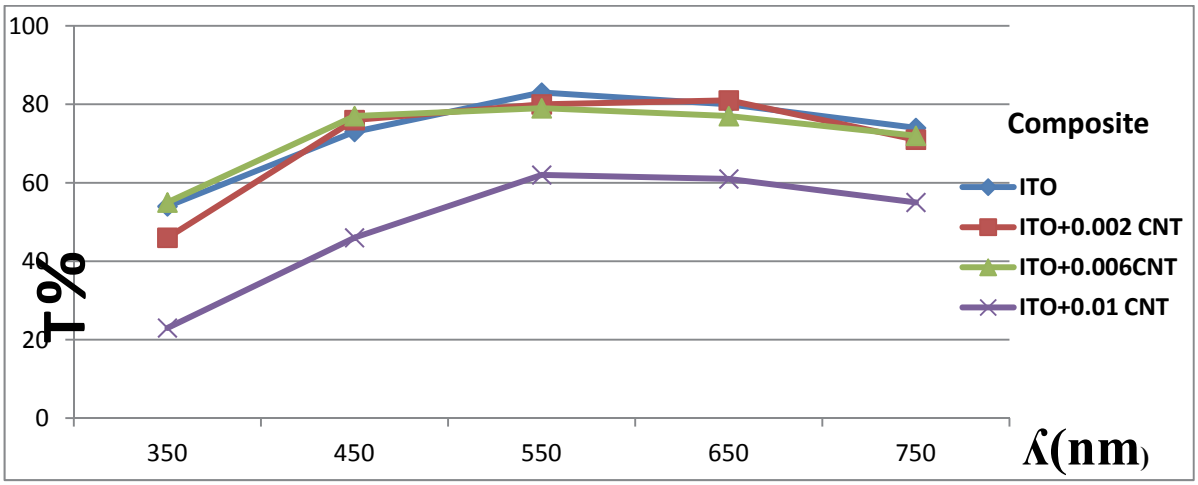


Fig.4: Transmittance spectra of CNTs/ITO nanocomposites at different percentage of CNTs.

Also, it shows that up to 0.006 % CNT has just 4 to 6 percent affect on reduction of transparency. So, the average transmittance at 550 nm is very close to that of pure ITO films. Increasing the concentration of CNT to above 0.008% causes a dramatic affect on transparency of the films. Also it was found that the average transmittance spectra on ITO modified CNTs films decreases as the ITO film thickness increases.

ITO is known to be lacking in mechanical robustness. So, bending tests was applied to find the mechanical flexibility of the ITO and CNTs/ITO composite films on PET substrate. It was found that by increasing the amount of CNT in CNTs/ITO composite, the mechanical flexibility increased significantly while the sheet resistance and transparency decreases by factors of about 8 and 5 percent respectively. Also, it was shown that bending to radii of 4 mm causes a huge increase in resistance which could be due to cracks in CNTs/ITO thin films.

Sheet resistance, surface roughness and average transmittance in 550 nm and dependence on the concentration of CNTs in composites are summarized in Table 1.

Table 1: Mechanical flexibility properties of ITO/CNT thin films.

Sample	Sheet resistance (Ω/ sq)	% Transmittance 550 nm	8mm bending test (Ω/ sq)	4 mm bending test (Ω/ sq)
ITO Sheet	950	84	800	11300
ITO/CNT (0.006)	520	82	650	10000
ITO/CNT (0.008 %)	630	74	80	10500
ITO/CNT (0.01 %)	1350	61	98	14000

4. Conclusion

A CNTs/ ITO composite which was then coated on a polymer and treated by ArF Excimer laser was developed. It had been concluded from the data obtained in this work that the optical conductivity of the films increased with the increasing CNTs concentration up to the 0.006% at which glomeration of the CNTs happened. Also it was concluded that small amount of CNT does not affect on transparency. In summary, CNTs doped ITO, using spin coating process as a simple, not expensive method improving conducting and strength of the films without significant affect on transparency. Treatment of CNTs/ITO films by excimer laser reduces the sheet resistance to less than 500 Ω/sq.

References

[1] I, Hamberg, and C.G. Granqvist, J. Applied Physics, 1986. **60** (11), (1986)123
[2] S. B. Rana, A. Singh, S. Singh, Int. J. Nanoelectronics and Materials**, 6** (2013) 45
[3] Y-H. Tak, K-B. Kim, H-G. Park, K-H. Lee, J-R. Lee, Thin Solid Films. **411** (2002) 12
[4] R. A. Ismail, O. A. Sultan, R. A. Al-Salam, Int. J. Nanoelectronics and Materials, 5 (1012) 31
[5] S. M. Al-Delaimy, A. R. Al-Kaerow, Int. J. Nanoelectronics and Materials, **5** (2012) 117
[6] M. K. Zamorskii, K. Nouneh, K. Kobayashi, M. Oyama, J. Ebothe, A. H. Reshak, Optics & Laser Technology, **4** (2008), 499
[7] K. G. Kanade, D. P. Amalnerkar, H. S. Potdar. B. B. kale, Material Chemistry and Physics, **117** (2009) 187
[8] M. A. Aziz, M. Oyama. Ali H. Reshak, E. Gondek, P. Armatys, A. Shebl, I. V. kityk, A. Wojciechowski, W. Otowski, Physica E. **44** (2012) 1182
[9] Y M. Sung, J Electr Eng Technol**, 2** (2007) 532
[10] A E. Delahoy, L. Chen, M. Akhtar, B. Sang, S. Guo, Sol Energy, **77** (2004) 785
[11] Y M. Sung, D-W. Han, Vacuum**, 83**(2009) 161
[12] L. R. P. Kassab, K. J. Plucinsk, M. Piasecki, K. Nouneh, I. V. Kityk, A. H. Reshak, R de A Pinto, Optics Communications, **281** (2008) 3721
[13] K. Ozga, T. kawaharamura, A. Ali Umar, M. Oyama, K. Nouneh, A. Slezak, S. Fujita, M. Piasecki, A. H. Reshak, I. V. Kityk, Nanotechnology, **19** (2008) 185609
[14] A. H. Reshak, J. Ebothe, A. wojciechowski, W. Kuznik, A. Popeda, Physica E. **42** (2010) 1769
[15] Z. Charifi, H, Baaziz, A. H. Reshak, Phys. Stat. Sol. (b), **244** (2007) 3154
[16] Z. Ben Aydai, L. Elmir, J. ElGhoul, K. Djessas, S. Alaya, J. Nanoelectronics aand Materials, **3 (**2010)87
[17] M. Gross, A. Winnacker, and P.J. Wellmann, Thin Solid Films, 2007. **515** (24): p. 8567-8572
[18] J. Li, L. Hu, L. Wang, Y. Zhou, G. Gruner, T J. Marks, Nano Lett**, 6** (11), (2006) 2472
[19] H S. Woo, R. Czerw, S. Webster, D L. Carroll, J W. Park, J H. Lee, Synth. Met, **116** (2001) 369
[20] C M. Aguing, S. Suvary, S. Pigeon, R. Izquierdo, P. Desjardins, R. Martel, App. Phys. Lett**, 88** (2006) 183104
[21] D. Zhang, R. Ryu, X. Liu, E. Polikapov, J. Ly, E. Tompson, C. Zhou, Nano Lett**, 6** (2006)1880

[22] A D. Pasquier, H E. Unalan, S M. Kanwal, M. Chhowalla, Appl Phys Lett**, 87** (2005) 203511
[23] M W. Rowell, M A. Topinka, D.McGeheem, H J. Prall, G. Dennler, S. Saricifteі, L. Hu, G. Gruner, Appl. Phys. Lett**, 88** (2006) 233506
[24] H. Salar Amoli, B. Fathi, J Sol-Gel Sci Technol**, 59** (2011) 32
[25] Y H. Tak, K E. Kim, H G. Park, K H. Lee, J R. Lee, Thin Solid Films**, 411** (2002) 12
[26] K. Lin, R S. Kumar, L S. Cheng, C S. Jin, Trans. Electron. Dev**, 56** (2009) 31