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Study of the junction characteristics of MWNT doped polymer composite films

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Interface Studies of Multi walled carbon nano-tube (MWNT) doped polymer (PS & PMMA) blends and n-type Si substrate has been reported in the manuscript. MWNT is commonly used as an electron acceptor in interpenetrated networks and an electron transport in photovoltaic cells. We have studied the guest–host approach to prepare MWNT doped polymer blend and found that the MWNT shows the junction characteristics with n-type Si substrate. The knee-voltage and dynamic resistance drastically varies with annealing temperature. The optical micrographs show the uniform dispersion of MWNT and it's blend in the form of crystallites having micron order size. These polymer thin films have also been characterized by optical and XRD measurements.

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1. Introduction

Polymer based molecular heterojunction cells were extensively studied over the decade, due of their potential advantages and low cost production process. The real advantage of these BHJ devices, which can be processed in solution, over vacuum deposition is the ability to process the composite active layer from solution in a single step, by using a variety of techniques that range from inkjet printing to spin coating and roller casting. However, regardless of the method of preparation, one feature that extends across all classes of organic solar cells is the almost ubiquitous use of fullerenes as the electron accepting component. The high electron affinity and superior ability to transport charge make fullerenes the best acceptor component currently available for these devices. CNT is a member of the fullerene family which is created when a carbon honeycomb sheet rolls in itself to form a cylinder. CNT films have emerged as an active and rapidly advancing area of research. CNT films have a number of potential advantages compared to the existing transparent conductor technologies such as Indium Tin Oxide (ITO). The gap between theoretical and real-world performance in terms of sheet resistance and optical transparency is probably still too large to allow CNT films to be incorporated into commercial solar cells. In that context, extensive studies have been done on semiconducting CNT and fullerene (C_{60}) as a promising candidate material in opto-electronic devices, including solar cells [1–6]. In addition to the research aimed purely at improving film performance, recent work has demonstrated advances in using CNT films in a wide variety of applications – for instance, transparent transistors [7], antistatic coatings [8], gas sensors [9], pH sensors [10], and solar cell electrodes [11].

Incorporation of CNT into a polymer has been recognized as a simple means of combining the unique properties of CNT with macromolecular characteristics [12- 14]. We are interested to investigate the electrical properties of incorporated CNT networks in conventional polymer matrices on silicon substrate. For this purpose, we have adopted a well-known method of dispersing the CNT by first dissolving that in a suitable solvent and then casting a thin film. For this purpose, we have used PS and PMMA as host polymers, which all of them contains sp3 hybridized backbones. However the quantum efficiencies of these devices are still considerably lower [15-20]. In the last decade, researchers fabricated inorganic–organic heterojunctions by depositing organic molecules (CNT, C_{60} and C_{70}) on inorganic bulk materials (Si [21-23], GaN [24, 25]) to form a plane interface. Weining wang et al. have reported PANI/n-type silicon heterojunction solar cell [26].

In this paper, we report our research on MWNT–Polymer blend/ n-type silicon heterojunction solar cells. The MWNT was blended with Polymer to provide mechanical strength and good processability. These MWNT-polymer composite were characterized by UV-VIS spectroscopy, XRD and optical microscopy.

2. Materials and sample preparation

The PMMA and PS were obtained from Good fellow, UK and MWNT from Aldrich, Germany. Initially the MWNT (1% wt) was dissolved in chloroform for 2 hours using ultrasonication for a homogeneous solution. PS and PMMA were stirred in chloroform for 2 hours separately and then MWNT solution mixed in PMMA and PS solution to make MWNT polymer blend. These blends have been characterized by XRD, UV-VIS and optical micrographs. The Si wafers of area 1×1 cm^2were used as a substrate. MWNT-polymer/n-type Si junction was prepared by spin coater at 1000 rpm by using the MWNT-polymer solution onto n-type Si substrate. The annealing of samples has been performed in vacuum at 100º C for 10 minutes. The contact of Al (100 nm) was deposited on spin coated Si substrate using thermal vacuum deposition technique at 10^{-5} torr.

4. Result and discussion

(a) UV-VIS Spectroscopy

UV-VIS spectrums of these blends were recorded using U-2900 Hitachi spectrophotometer. The measurements show that the absorption edge is shifted towards longer wavelengths and absorption is increased after doping of MWNT in PS and PMMA in comparison to pure polymer film as shown in Fig. 1 which may be due to uniform distribution of MWNT in polymers. Therefore the band gap of blend is decreased, which also confirms the presence of MWNT in polymer matrix.

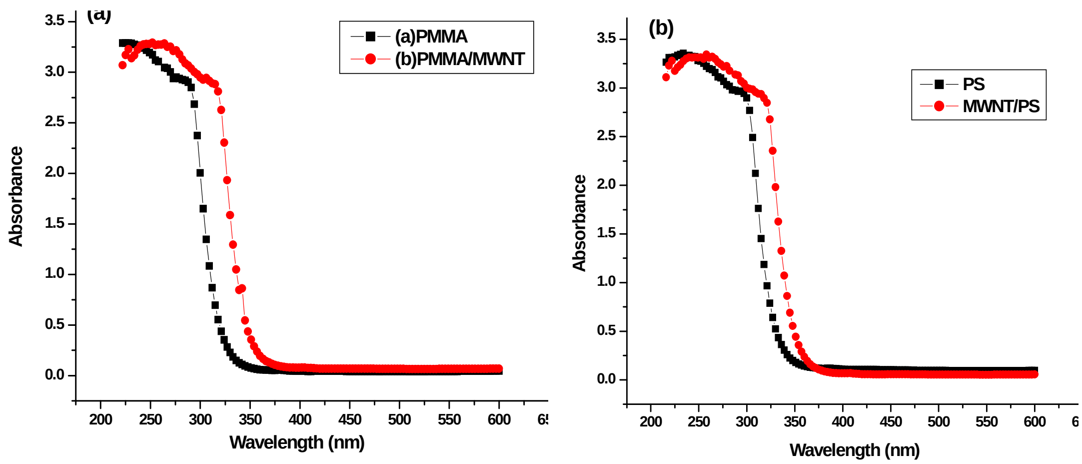

Fig. 1. UV-VIS spectrums for (a) Pure PMMA & MWNT/PMMA and (b) pure PS & MWNT/PS.

(b) XRD

X-ray diffraction measurements have been performed using Panalytical system having CuK_{α} as a radiation source of wavelength λ=1.5402 Å within $2\theta = 10^0$- 40^0 at the scan speed 0.4^0 /minute. Fig. 2 shows the X-ray diffraction pattern of pure PS, PMMA and their blends with MWNT on glass substrate. In case of pure PS and PMMA, a broad hump has been found around 2θ= 15º-20º which explain amorphous nature of polymers. A small sharp peak has been appeared at 2θ = 26º in case of MWNT/polymer blends, which confirms the presence of MWNT in polymer matrix.

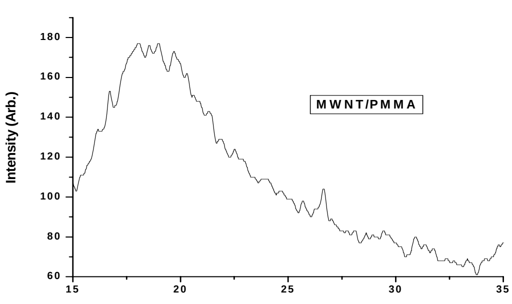

Fig. 2. XRD spectra of MWNT/PMMA blend.

(c) I-V Characteristics

Typical I-V characteristics of MWNT doped polymer on n-type Si substrate are shown in Fig. 4. As one can see that the current increases exponentially at a forward applied voltage, but very small current flows under a reversed applied voltage. This indicates that a rectifying effect of the heterojunction was observed. It may be due to low work function of Ag in comparison n-type Si, which behaves here as a electrode. The effect of vacuum annealing (at 50°C, 75°C and 100°C) on the junction also shows a further enhancement of the knee voltage, Which has been attributed to the formation of a junction.

(d) Optical micrograph

Optical micrograph images of these samples were recorded using labomad optical microscope at 10x magnification. Fig. 3 represents the optical micrographs of (a) PS (b) MWNT/PS (c) PMMA and (d) MWNT/PMMA blend thin films. In both case MWNT shows an uneven cluster structure which are uniformly distributed in polymer matrix and smoothness of blend film increased.

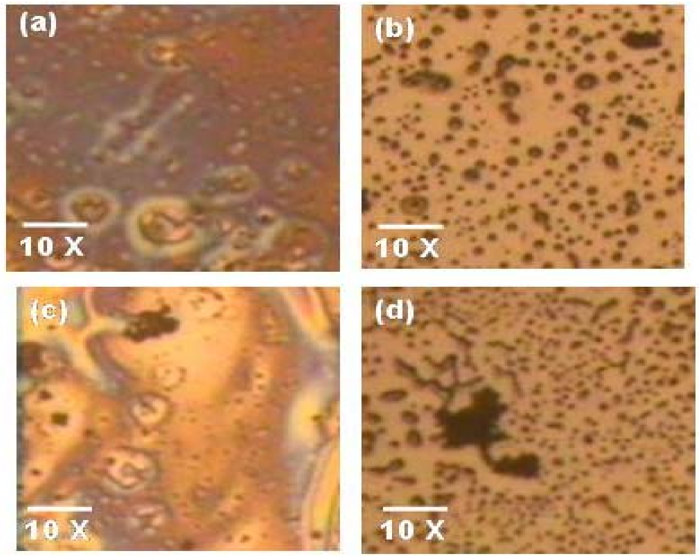

Fig. 3. Optical micrographs for (a) Pure PS and (b) MWNT/PS (c) Pure PMMA and (d) MWNT/PMMA.

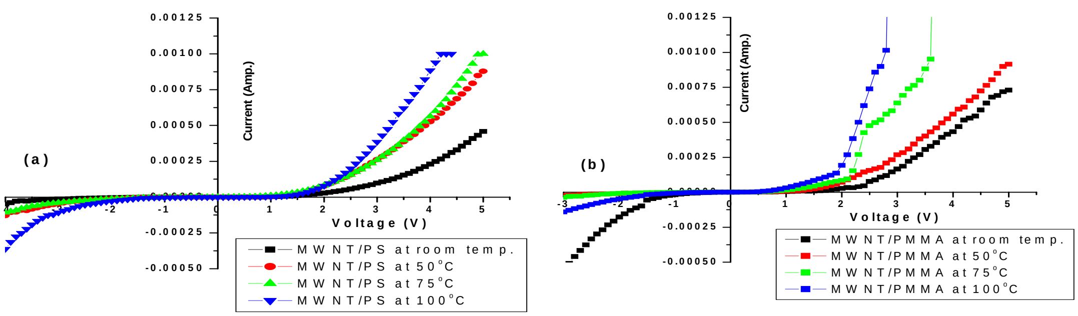

Fig. 4. I-V characteristics for (a) MWNT/PS blend and (b) MWNT/PMMA blend at different temperatures.

5. Conclusions

We have found that MWNT/PMMA blend on n-type Si shows rectifying nature. We have also fabricated MWNT/PMMA blend / n-type silicon heterojunction. I-V characteristics indicate that conductivity of blend is increased with the doping of MWNT in blend, as well as after annealing, which may be due to an increase injection of charge carriers through the heterojunction. The XRD, UV-VIS and optical micrograph results confirm the presence of MWNT in polymer matrix.

References

[1] A. J. Heeger, J. Phys Chem B **105**, 8475 (2001).
[2] M. Taguchi, K. Kawamoto, S. Tsuge, T. Baba, H. Sakata, M. Morizane, K. Uchihashi, N. Nakamura, S. Kiyama, O. Oota, Prog. Photovoltaics **8**, 503 (2000).
[3] M. A. Green, K. Emery, D. L. King, Y. Hishikawa, W. Warta, Prog. Photovoltaics **15**, 35 (2007).
[4] Barry C. Thompson, Jean M. J. Frechet, Angew. Chem. Int. Ed., **47**, 58 (2008).
[5] M. Fahlman, W. R. Salaneck, Surf. Sci. **500**, 904 (2002).
[6] K. Petritsch, I. J. Dittmer, E. A. Marseglia, et al., Sol. Energy Mater. Sol. Cells **61**, 63 (2000).
[7] T. Takenobu, T. Takahashi, T. Kanbara, K. Tsukagoshi, Y. Aoyagi, Y. Iwasa, Applied physics letters, **88**(3), 33511 (2006).
[8] K. Watson, S. Ghose, D. M. Delozier, J. G. Smith, J. W. Connell, Polymer. **46**(7), 2076 (2005).
[9] K. Parikh, K. Cattanach, R. Rao, D. S. Suh, A. M. Wu, S. K. Manohar, Sensors and actuators. B, Chemical, **113**(1), 55 (2006).
[10] M. Kaempgen, S. Roth, Journal of electroanalytical chemistry and interfacial electrochemistry, **586**(1), 72 (2006).
[11] Pasquier Aurelien, Du Unalan, Husnu Zmrah, Kanwal Alokik, Miller Steve, Chhowalla Manish, Applied physics letters, **87**(20), 1 (2005).
[12] M. Prato, J. Mater. Chem., **7**(7), 1097 (1997).

[13] K. E. Geckeler, Trends Polym. Sci., **2**, 355 (1994).
[14] Hirsch, Adv. Mater., **5**, 859 (1993).
[15] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, Nature. **347**, 354 (1990).
[16] H. W. Kroto, A. W. Allaf, S. P. Balm, Chem. Rev. **91**, 1213 (1991).
[17] J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti, A. B. Holmes, Appl. Phys. Lett. **68**, 3120 (1996).
[18] B. Miller, J. M. Rosamilia, G. Dabbagh, R. Tycko, R. C. Haddon, A. J. Muler, W. Wilson, D. W. Murphy, A. Hebard, J. Am. Chem. Soc., **113**, 6291 (1991).
[19] P. C. Eklund, A. M. Rao, Springer, Berlin, 1999.
[20] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, F. Wuld, Appl. Phys. Lett, **62**, 585 (1993).
[21] S. H. Yang, C. L. Pettiette, J. Conceicao, O. Cheshnovsky, R. E. Smalley, Chem. Phys. Lett, **139**, 233 (1987).
[22] H. Ajie et al., J. Phys. Chem, **94**, 8630 (1990).
[23] (a) M. Prato, J. Mater. Chem., **7** (7), 1097 (1997). (b) K. E. Geckeler, Trends Polym. Sci., **2**, 355 (1994).
[24] A. Hirsch, Adv. Mater., **5**, 859 (1993).
[25] R. A. Marcos, M. T. Rispens, J. C. Hummelen, R. A. Janssen, J. Synth. Met., **119**, 171 (2001).
[26] P. C. Eklund, A. M. Rao, Fullerene Polymers and Fullerene Polymer Composites, Springer Berlin, 1999.

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