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Microwave Hall mobility studies on polymer-single walled carbon nanotube composite fibers

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Composite fibers of single walled carbon nanotubes dispersed in poly(methyl methacrylate) and polystyrene are prepared using electrospinning. The single fiber electrical conductivity is measured as a function of the composition of carbon nanotubes. A noncontact method of measuring the carrier mobility at microwave frequency (14 GHz) using bimodal cavity is employed. The mobility measurements indicate lower percolation threshold for mobility compared to electrical conduction. For higher concentrations of carbon nanotubes, the mobility is found to decrease indicating possible carrier-lattice scattering. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2939575]

In general, the measurement of electrical properties of materials requires direct ohmic contacts to be made on the sample. It is difficult to obtain reliable electrical parameters in the case of materials such as semiconductors, heterostructures, biological substances, and those in the form of powders, thin films, and nanofibers. In this context, noncontact microwave techniques provide an alternative for the electrical characterization of materials. Subramanian *et al.* have applied cavity perturbation technique for the study of transient microwave conductivity in semiconductors and organic liquids under optical excitation.[1] Microwave Hall effect (MHE) is one other scheme for the measurement of mobility of charge carriers in similar systems.

One of the sensitive measurement methods for microwave Hall mobility employs bimodal cavity.[2–4] Here two orthogonal modes resonate at the same frequency. The sample, mounted on a poly-tetrafluoroethylene sample holder, is placed where both the modes have their maximum electric field. One of the modes is excited using the input port of the cavity. The carriers oscillating due to the input microwave power is subjected to an external static magnetic field. This couples the microwave power to the orthogonal mode, the magnitude of which depends on the mobility of the carriers. Thus, the change in the transmission coefficient between the two modes due to the applied magnetic field is related to the mobility of the carriers.

Carbon nanotubes (CNTs) based polymer nanocomposites have attracted much attention due to their unique structure and excellent mechanical, electrical, and thermal properties.[5,6] Electrospinning is an ideal method for the preparation of ultrafine fibers of polymer composites with CNTs as filler.[7,8] Both single walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs) play an important role in the enhancement of the electrical conductivity in these systems. Since it is difficult to obtain good electrical contacts on the fibers due to their high resistance and also to improve the signal to noise ratio in the mobility measurements, noncontact microwave Hall mobility technique at 14 GHz is employed. Here the composite fibers are electrospun using SWCNTs disbursed in two different polymer matrices, namely, poly (methyl methacrylate) (PMMA) and polystyrene (PS).

The SWCNT of 90% purity, obtained from Chengdu Organic Chemicals, Chinese Academy of Sciences, China, were used without further purification. The bulk electrical conductivity of the SWCNTs was 10^4 S/m and the diameter was within 1 – 2 nm. The average molecular weights of PS (LG Chemicals, India) and PMMA (Sigma-Aldrich, USA) were 25 000 and 99 600, respectively. The solutions of PMMA-SWCNT with concentrations of 0.1%, 0.5%, 0.75% w/w and PS-SWCNT with concentrations of 0.05%, 0.1%, 0.5%, and 1.0% w/w were prepared and electrospun using the setup described elsewhere.[7] The diameter of the fibers was in the range of 0.1–8 μm.

The block diagram for the measurement of mobility using the MHE is shown in Fig. 1. This consists of a microwave network analyzer (Agilent make N5230A) used to obtain the transmission and reflection parameters, a canceling channel (to remove the nonideal mode coupling), and a bimodal cavity. A TE_{111} *P*-band dual mode cylindrical cavity with radius and height of 1.1 and 1.3 cm, respectively, was designed and fabricated. Probe coupling was chosen for the excitation of the cavity. The cavity resonated at 14 GHz and unloaded quality factor was 3109. The sample was kept at

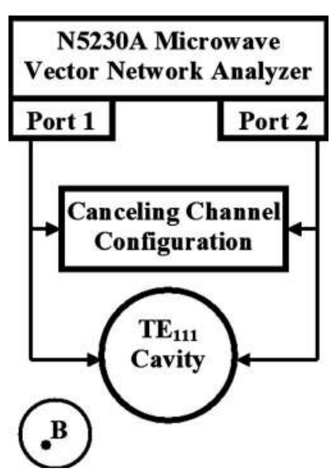

FIG. 1. Block diagram of the experimental arrangement for MFE technique.

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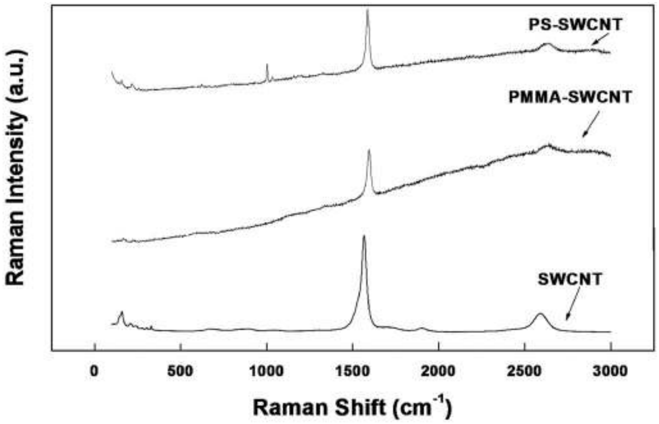

FIG. 2. Raman spectra for SWCNT, 0.5% w/w loaded SWCNT in PS and 0.5% w/w loaded SWCNT in PMMA.

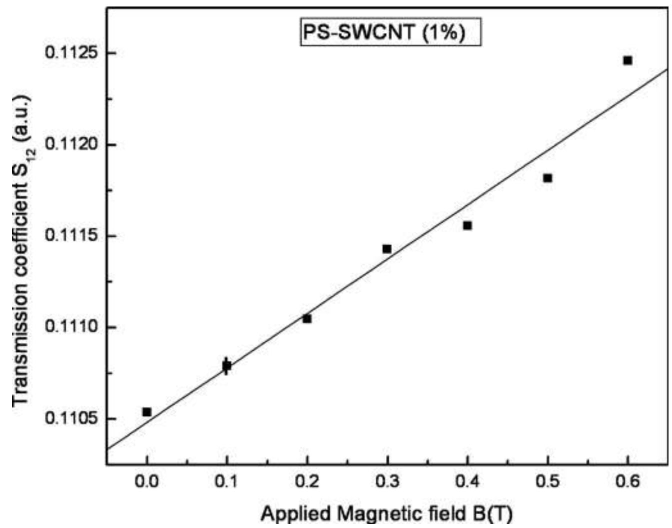

FIG. 3. Variation in transmission coefficient with respect to the applied magnetic field for the PMMA-SWCNT (1%) composites. The vertical line indicates the error in the measurement.

the geometrical center of the cavity and the static magnetic field was applied along the axis of the cavity. The details of the experimental procedure are provided elsewhere.[9] The relation for the evaluation of the Hall mobility (μ) of the carriers at microwave frequency for nonequal input and output coupling is given by the following equation:[10–12]

$$\mu = KA(S_{21}/B), \tag{1}$$

where $A=\{[1-(Q_{11}/Q_{10})][1-(Q_{21}/Q_{20})](1-\Gamma_{11})(1-\Gamma_{21})\}^{-1/2}$; Q_{10}, Q_{20},Q_{11}, and Q_{21} are the unloaded and loaded quality factors while Γ_{11} and Γ_{21} are the loaded reflection coefficients at the ports 1 and 2, respectively; S_{21} is the change in the transmission coefficient due to the application of magnetic field; $K(=2.08\times 10^9)$ is the calibration constant obtained using standard semiconductor samples; B is the static magnetic field.

The radial breathing mode ($\sim$100 – 500 cm–[1]), G band ($\sim$1600 cm^{-1}), and G' band (2650 cm^{-1}) observed in the Raman spectra of fibers (Fig. 2) confirmed the presence of SWCNT in the composite fibers.

The electrical conductivity of a single fiber was measured using a Keithley 238 current source and Keithley 617 electrometer in voltage mode. The single fiber was obtained over a precleaned glass plate through a window on an aluminum foil while electrospinning. Gold electrodes with a separation of $\sim$500 μm were coated over the single fiber through mask evaporation. Table I indicates that the conductivity increases due to the presence of CNTs by nearly twelve orders of magnitude from that of pure PMMA (10^{-12} S/m) and by nearly sixteen orders of magnitude from that of pure PS (10^{-16} S/m).[13] This shows that the concentration of SWCNT is well above the percolation threshold in both PMMA-SWCNT and PS-SWCNT composite fibers even for the lowest loading.

The variation of the microwave transmission coefficient with respect to the applied magnetic field for all the composites was linear in nature. Figure 3 presents the variation in the transmission coefficient with the applied magnetic field for the PMMA-SWCNT (1% w/w) composite fiber. From Table II, it is clear that there is a decrease in the mobility of the carriers as the concentration increases. For a given concentration, the Hall mobility of PS-SWCNT is higher than that of PMMA-SWCNT. This is also evident from the higher dc conductivity values for PS-SWCNT than PMMA-SWCNT. The measured microwave Hall mobility does not correspond to any preferred alignment of the fibers with the microwave electric field since the fibers in the bunch are not perfectly aligned. However, the measured microwave mobility is known to correspond to the highest value in the sample.[11]

For the pure polymer, one expects almost negligible mobility. With an addition of 0.1% and 0.05% w/w of SWCNT in PMMA and PS, the mobilities are 56 and 59 cm^2/V s. respectively. Further, the microwave mobility decreases as the concentration increases. Hence, there must be a critical concentration at which the mobility shows a maximum. However, further decrease in SWCNT concentration does not

TABLE I. dc conductivity values of a single fiber of SWCNT in PMMA and PS.

Amount of SWCNT in the composite fibers (%)	PMMA-SWCNT (S/m)	PS-SWCNT (S/m)
0.05	0.075	0.009
0.1	0.13	0.050
0.5	0.15	0.085
1	0.17	0.103

TABLE II. MHE measurements on composite fibers.

Material	Amount of SWCNT in the composite fibers (%)	A	S_{21}/B (a.u./G)	Microwave Hall mobility μ_H (cm^2/V s)
PMMA-SWCNT	0.1	2.47	1.09×10^{-8}	56
	0.5	2.56	3.98×10^{-9}	21
	0.75	2.85	1.80×10^{-9}	11
PS-SWCNT	0.05	4.80	5.88×10^{-9}	59
	0.1	3.83	3.48×10^{-9}	28
	0.5	2.88	2.02×10^{-9}	12
	1	3.62	1.3×10^{-9}	9

give consistent values due to scanty samples used in the measurement.

It is well known that above the percolation threshold, the conductivity does not proportionally increase with the concentration SWCNT which points to the presence of scattering of the carriers either by other carriers or by the lattice. The mobility thus varies based on the competing influences between the response of the carriers to the applied microwave field and the scattering process. At room temperature, the carrier-lattice scattering is the dominant process. In the case of high frequency mobility measurements, the scattering process is much more significant since the crossed electric and magnetic fields increases the effective electrical length. This dominates even at lower concentrations and, therefore, the percolation threshold for the mobility is lower than that of dc conductivity. Thus, the carrier-lattice scattering may be one of the reasons for the decrease in the mobility of the carriers in the composite. It might be necessary to study the temperature and frequency dependence of the microwave Hall mobility to understand the nature of this variation.

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