Microwave Hall Mobility Studies on Polymer–Metal Oxide Nanocomposites

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ABSTRACT: Films of polymer metal oxide composites with poly(methyl methacrylate) and metallic powders (CuO, Ni, and brushed Fe_3O_4) were prepared with a spin-casting method. Electric transport studies indicated that the compositions surpassed the percolation threshold limit. Alternating current (AC) conductivity studies confirmed a hopping mechanism with power-law behavior in frequency. For the first time, the mobility values of the carriers in these films were measured by the contactless microwave Hall effect technique with a bimodal cavity operating at 14 GHz. In this technique, a circular bimodal cavity is used to measure the change in the transmission coefficient (proportional to the carrier mobility) due to the application of a static magnetic field perpendicular to the microwave electric fields. The mobility measurements indicated a decrease in mobility with increasing quantity of CuO and Ni and showed an increase in the carrier–lattice scattering, whereas the mobility increased with increasing Fe_3O_4 due to the negative magneto resistance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1967–1972, 2008

Key words: composites; films; metal-polymer complexes; nanocomposites

INTRODUCTION

The study of carrier kinetics is very important for the characterization of semiconductors and other samples for the development of devices. One such important transport property is the mobility of carriers. The measurement of mobility is generally performed with the direct current (DC) Hall effect, which requires the use of contacts on the sample. DC Hall effect measurements on organic semiconductors (e.g., copperpthalocyanine) and quasi one-dimensional conducting materials are difficult because of the needle shape of the samples. In this case, the application of contacts is a critical step in the measurement process and also makes the sample unusable. Therefore, it is better to use contactless and nondestructive techniques for this purpose. It is well known that most measurements at microwave frequencies are generally contactless and nondestructive in nature. For the nondestructive evaluation of the Hall mobility, one can use the microwave Hall effect technique.

To observe or measure the Hall mobility at microwave frequencies with the microwave Hall effect arrangement, a circular bimodal cavity is used. The sample is kept in a bimodal cavity at a position where the electric field is maximum and common to both the modes with the help of a sample holder, which fits exactly into the cavity. The excitation of one mode results in an electric field that causes the carriers to oscillate at the microwave frequency in the sample. The application of the external static magnetic field (perpendicular to both the modes) results in the coupling of microwave power to the other mode due to the Hall effect. Therefore, there is a change in the transmission coefficient with the application of an external static magnetic field that is directly proportional to the mobility of carriers.

The microwave Hall effect was first observed by Cooke,[1] who used it to determine the carrier mobility in semiconductors. Several workers developed this technique further by using a circular bimodal cavity.[2–6] This technique is useful for measurement of the carrier mobility of bulk semiconductors, organic semiconductors,[7] powdered materials,[8] perovskites,[9] fine magnetic materials,[10] pyrite crystals,[11] and heterostructures.[12] The microwave Hall effect is applied in the investigation of biological and polymeric materials. The microwave Hall effect method is the only available technique for quantitatively evaluating the carrier mobility for the aforementioned samples.

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Polymer-based composite films are used in a variety of applications, ranging from reversible fuses and resistive heating tapes to the housing of electronic equipment to shield against electromagnetic interference. Special interest has been focused on the poly(methyl methacrylate) (PMMA) polymer because of its versatile use in semiconductor research. The electrical properties of PMMA are very sensitive to its chemical composition. To functionalize polymer films, different materials can be mixed with these polymers. The properties of PMMA–copper semiconductive composite polymer compositions were synthesized and evaluated by Abu-Ayana et al.[13]

To enhance the electrical properties of PMMA, metallic powders (Ni, CuO, and Fe_3O_4 brushes) can be doped in the polymer. As mentioned earlier, it is very essential to measure the electrical transport properties, including conductivity (DC and alternating current (AC)), and mobility of these materials. In this article, we present the DC and AC conductivity studies and microwave Hall mobility values measured by the microwave Hall effect arrangement with a bimodal cavity operating at 14 GHz for PMMA–CuO, PMMA–Ni, and PMMA–Fe_3O_4 composite films.

EXPERIMENTAL

Materials

PMMA was obtained from Union Carbides (Bhopal, India), and tetrahydrofuran (THF) was from Sisco Research Laboratories (Mumbai, India). CuO and nickel oxide nanoparticles were obtained from Argonide Corp. (Stanford, FL). The particle sizes of these metal powders were around 100 nm.

Synthesis of the polymer composite thin films (CuO–PMMA, Ni–PMMA, and Fe_3O_4–PMMA)

The concentration of the solution of PMMA in THF was optimized to obtain relatively uniform films and was found to be 15% (w/w). At first, a 15% PMMA solution in THF was prepared. This solution was stirred for nearly 2 h. After that 20, 30, 40, and 50% (w/w) CuO nanopowders were added to this solution and stirred with a magnetic stirrer for about 8 h and sonicated for 30 min. Immediately after sonication, the solution was put into a syringe (Dispo van, Faridabad, India) and poured onto a clean glass slide, which was rotated at a speed of 1350 rpm. After drying, the film and the glass slide could be easily separated. This separated film was used for further characterizations. A similar procedure was adopted for the preparation of the Ni–PMMA and Fe_3O_4–PMMA composite films. In the case of the Ni–PMMA films, the nickel nanopowder was used for the preparation of the solution, whereas in the case of the Fe_3O_4–PMMA composite films, Fe_3O_4 brushes were used for the preparation of the solution. The details on the preparation of the Fe_3O_4 brushes are given elsewhere.[14] The thickness of these films was roughly 200 μm.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns were recorded on the polymer metal composite films at room temperature with a Philips Pan Analytical X'PERT PRO diffractometer (Almelo, The Netherlands) with Cu Kα radiation (λ = 1.5406 Å) in the 2θ range 20–90°. The XRD patterns of the PMMA–CuO, PMMA–Ni, and PMMA–Fe_3O_4 films confirmed the presence of the CuO, nickel and Fe_3O_4. A typical XRD pattern of the PMMA–Ni composite film is shown in Figure 1.

The DC and AC conductivity measurements were performed with a two-probe technique. The composite films were cast on aluminum-coated glass slides with an interelectrode distance of approximately 1 mm. A Keithley 617 programmable electrometer (Cleveland, OH) was used for DC conductivity measurements, and an HP 4192A impedance analyzer (Santa Clara, CA) was used for the capacitance and impedance studies to evaluate the AC conductivity in the frequency range 6 Hz–13 MHz.

Table I presents the DC conductivity of the composites. The conductivity increased with increasing CuO, Ni, and Fe_3O_4 in the PMMA polymer material. An increase in the conductivity by nearly six orders of magnitude from pure PMMA (10^{-12} S/m)[15] indicates that the conductivities of composite films are above the percolation threshold. As the concentration of the metal oxide powders was higher than the percolation threshold, the sample could be assumed to have a continuous path for conduction. In this

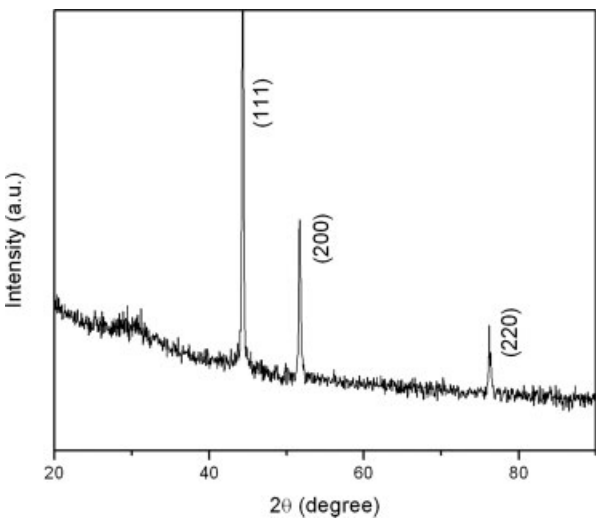

Figure 1 XRD pattern of a PMMA–Ni composite film.

TABLE I
DC Conductivity and Fitting Parameters for the AC Conductivity of Polymer Composite Films

Composition of metal powder in the polymer (%)	PMMA + Fe_3O_4			PMMA + CuO			PMMA + Ni		
	DC conductivity (S/m)	Fitting parameters for the AC conductivity		DC conductivity (S/m)	Fitting parameters for the AC conductivity		DC conductivity (S/m)	Fitting parameters for the AC conductivity	
		n	A_1 ($S\ m^{-1}\ rad^{-n}\ s^n$)		n	A_1 ($S\ m^{-1}\ rad^{-n}\ s^n$)		n	A_1 ($S\ m^{-1} rad^{-n}\ s^n$)
20	6.10×10^{-5}	0.46	5.64×10^{-7}	6.52×10^{-5}	0.51	6.23×10^{-8}	6.725×10^{-5}	0.63	8.36×10^{-9}
30	8.01×10^{-5}	0.65	8.19×10^{-7}	7.94×10^{-5}	0.57	2.96×10^{-9}	8.124×10^{-5}	0.57	3.24×10^{-8}
40	8.52×10^{-5}	0.50	1.52×10^{-7}	8.16×10^{-5}	0.51	1.29×10^{-8}	8.821×10^{-5}	0.59	1.73×10^{-8}
50	8.62×10^{-5}	0.46	5.64×10^{-7}	8.53×10^{-5}	0.48	3.60×10^{-8}	8.901×10^{-5}	0.60	4.44×10^{-8}

case, the increase in DC conductivity could be attributed to the nature of the path of conduction and also to the increase in the concentration of conducting nanopowders. Although one has to employ statistical considerations to account for the increase in the conduction process with concentration, it is important to note that the increase in the concentration played a major role. Moreover, the conductivity depended on the carrier transport through the metal oxide nanopowders. Therefore, the mobility of the carriers definitely indicated that a scattering process was involved. As it is difficult to use the conventional DC Hall effect for these types of samples, one has to rely on a noncontact methodology.

A typical variation of the AC impedance plot for PMMA–CuO composite film is shown in Figure 2. Similar observations were made for all of the other composites. The linear fit in the impedance plot could be represented as a series combination of the resistance and the capacitor. This provided information regarding the capacitance nature of the films.[16]

A typical variation of the AC conductivity with respect to frequency of the PMMA–CuO (20%) composite film is shown in Figure 3. To account for the high frequency dispersion, the conductivity spectra could be modeled with Jonscher's universal law.[16]

$$\sigma(\omega) = \sigma(0) + A_1\omega^n \quad (1)$$

where A_1 is a weakly temperature-dependent parameter, $0 < n < 1$ is a dimensionless frequency exponent, and $\sigma(0)$ is the DC conductivity of the sample. The fitting parameters A_1 and n for the PMMA–CuO, PMMA–Ni, and PMMA–Fe_3O_4 films are given in Table I. The goodness of fit was satisfactory. The values of n indicated that AC conduction followed a hopping mechanism, which is known for disordered (polymer) films.

The mobility studies at microwave frequencies were performed with the bimodal cavity technique. A block diagram of the microwave Hall effect arrangement is shown in Figure 4. This consisted of a N5230A microwave network analyzer (Santa Clara, CA), which was used to observe the transmission and reflection parameters, a canceling channel and the bimodal cavity. The canceling channel consisted of Agilent 87300B (10 dB) coaxial directional couplers, Agilent 8495B (0–70 dB) and 8495B (0–11dB)

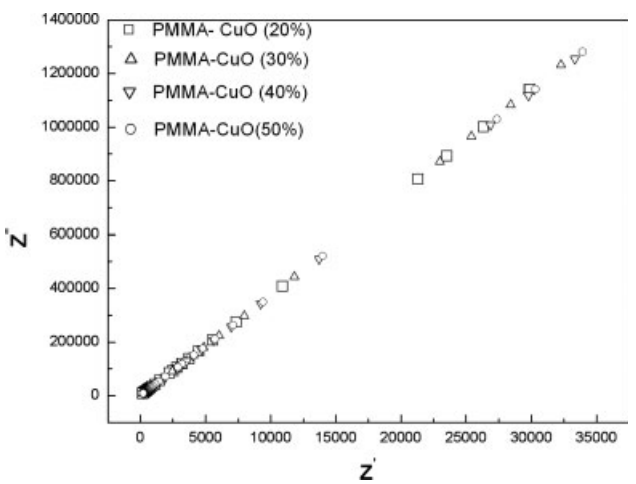

Figure 2 Variation of imaginary part (Z″) with real part (Z′) of the impedance for PMMA-CuO films.

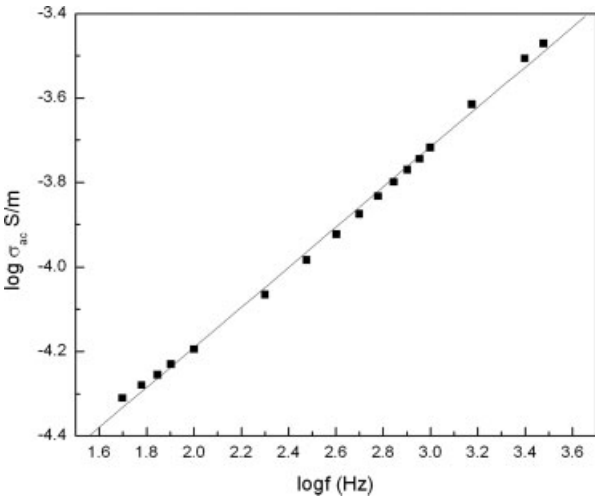

Figure 3 Variation of the (AC) conductivity (σ_{ac}) with frequency (f) for a PMMA–CuO (20%) film.

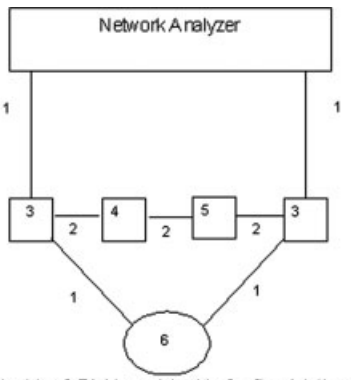

Figure 4 Experimental arrangement of the microwave Hall effect technique.

coaxial step attenuators, and a Spectrum Elecktrotechnik GmbH LS-M018-2121 (Munich, Germany) coaxial phase shifter. The canceling channel was necessary for the removal of the nonideal mode coupling.

A transverse electric with 111 mode (TE_{111}) P-band dual-mode cylindrical cavity with a radius of 1.1 cm and a height of 1.3 cm was designed and fabricated.[17] Probe coupling was chosen for the excitation of the cavity. Tuning probes were placed at each 45° to obtain mode degeneracy and orthogonality. Brass screws 2 mm in diameter were chosen for tuning. The resonant frequencies of both the primary and secondary modes may not resonate at the same frequency due to the imperfections in the cavity fabrication. To have mode degeneracy, a necessary tuning procedure is required. Tuning probes 1, 2, 3, and 4 were capacitive in nature; these were used to attain the mode degeneracy. Tuning probes 5 and 6 were resistive in nature; these were used to attain equal quality factors at both of the ports. The use of these probes ultimately led to a decrease in quality factors of the bimodal cavity. The cavity resonated at 14 GHz, and the unloaded quality factor was measured as 3109. A typical circular bimodal cavity is shown in Figure 5.

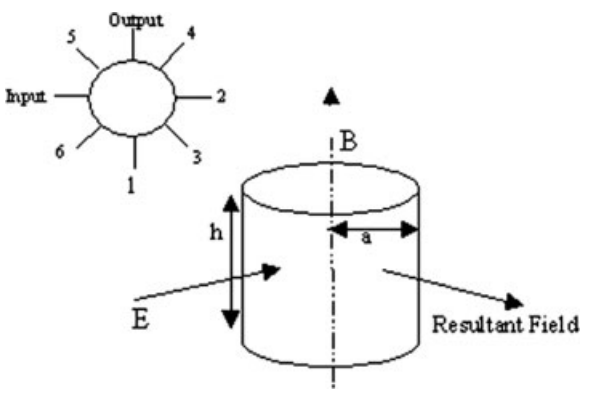

Figure 5 Schematic diagram of the transverse electric with 111 mode (TE_{111}) dual-mode degenerate cylindrical cavity.

The relation for the evaluation of the Hall mobility (μ) of the semiconductor sample at microwave frequencies for nonequal input and output coupling is given by the following equation:[18–20]

$$\mu = \frac{K}{B}\left[\left(1-\frac{Q_{11}}{Q_{10}}\right)\left(1-\frac{Q_{21}}{Q_{20}}\right)(1-\Gamma_{11})(1-\Gamma_{21})\right]^{-\frac{1}{2}} S_{21} \quad (2)$$

The previous equation can be written as follows:

$$\mu = KA\left(\frac{S_{21}}{B}\right) \quad (3)$$

where $\sigma(\omega)$ is the AC conductivity at frequency ω, $A = \left[\left(1-\frac{Q_{11}}{Q_{10}}\right)\left(1-\frac{Q_{21}}{Q_{20}}\right)(1-\Gamma_{11})(1-\Gamma_{21})\right]^{-\frac{1}{2}}$; Q_{10}, Q_{20}, Q_{11}, and Q_{21} are the unloaded and loaded quality factors at ports 1 and 2, respectively; Γ_{11} and Γ_{21} are the loaded reflection coefficients of input 1 and output 2, respectively; S_{21} is the change in the transmission coefficient; K (2.08×10^9) is the calibration constant obtained with a standard semiconductor sample; and B is the static magnetic field. The previous equation is valid only if the skin depth is greater than the thickness of the sample. One can also evaluate the conductivity data simultaneously by the previous measurements if he or she knows the geometry of the sample.

Al Zoubi[21] reported that there would be an empty cavity signal upon the application of the static magnetic field. However, in our measurements, we did not observe the empty cavity signal. Moreover, all of our samples were checked for skin depth, and we found that the skin depth was greater than the thickness of the sample.

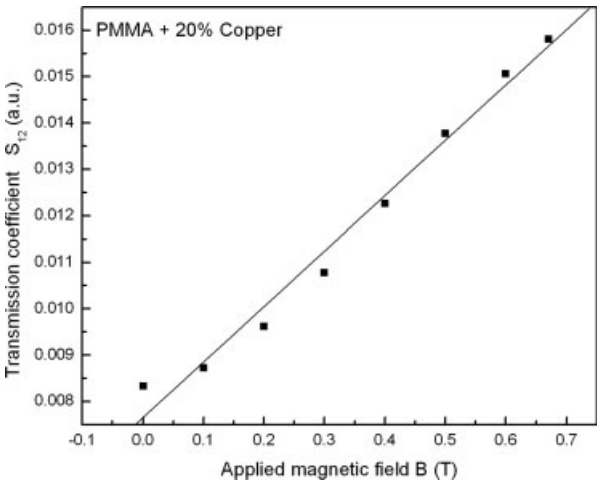

Figure 6 Variation of the transmission coefficient with the applied magnetic field for a PMMA–CuO (20%) film.

TABLE II
Data Obtained for the PMMA–Fe_3O_4, PMMA–CuO, and PMMA–Ni Films with Microwave Hall Effect Measurements

Composition of metal powder in the polymer (%)	PMMA–Fe_3O_4			PMMA–CuO			PMMA–Ni		
	A	S_{21}/B (au/Gauss)	Microwave Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	A	S_{21}/B (au/Gauss)	Microwave Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	A	S_{21}/B (au/Gauss)	Microwave Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)
20	6.39	2.00×10^{-10}	3	7.97	5.43×10^{-10}	9	6.05	1.40×10^{-9}	20
30	5.94	4.10×10^{-10}	5	4.57	4.25×10^{-10}	4	7.09	1.11×10^{-9}	16
40	5.49	6.90×10^{-10}	8	3.80	2.21×10^{-10}	2	3.35	1.89×10^{-9}	13
50	5.47	9.60×10^{-10}	11	5.04	5.10×10^{-11}	0.5	3.80	5.63×10^{-10}	5

The variation of the transmission coefficient with respect to the applied magnetic field is given in Figure 6 for the PMMA–CuO 20% composite film. A similar such variation was observed for other compositions and also for PMMA–Ni and PMMA–Fe_3O_4 films. Table II presents the value of A (which depended on the quality factor and reflection coefficient at ports 1 and 2), the change in the transmission coefficient from port 1 to port 2 in the presence of a magnetic field, and the evaluated microwave Hall mobility values from these values for the polymer composite films.

In PMMA–CuO and PMMA–Ni composite films, the microwave Hall mobility decreased with increasing amount of CuO and Ni. We already mentioned that DC conductivity increased with increasing amount of CuO and Ni and that this may have been due to the increase in the concentration of the carriers. If mobility of the carriers were assumed to remain constant with the increase in the composition of CuO or Ni, the DC conductivity would be expected to vary linearly with concentration. This means that $\sigma_2/\sigma_1 = n_2/n_1$. Therefore, for 30, 40, and 50% compositions, the values of n_2/n_1 were 1.5, 2, and 2.5, respectively, with respect to the concentration at 20%. Therefore, for both CuO and Ni additions, the values of σ_2/σ_1 were also expected to increase accordingly. However, the experimental observations indicated that the σ_2/σ_1 values were 1.21, 1.25, and 1.31 for CuO films and 1.21, 1.31, and 1.32 for Ni films. Hence, it is clear that mobility must have decreased with increasing carrier concentration. It is well known that an increase in the number of carriers will result in a higher carrier–carrier and carrier–lattice scattering rate. Because the measurements were performed at room temperature, carrier–lattice scattering dominated. This was expected to decrease the mobility of the carriers. Microwave Hall mobility measurements supported this because there was a decrease in mobility up to 90% for CuO and 75% for Ni with increasing concentration of oxide powder.

Interestingly, in the case of the PMMA–Fe_3O_4 films, the DC conductivity and microwave Hall mobility values increased with increasing Fe_3O_4 concentration. Although the increase in the conductivity was due to the increase in the number of carriers, it was also expected to increase the carrier–lattice scattering to decrease the mobility. Because Fe_3O_4 is well known to possess negative magneto resistance, the application of a magnetic field assisted the process of conduction. This increased the microwave Hall mobility values dominating the scattering process.

CONCLUSIONS

Polymer composite films (PMMA–CuO, PMMA–Ni, and PMMA–Fe_3O_4) were prepared with a spin-casting method. The DC conductivity of the films increased with increasing concentration of the dopant in all of the films. The composite films showed an increase of six orders in the electrical conductivity well above the percolation threshold. Jonscher's universal power law was used to analyze the AC conductivity of the films. The microwave Hall effect studies on the PMMA–CuO and PMMA–Ni films showed that the mobility values decreased with increasing concentration, and this was attributed to the enhanced carrier–lattice scattering. In the case of the PMMA–Fe_3O_4 films, the carrier mobility values increased with increasing concentration due to the magnetically assisted enhancement in conductivity due to the presence of Fe_3O_4.

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