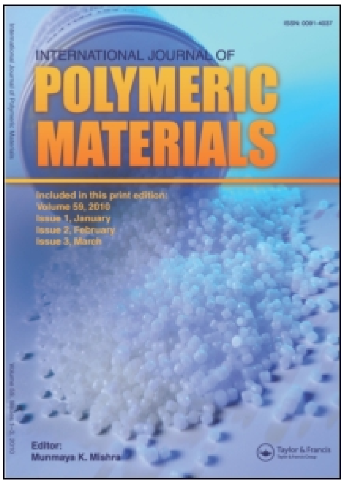

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Thermal Diffusivity of Plasma-Polymerized Polyaniline Films by Transverse Probe Beam Deflection Method

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Undoped and iodine-doped polyaniline films were prepared by radio frequency plasma polymerization technique. The dependence of the thermal diffusivity of these films on doping and the reactor pressure is investigated by transverse probe beam deflection method in the skimming configuration.

Keywords: photothermal, polyaniline, thermal diffusivity

INTRODUCTION

Conducting polymer films have been of much interest over the last couple of decades because of their role in diverse fields extending from microelectronics to sensor technology [1–5]. Many of the studies focused on the conduction mechanisms in these polymers. Most of these polymers are prepared by conventional chemical or electrochemical synthesis routes. Usually, such polymer samples are made conducting by a suitable doping process [6]. In the case of films, plasma polymerization is a widely used technique for the polymerization of organic and inorganic monomers. Among plasma polymerization techniques, radio frequency (RF) plasma polymerization enjoys the unique advantage of producing pinhole-free films. But these films

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are usually of the highly crosslinked type, unlike those obtained from the conventional chemical synthesis route.

In applications where thin films play a significant role, their thermal characteristics are of high priority, as a poor thermal design may result in a device failure. For a proper thermal design, it is desirable to have a prior knowledge of the thermal parameters of the films. An account of the heat diffusion in a film can be adequately represented by its thermal diffusivity, α, value. It is defined as the ratio of thermal conductivity to the thermal capacity per unit volume, given by $\alpha = k/\rho C$, where k, ρ and C are the respective thermal conductivity, density and specific heat capacity values of the material. There are several well-established methods for thermal characterization of a substance and some of these are nondestructive. Photothermal methods are, in general, noninvasive. Of the various photothermal methods in use, transverse probe beam deflection (PBD) technique is a superior noncontact, nondestructive method for optical and thermal characterization [7–9]. Its contactless nature makes it particularly suitable for thin films and single crystals.

Thermal diffusivity measurements constitute one of the most successful applications of the photothermal technique. This method can be applied to both bulk and thin film samples. This technique is based on the periodic heating produced by an intensity-modulated laser beam (called the pump beam) focused on to the sample surface. The induced oscillating temperature distribution gives rise to thermal waves in the sample. These waves are of the same frequency as the modulating pump beam and have wavelengths determined by the modulating frequency and the thermal diffusivity of the sample. The thermal waves propagating along the surface of the sample give rise to a refractive index gradient in the fluid medium adjacent to the sample surface. A second laser beam (probe beam) directed parallel to the sample surface is deflected at the same frequency as the thermal wave. The magnitude and phase of the deflection is closely related to the thermal wave. The thermal diffusivity of the sample can be determined from the phase data.

Polyaniline (PANI) in the bulk as well as film form is a widely probed conducting polymer because of its applications in diverse fields. Among its various forms, only one form, the partially oxidized protonated emeraldine, is conducting in the undoped condition. The electrical conductivity of PANI is tailored by different doping techniques [10]. It is well-established that doping increases the electrical conductivity by several orders of magnitude. Iodine doping is a popular technique used in the case of PANI. The variation of heat diffusion properties with doping, though relevant in thermal design, is not much explored. Also in the case of thin polymer films, the preparation conditions play an important role in determining their structure and properties. Although the film structure and composition depend primarily on the monomer, in RF plasma polymerization the deposition parameters, such as monomer flow rate, the reactor pressure, RF power and substrate temperature, are equally relevant in determining the structure as well as the thermo-physical properties of the film [11,12]. The present study is focused on investigating the dependence of thermal diffusivity of PANI films on iodine doping as well as on the monomer pressure in the reaction chamber.

EXPERIMENTAL

Preparation of Films

PANI films are prepared by RF plasma polymerization technique using a capacitively coupled plasma reactor. The reactor consists of a tubular glass chamber of about 40 cm in length and 6 cm in diameter. A tuned plate oscillator is used for generating the required RF power. Capacitive coupling is employed for delivering the RF power to the reaction chamber.

PANI films are prepared on ultrasonically cleaned glass substrate at different reactor pressures. In-situ iodine doping is employed to study the effect of doping on heat diffusion in these films.

Thermal Diffusivity Measurements

The experimental setup for the probe beam deflection method consists of a sample cell mounted on a platform attached to an XYZ translator. A 20 mW He-Ne laser (Melles Griot) delivers the pump beam at 632.8 nm. A mechanical chopper (SR 540 – Stanford Research Systems Inc.) modulates the pump beam. The probe beam is supplied by a 5 mW He-Ne laser. A bi-cell acts as the position-sensitive detector. The detected output is amplified and fed to a lock-in amplifier (SR 830 DSP—Stanford Research Systems Inc.).

PANI film on glass substrate is mounted on a sample holder and kept inside a quartz cuvette sample cell. Carbon tetrachloride is used as the coupling medium. Intensity modulated 632.8 nm radiation from the pump laser is allowed to fall on the sample. The probe beam runs parallel and close to the sample surface and is directed perpendicular to the pump beam. The probe beam gets deflected due to the thermal gradient induced in the coupling medium close to the sample surface, with deflection components both perpendicular and parallel to the sample surface. The transverse component of the photothermal signal, which is perpendicular to the pump beam and parallel to sample surface, describes the heat diffusion process parallel to the surface. This transverse component is detected by the position-sensitive detector.

The probe beam is made to scan a region on either side of the pump beam in the skimming configuration, recording the phase of the photothermal signal. In the phase method for determining the thermal diffusivity of a sample, the phase of the transverse component of the photothermal deflection signal is plotted against the pump-probe offset. A fairly linear relation exists between the phase of the deflection signal and the offset [13,14]. Thermal diffusivity α is obtained from the slope of this plot as $\alpha = \pi f/m^2$, where f is the modulating frequency and m is the slope of the graph.

RESULTS AND DISCUSSION

The phase – offset plot for undoped PANI film prepared at reactor pressure 0.4 mbar is shown in Figure 1. The value ($4.377\times 10^{-7}\, m^2s^{-1}$) of thermal diffusivity obtained is much smaller than the corresponding value for the bulk sample prepared by the conventional chemical synthesis. This reduction is in agreement with the general observation that heat diffusion in thin films is impeded by several factors.

The variation of phase of the photothermal signal with pump-probe offset for iodine-doped film is shown in Figure 2. The value

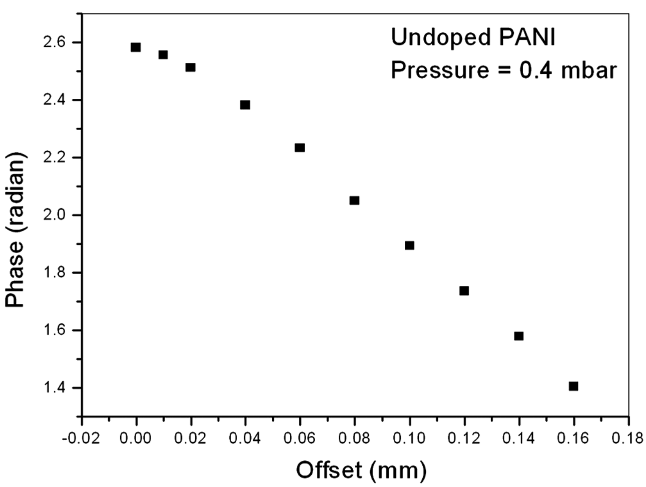

FIGURE 1 Phase – offset plot for PANI prepared at 0.4 mbar.

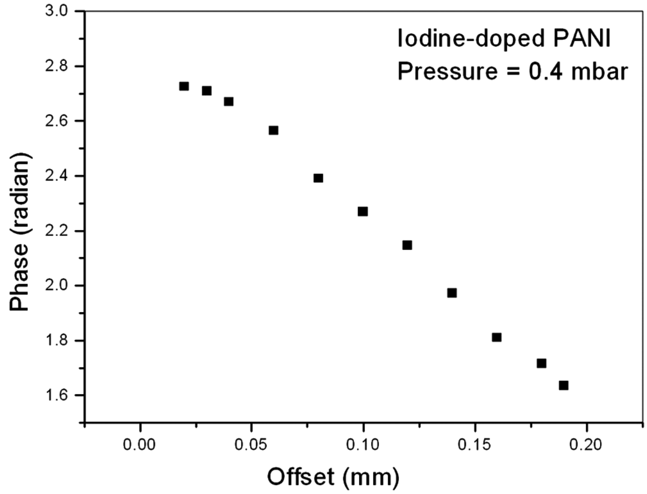

FIGURE 2 Phase – offset plot for iodine-doped PANI prepared at 0.4 mbar.

($3.487 \times 10^{-7}\,m^2s^{-1}$) of thermal diffusivity obtained in this case is smaller than that in the undoped case. This reduction is in contrast to the general observation of enhancement in electrical conductivity of the film upon doping with iodine. The presence of iodine in the film increases the electrical conductivity, whereas it contributes to

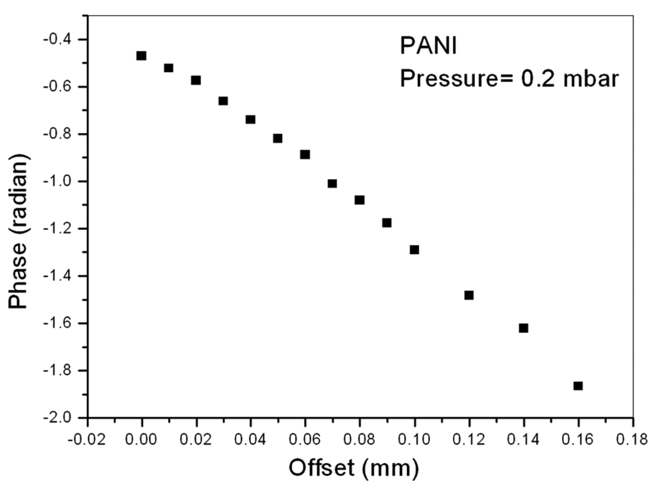

FIGURE 3 Phase – offset plot for PANI prepared at 0.2 mbar.

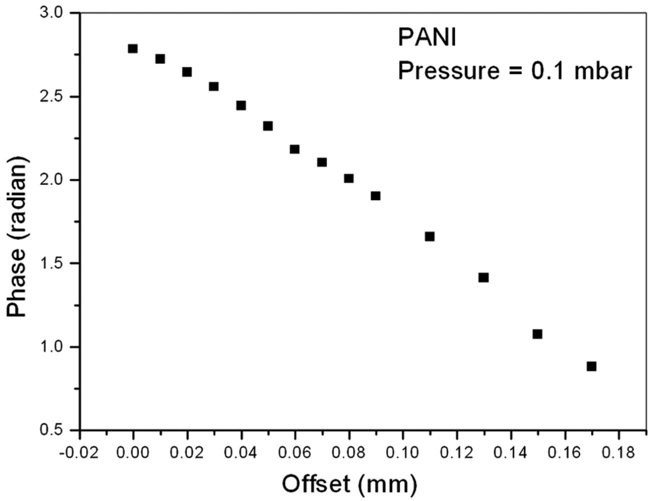

FIGURE 4 Phase – offset plot for PANI prepared at 0.1 mbar.

considerable phonon scattering, resulting in a decrease in heat conduction in the film.

The plots for PANI films prepared at reactor pressure 0.4, 0.2, 0.1, and 0.06 mbar are shown in Figure 1 and Figures 3–5 respectively. The thermal diffusivity values obtained in these cases are given in Table 1.

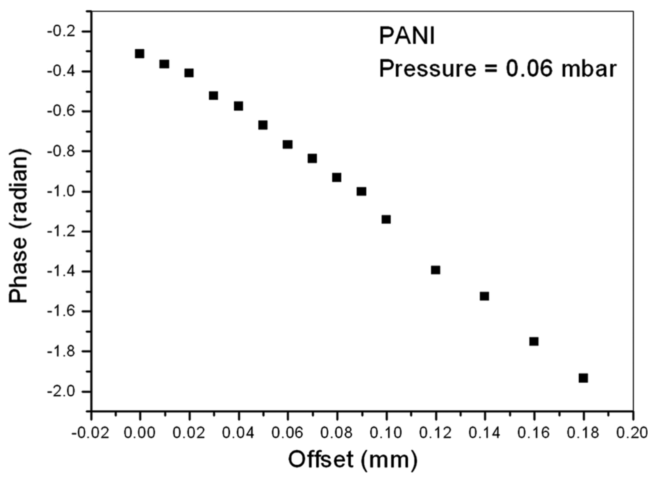

FIGURE 5 Phase – offset plot for PANI prepared at 0.06 mbar.

TABLE 1 Variation of Thermal Diffusivity with Reactor Pressure

Pressure (mbar)	0.4	0.2	0.1	0.06
α ($\times 10^{-7}\,m^2s^{-1}$)	4.377	3.653	2.399	2.187

A close examination of the values reveals a marked reduction in the diffusivity value at 0.1 mbar. A general feature of most of the RF plasma polymerized films is their highly crosslinked nature. Also there is higher fragmentation at lower pressures. The marked reduction in diffusivity value for films prepared at lower pressures is attributed to the above two factors. This establishes the fact that film properties, particularly thermal properties, depend on the preparation conditions.

CONCLUSIONS

PANI films were prepared by the RF plasma deposition technique. Thermal diffusion in undoped and iodine-doped films was explored by photothermal beam deflection method. In contrast to the behavior of electrical conduction, heat diffusion is found to be dampened in iodine-doped samples. The presence of iodine in the PANI structure reduces heat diffusion by enhanced phonon scattering at these sites, with no electronic contribution to thermal conductivity.

In agreement with the fact that the various deposition parameters can affect the structure and properties of plasma-polymerized films, the present study points to a decrease in the diffusivity value at low reactor pressures. This reduction is attributed to changes in the basic nature of the film at low pressure. As is evident from the plot, the variation of thermal diffusivity with pressure is not uniform. There is a marked decrease in the value of thermal diffusivity when the pressure is reduced from 0.2 to 0.1 mbar. Higher degrees of fragmentation and crosslinking are the possible causes that lead to this reduction in thermal diffusivity at low values of reactor pressure.

REFERENCES

[1] Nagagawa, K., *J. Appl. Polymer Sci.* **41**, 2049 (1990).
[2] Koike, Y., Nihei, E., Tanio, N., and Ohtsuka, Y., *Appl. Opt.* **29**, 2686 (1990).
[3] Pei, Q., Yang, Y., Yu, G., Zhang, C., and Heeger, A. J., *J. Am. Chem. Soc.* **118**, 3922 (1996).
[4] Yue, J. and Epstein, A. J., *J. Chem. Soc., Chem. Comm.* **21**, 1540 (1992).
[5] Tsumura, A., Koezuka, H., and Ando, T., *Synth. Met.* **25**, 11 (1988).

[6] Bott, D. C. and Skotheim, T. A. Eds. (1986). *Handbook of Conducting Polymers*, Marcel Dekker, New York, pp. 1191.
[7] Boccara, A. C., Fournier, D., and Badoz, J., *Appl. Phy. Lett.* **36**, 130 (1980).
[8] Jackson, W. B., Amer, N. M., Boccara, A. C., and Fournier, D., *Appl. Opt.* **20**, 1333 (1980).
[9] Salazar, A., Sanchez-Lavega, A., and Fernandez, J., *J. Appl. Phys.* **69**, 1216 (1991).
[10] Bhat, N. V. and Joshi, N. V., *Plasma Chem. Plasma Process* **14**, 151 (1994).
[11] Shi, F. F., *Surf. Coat. Technol.* **82**, 1 (1996).
[12] Kim, H. Y. and Yasuda. H. K., *J. Vac. Sci. Technol. A* **15**, 1837 (1997).
[13] Bertolotti, M., Li Voti, R., Liakhou, G., and Sibilia, C., *Rev. Sci. Instrum.* **64**, 1576 (1993).
[14] Bertolotti, M., Li Voti, R., Liakhou, G., and Sibilia, C., *Rev. Sci. Instrum.* **66**, 277 (1995).