Progress In Electromagnetics Research M, Vol. 18, 197–207, 2011

DETERMINATION OF OPTICAL TRANSMISSION LOSS IN POLY (3-METHYL THIOPHENE) THIN FILM PLANAR WAVEGUIDE: EFFECT OF VAPOUR CHOPPING

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Abstract—This article reports the effect of vapour chopping technique on the properties of vacuum evaporated poly (3-methyl thiophene) thin films such as surface morphology, optical transmittance, band gap, refractive index and optical transmission loss. Vapour chopping gives smooth surface morphology with smaller grain size reduced roughness than non chopped thin films, while the transmittance of the thin film increases with simultaneous decrease in the refractive index, band gap and optical transmission loss decreases due to vapour chopping.

1. INTRODUCTION

Conducting polymers have been studied extensively during the last two decades as an important semiconductor material because of their interesting chemical and physical properties [1–3] useful for various applications. A characteristic feature is that the conductivity of these polymers can be varied from conducting to insulating range by means of proper doping. Polythiophenes distinguished as promising materials among various classes of conducting polymers, because of their good thermal and chemical stability, as well as of their optical and electronics properties, useful for various device applications such as LED [2],

Received 25 March 2011, Accepted 31 May 2011, Scheduled 8 June 2011
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field effect transistors [3], optical waveguides [4], in optoelectronic devices [5], photovoltaic and photoconductive devices and optical modulator devices [6]. Polythiophenes have also been exploited in sensor applications [7]. Due to the poor solubility of this polymer the commercial applications of unsubstantiated polythiophenes are limited [2], also the presence of inert sulphur atom in thiophene increases the oxidation potential which makes the preparation of polythiophene more difficult [7]. Alkyl substituted polythiophenes are soluble in most organic solvents, besides alkyl substituents strongly influences the polythiophenes properties. It is reported that alkyl substituted polythiophenes shows good environmental stability [8]. Poly (3-methylthiophene) belongs to polythiophene family having good chemical and environmental stability. Although a lot of work has been done on the synthesis of poly (3-methylthiophene), there are very few reports available on vacuum deposition of poly (3-methyl thiophene) thin films and their optical properties. Also to the author's knowledge the study of the refractive index of poly (3-methyl thiophene) thin films is not reported yet. Several methods are available for the polymerization of poly (3-methylthiophene) among which the simple chemical oxidation polymerization of poly (3-methylthiophene) with iron chloride in chloroform gives soluble, high molecular weight compounds with high yield. [9], also it has been reported earlier that the nature of the dopant plays an important role in changing the properties of poly (3-methylthiophene) [10].

In an optical communication system light transports the information between different users by means of various devices modulators, detectors, and demodulators which can be mounted on single substrate, and such planar substrate is known as the planar waveguide which is the basic element of integrated optics. Series of waveguide transitions where the cross section of a waveguide structure changes in the direction of optical propagation are widely used in the design of integrated optical circuits, for example, junctions, tapers, and branches [11, 12], also in thermo-optic switches [13]. It consists of two layers with slightly different refractive indices the optical signal guides along the higher refractive index layer by means of total internal reflection. The aim of this work is to reduce the optical transmission loss in the poly (3-methyl thiophene) and to use it in the development of integrated optics.

In the present article the properties of poly (3-methylthiophene) thin films prepared by vacuum evaporation are reported, and the effect of the vapour chopping technique on the properties of poly (3-methylthiophene) such as surface roughness, transmittance, band gap and refractive index and optical transmission loss are reported.

2. EXPERIMENTAL PROCEDURE

Poly (3-methylthiophene) was synthesized by an oxidation polymerization method using iron chloride discussed elsewhere [3]. The monomer solution was obtained by dissolving 0.25 M of (3-methylthiophene) (AR, Alfa Aesar) in 100 ml of chloroform. The oxidant solution was prepared by dissolving 0.75 M of $FeCl_3$ (Sd-Fine) in 100 ml chloroform which was kept under constant stirring for half hour, in which the monomer solution of thiophene was added drop wise for 8 hours, under nitrogen atmosphere and constant stirring. After complete addition of the monomer the reaction mixture was kept at room temperature under constant stirring for 24 hours. The dark brown precipitate of poly (3-methyl thiophene) was formed and a known quantity of methanol was poured in the precipitate. The precipitate was further washed by methanol, chloroform and HCl repeatedly to remove residual oxidant and unreacted monomer and collected in a filter paper. During this process the dark brown colour of precipitate changes to brown, then the precipitate was deprotonized by 0.5 M ammonia, the precipitate was further washed with 0.5 M of HCl, acetone and chloroform. The obtained poly (3-methylthiophene) powder was dried under vacuum at 60°C for 24 hours.

The poly (3-methyl thiophene) thin films were deposited by using resistive heating vacuum deposition technique at 10^{-3} Torr on glass substrates (refractive index $\sim$ 1.515) placed on substrate holder at a distance 12.5 cm from the substrate material. The deposition was taken for 6 minutes with deposition rate 3–4 A°/S. The effect of vapour chopping [14] was studied for poly (3-methyl thiophene) thin films. The vapour chopping technique consists of a vane of thin metal sheet of aluminium cut into circular shape of 10 cm diameter. This circular sheet was given a V-cut (155°) shape. This thin circular vane was fixed to a light aluminium rod of 6.5 cm height. This aluminium rod was attached to the shaft of 3 V DC motor having a broad base so that it could be kept inside the vacuum system. The variable power supply of 0–4 V (DC) was used to vary the voltage by means of which the speed of rotation could be controlled and hence the chopping speed. Chopper provides growth flux interruption at constant rate. The speed of the rotation of the chopper was $\sim$ 5–6 rot/sec.

FTIR spectra of poly (3-methylthiophene) powder and thin films were recorded by using a Perkin-Elmer's Spectrum Spectrophotometer in the range of 400–4000 cm^{-1}. For FTIR, these films were scratched from glass substrate and mixed with KBr. The optical absorption in the wavelength range 350–850 nm of poly (3-methylthiophene) thin films was measured by UV-vis spectrophotometer (U-2800, Hitachi, Japan). Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) technique were used for surface morphology inspection. Thickness of the film was ($\sim$ 1000 A°) as measured by Tolansky interferometric method, the error in the thickness is ($\sim$ 15 to 25 A°). While the refractive indices of the thin films were determined by Abele's method [15] as well as analytical method [16]. The optical transmission loss was measured by prism coupling technique [10]. Three identical films of nonchopped and vapour chopped were used for the present study. The refractive index and optical transmission loss was measured for 5 times for each nonchopped and vapour chopped films (i.e., 15 times).

3. RESULT AND DISCUSSIONS

The FTIR spectra of the vapour chopped and nonchopped poly (3-methyl thiophene) thin films are as shown in Fig. 1. The peak at 3408 cm^{-1} in both vapour chopped (VC) and nonchopped (NC) films is due to humidity in KBr [17]. The low intensity peaks located at 2926 cm^{-1} and 2850 cm^{-1} are assigned to C-H symmetric and C-H asymmetric stretching vibrations respectively.

The bands at 1631 cm^{-1} and 1448 cm^{-1} in nonchopped thin films were slightly shifted in the vapour chopped thin films at 1640 cm^{-1} and 1446 cm^{-1} representing C = C symmetric and asymmetric stretching vibrations in poly (3-methyl thiophene) [1], this shift may be due to cross-linking of polymers [18] during deposition which can be seen from AFM images. The range of 600–1500 cm^{-1} is the finger print region of

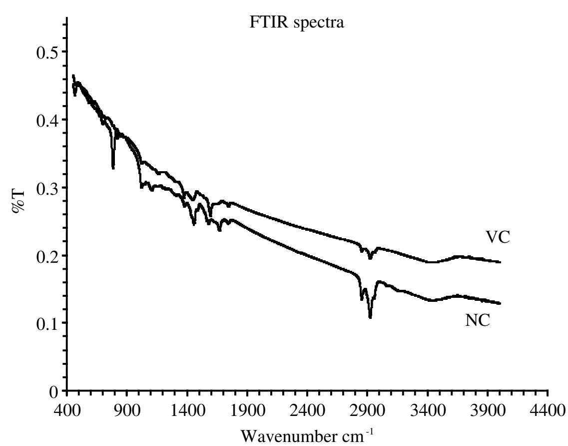

Figure 1. FTIR spectra of poly (3-methylthiophene) thin films.

poly (3-methyl thiophene), an extra absorption band was observed in the case of vapour chopped films at 1156 cm^{-1} representing the out-of-plane deformation in poly (3-methyl thiophene), and the band at 1014 cm^{-1} and 1025 cm^{-1} are produced by C-H wagging vibrations. The peak at 814 cm^{-1} in nonchopped and at 819 cm^{-1} in vapour chopped film corresponds to C-S stretching vibrations [19], where as the peak at 604 cm^{-1} in nonchopped film assigned to C-S-C ring deformation [19] is slightly shifted to 617 cm^{-1} in the vapour chopped thin films.

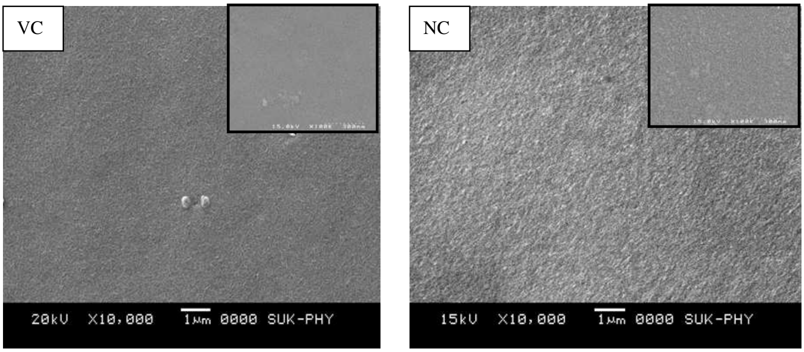

Figure 2. SEM images of poly (3-methylthiophene) thin films (inset FESEM images).

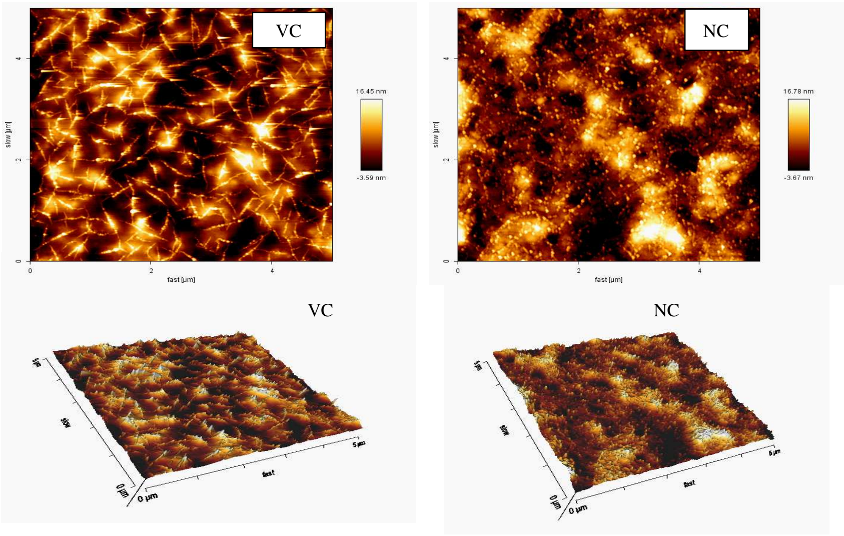

Figure 3. AFM images of poly (3-methyl thiophene) thin films.

Figure 2 shows the SEM images of vapour chopped and non chopped poly (3-methyl thiophene) thin films. The vapour chopped thin films shows more smooth surface morphology with reduced grain size. It is seen that the roughness of the vapour chopped thin films is lesser as compared to the nonchopped thin films.

Nonchopped thin films consist of rounded grains [20] while in the vapour chopped thin films clear indication of the cross-linking of polymer chain with presence of short chain oligomers with rounded grains with smaller size is observed (Fig. 3). The nonchopped thin films show large scattered grains showing nonuniform deposition. It is seen that the roughness of the vapour chopped thin films is lesser

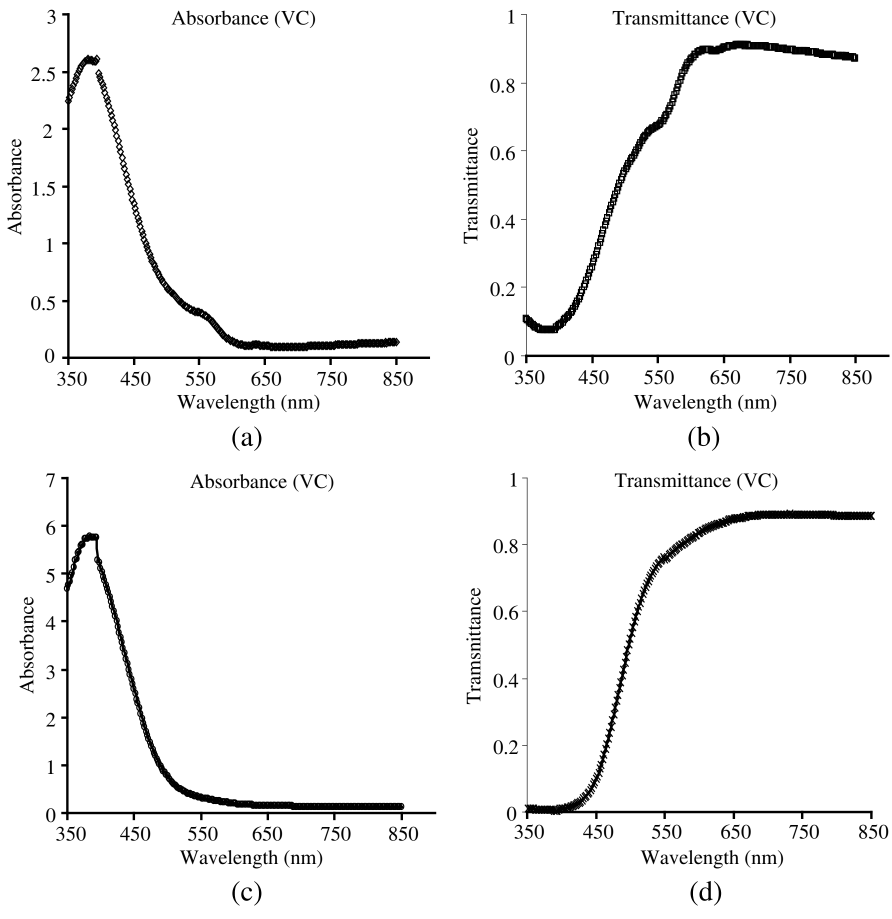

Figure 4. Absorbance and transmittance spectra of poly (3-methyl thiophene) thin films.

as compared to the nonchopped thin films. The grain size is observed $\sim$ 16 nm for nonchopped and 13 nm for vapour chopped thin films. Which is smaller than the electrochemically prepared poly (3-methyl thiophene) thin films having grain size 0.1–0.3 μm [21].

The optical absorption of the poly (3-methyl thiophene) thin films in the range of 350–850 nm is illustrated in Fig. 4. In this figure the absorption peak observed at 398 nm in nonchopped [4(c)] thin film is due to π–π^* transitions in thiophene ring [22], while it shifts at 392 nm in the vapour chopped films [4(a)]. The absorption peak in the vapour chopped thin films at 553 nm is due to molecular electronic transitions due to short chain oligomers. The transmission of the vapour chopped and non chopped thin films of P3MeT are also shown in Figs. 4(b) and 4(d). From the figure it can be seen that the vapour chopped thin films show higher transmittance as compared to the nonchopped thin films.

Figure 5 shows the graph of $(\alpha thv)^2$ as a function of hv. From the absorption data, the band gap energy was calculated using formula

$$\alpha = [\alpha_o(hv - Eg)^n]\,(hv) \tag{1}$$

where 'Eg' is the separation between bottom of the conduction band and top of the valence band, α — absorption of thin film and α_o — a constant (independent on photon energy hv) and n is a power factor. The value of Eg is obtained from the plot of $(\alpha thv)^2$ Vs hv. Where "t" — the thickness of the film and hv — photon energy. The observed values of band gap of poly (3-methyl thiophene) thin films are tabulated in Table 1. From the table it is seen that there is a decrease in the band gap of the poly (3-methyl thiophene) thin films due to vapour chopping.

The refractive indices (n) of the nonchopped and vapour chopped poly (3-methyl thiophene) thin films were measured by Abele's

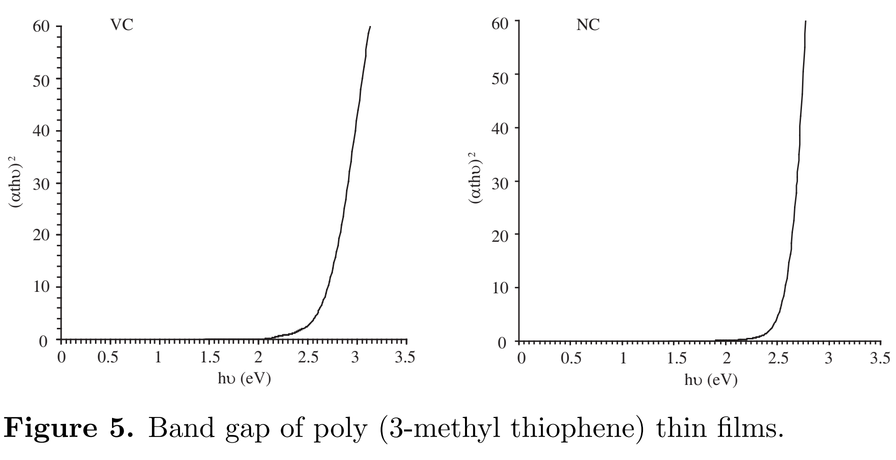

Figure 5. Band gap of poly (3-methyl thiophene) thin films.

Table 1. Refractive index, band gap and optical transmission loss of poly (3-methyl thiophene) thin films.

Poly (3-methy 1 thiophene) thin film thickness ($\sim 1000\,\text{A}^\circ \pm 20\,\text{A}^\circ$)	Refractive Index		Band Gap	Optical Transmission Loss dB/cm
	Analytical method	Abele's method		
Vapour chopped	1.82 ± 0.007	1.71 ± 0.005	2.64 ± 0.004	4.28 ± 0.02
Nonchopped	1.89 ± 0.006	1.80 ± 0.006	2.71 ± 0.003	3.94 ± 0.02

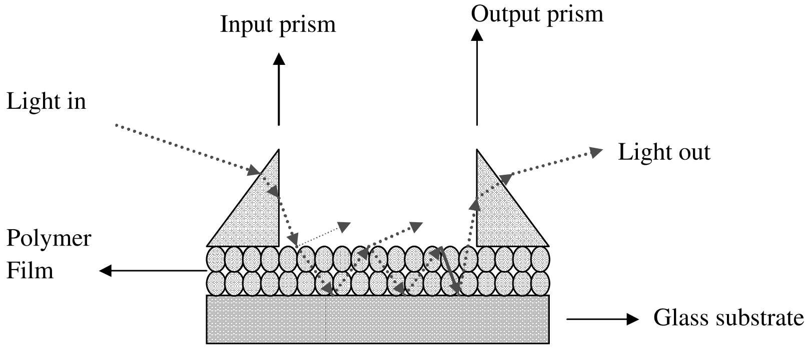

Figure 6. Schematic representation of prism coupling method.

method [15] and also calculated by using analytical method using following formula [16]. Three identical nonchopped and vapour chopped thin films were used for the calculation of the refractive index and the reported values of the refractive indices are the average values of these measurements.

$$n = \left[\frac{n_s^2 T_f + n_s\left(1 + \sqrt{R_f}\right)^2}{T_f + n_s\left(1 - \sqrt{R_f}\right)^2}\right]^{1/2} \tag{2}$$

where, n_s is refractive index of the substrate, T_f is transmittance, R_f is reflectance.

The refractive index values of the vapour chopped and nonchopped thin films are tabulated in the Table 1. Vapour chopping strongly affects the refractive index of the thin films; it is observed that there is decrease in the refractive index of the vapour chopped thin films.

The Figure 6 shows the schematic representation of the prism coupling method for the measurement of optical transmission loss [23]. This set-up consisted of He-Ne laser (632.8 nm), spectrometer, polarizer, two special prisms, prism mount and detector. The two were right angled prisms made of extra dense glass with refractive index of 1.79. The prisms were at a distance of 1.5 cm from each other. Only the lowest mode number $m = 0$ has been studied. Precise adjustment of angle of incidence for obtaining $m = 0$ mode was done. This was done after obtaining the m lines on the screen and adjusting the bright spot for the largest angle of incidence. The input prism was set stationary and prism table rotated for accurate identification of the angle for $m = 0$ mode. The input light intensity was measured at the region of the coupling spot where actual launching into waveguide takes place. The intensity was measured in terms of current through a photo diode. The calculated values of optical transmission loss are tabulated in Table 1. The reported value of optical transmission loss includes the prism coupling loss. Three identical vapour chopped and nonchopped films were used for this study. The Optical Transmission Loss was calculated for 5 times for each of nonchopped and vapor chopped film (i.e., 15 times for vapour chopped and 15 times for nonchopped) and the reported value is the average of these 5 values. The error obtained in this measurement is ± 0.02. The difference of optical transmission loss between vapour chopped and nonchopped film is 0.33 which is higher than error obtained in the measurement.

The optical transmission loss was calculated using formula

$$\text{OTL} = 10 \log (\text{Input intensity})/(\text{output intensity})\, \text{dB/cm}. \qquad (3)$$

4. CONCLUSION

The poly (3-methylthiophene) thin films were successfully deposited by vacuum evaporation. Vapour chopping technique gives smooth surface morphology and reduces scattering losses. The grain size of both vapour chopped and non chopped poly (3-methyl thiophene) thin films obtained was observed small (16 nm and ~ 13 nm). The increase in the transmittance and decrease in the refractive index also the decrease in the optical transmission loss (OTL) of the vapour chopped thin films may be useful for the waveguiding applications and fabrication of optoelectronics devices.

ACKNOWLEDGMENT

The author S. V. Kamat is thankful to Council of Scientific and Industrial Research (CSIR) for the award of Senior Research Fellowship (SRF). One of the authors Vijaya Puri gratefully acknowledges the award of Research Scientist from University Grant Commission (UGC), India.

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