

Synthesis, DC conductivity and dielectric properties of rf-plasma polymerized poly (3-methyl thiophene) thin films

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ABSTRACT

The thin films of Poly (3-methyl thiophene) on glass substrate are prepared by rf plasma polymerization method. The Arrhenius plot of DC conductivity shows straight line behaviour. The optical properties as UV-visible absorption and reflection studies, optical band gap and refractive index studies have been carried out on these samples. The refractive index of the films is determined to be 1.49, dielectric constant 2.24 and band gap to be 2.49 eV at a wavelength 620 nm in the visible region. To check the surface uniformity SEM studies have been carried out of thin films. XRD shows the amorphous nature of Poly (3-methyl thiophene) thin films.

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Introduction:

Semiconducting polymers have potential applications in various optical, electronic and optoelectronic and sensory devices [1-3]. These polymers can be synthesized by chemical polymerization which results in powders of these polymers. But device applications always need films [4]. Many of these polymer powders are insoluble in common organic solvents which makes their processability difficult. Plasma polymerization is a novel method to achieve thin films of these polymers, including those polymers which cannot be synthesized under normal chemical conditions. Plasma polymerization can be done using DC, AC and RF plasma methods [5-9]. Generally these films show stable physical and chemical characteristics due to their high cross-linking nature [6]. Input power and deposition time affect the morphology, thickness and structural characterization of these films [10]. Recently polyaniline thin films were prepared by RF-plasma polymerization and characterized by various techniques like XRD, FTIR, UV-Visible absorption and reflection, ellipsometry and SEM [11]. Plasma polymerized materials are characteristic of being highly cross-linked and amorphous. The band gap is found to lie between 1.4 to 2.5 eV, indicating semiconducting behavior of the

samples [12- 15]. In the present work we incorporated suitable modification in the RF-sputtering set up for synthesis of plasma polymerized poly (3-methyl thiophene) films. The films are characterized by FTIR, XRD, UV-Vis spectroscopy and Ellipsometry.

Experimental:

Plasma polymerized thin films of poly (3-methyl thiophene) on ultrasonically cleaned glass substrates were obtained by polymerizing 3-methyl thiophene monomer (99.9 % purity) under radio frequency (rf) plasma discharge in a home built set up. This is a custom-manufactured glass deposition chamber, coupled to a vacuum system, RF amplifier and a monomer feed-through set up. For maximum deposition, a novel set up has been designed. The position from where evacuation takes place and the position of monomer feed through from where monomer is injected into the chamber are crucial in this set up; a schematic of which shown in figure 1. The system was evacuated to lower than 10⁻³ torr and argon gas was introduced into the chamber for plasma pre-treatment for 20 s. The RF power applied was 15 W for about 1 h. Fragmentation of monomer takes place because of the Ar plasma created between the electrodes. The conditions of polymerization have been standardized and optimized and it has been found that

good quality films can be deposited under a certain monomer vapour pressure. The deposition rate is estimated to 3.33 nm/min and under constant deposition conditions, the thickness of the film is estimated to be 200 nm by ellipsometry [16, 17]. The DC conductivity measurements have been carried out for the thin films of material at 305-398 K temperature range at a constant voltage of 1.5 V in a vacuum of 10^{-3} torr in the specially designed metallic sample holder. The resultant current is measured with a pico-ammeter. Silver electrodes have been used for electrical contacts. UV-Visible Spectroscopy of the samples has been carried out using CamSpec M550 double beam UV-Visible Spectrophotometer. FTIR has been carried out by using NEXUS-670 FTIR spectrometer of thin films of poly(3-methyl thiophene), deposited on Si substrate (polished from both the sides). X-ray diffraction (XRD) studies have carried out by using a Panalytical (PW 3710) X-ray powder diffractometer with Cu K α radiation. The sample is scanned in angular range of 0-700 with scan speed of 0.020/s under similar conditions.

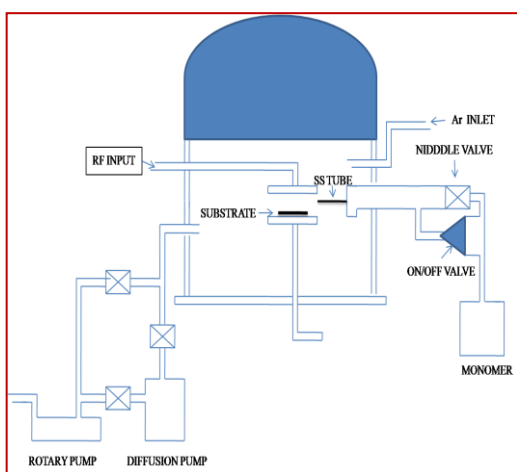


Figure 1. the RF-plasma polymerization set up.

Results and discussion:

DC conductivity:

For semiconducting materials, the DC conductivity can be expressed by Arrhenius relation [18]

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E_a/kT) \quad (1)$$

Here ΔE_a is the activation energy, σ_0 is the pre exponential factor related to the material, k is known as Boltzmann constant and T is the temperature. The value of the activation energy (ΔE_a) is estimated with the help of the slope of $\ln\sigma$ versus $1000/T$ plot. Figure 2 shows the dependence of $\ln\sigma$ on $1000/T$. The slope of the curve is estimated by using the linear fit [19-21]. The Plasma

polymerized thin films of poly (3-methyl thiophene) shows a higher conductivity (1.33×10^{-6} S/cm); this may due to the fact that during RF plasma polymerization, a large amount of energy is deposited to the target system within a small period of time along the ion path (track). The energy is so high that it can break all the chemical bonds along the track. The energy dissipates to the surrounding regions within a few nanoseconds. This energy leads to bond breaking, chain scissoring, cross-linking, radical formation, etc., which in turn cause molecular rearrangements in the polymer. Collective excitation (plasmons), which produces a large excited volume resulting in coercive interaction among the ions and radical pairs produced in the adjacent chains within the volume as a result of an electron stopping mechanism, is responsible for cross-linking of the polymer chains. Inter-chain electron hopping required for conduction between two chains is facilitated due to the cross-linking of the polymer chains after RF plasma polymerization. Defect sites in the molecular structure of the polymer chain created by RF plasma polymerization also contribute to higher dc conductivity as charge accumulation takes place, which produces charge carriers. In poly (3-methyl thiophene), the dominating charge carriers are polarons and bipolarons [22-24].

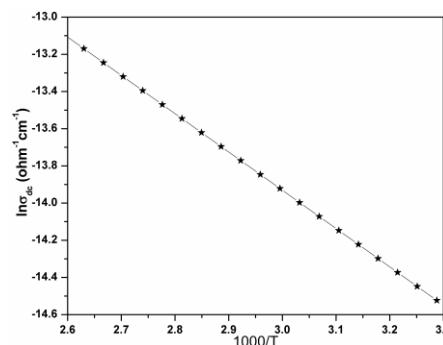


Figure 2. DC conductivity of plasma polymerized poly (3-methyl thiophene)

UV-Visible studies:

The UV-Visible absorption spectrum of poly(3-methyl thiophene) thin films is given in figure 3. The increase in absorption coefficient with wavelength and broadening of absorption peak shows the increase in conjugation and the widening of spectrum of the polymer films. From UV-Visible absorption spectrum the optical band gap has been measured by Tauc's relation [16, 17],

$$(\alpha h\nu) \propto (h\nu - E_g)^n \quad \text{where } n=1,2,3,\dots \quad (2)$$

'E_g' is the optical band gap. At the fundamental edge of amorphous materials two types of optical transitions can take place. In both types of optical

transitions, the photon interacts with the electron in the valence band and raises it to the conduction band. There is no interaction with lattice in the direct transition and the photon interacts with lattice in indirect transition. In the given equation 'n' decides the transition, for $n = 1/2$ the transition is direct allowed, $n = 2$ for indirect allowed transition, $n = 3$ for indirect forbidden and $n = 3/2$ for direct forbidden band gap. After applying all values of n, for the composites $n = 2$ indirect transition is found most suitable to calculate the band gap. α is given by,

$$\alpha = O_d/t, \quad (3)$$

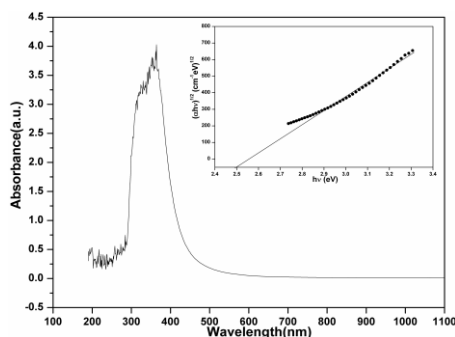


Figure: 3. UV-Visible absorption spectrum of poly (3-methyl thiophene)

where O_d is the optical density measured at a given film thickness (t), and the extinction coefficient (k) is given by

$$k = \alpha \lambda / 4\pi, \quad (4)$$

where λ is wavelength of incident photon. The optical band gap of poly (3-methyl thiophene) thin films have been measured by plotting $(\alpha hv)^{1/2}$ versus energy and extrapolating the linear portion of $(\alpha hv)^{1/2}$ to zero [17]. The peak around 361 nm is attributed to strong inter band $n-\pi^*$ transition, due to excitation in the aromatic ring. The other humps in the graph are attributed to $\pi-\pi^*$ transitions [25, 26]. The optical band gap is determined from the absorption spectrum. The value of k estimated at 420 nm is around 0.125. The allowed indirect transition optical gap is found to be 2.49 eV for the poly (3-methyl thiophene) films.

The UV-visible reflection spectrum is given in figure 4. From reflection and absorption spectra the refractive index, dielectric constant and dielectric loss in the visible region were measured by the following relations

The refractive index (n) has been determined by using following relation

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2] \quad (5)$$

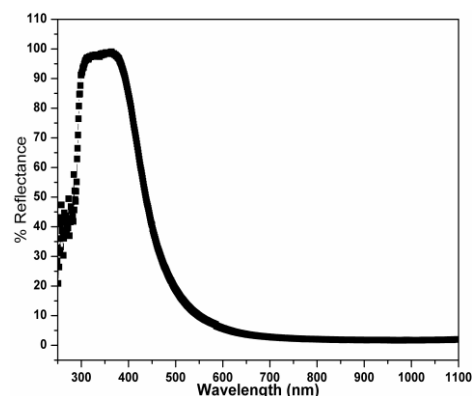


Figure: 4. UV-visible reflection spectrum of poly (3-methyl thiophene)

The values of dielectric constant (ϵ') and dielectric loss (ϵ'') are estimated by using the following relations [11, 18]

$$\epsilon' = n^2 - k^2 \quad (6)$$

$$\text{and } \epsilon'' = 2nk \quad (7)$$

The optical parameters have been plotted versus photon energy in figures: 5 (a, b, c). The value of refractive index at 640 nm is 1.498 and optical dielectric constant is 2.24. The value of refractive index measured by ellipsometry is 1.499 which matches well with value extracted from reflection spectra. From the reflectance data in figure 3, it is clear that the reflectance is constant in the wavelength range of 600 nm to 1100 nm. The dielectric constant has low value (2.24) in this range. So, these films will have applications in fabricating Schottky devices, storage batteries, LEDs, sensors, super-capacitors and for EMI shielding. The dielectric loss increases with increase in photon energy as shown in figure 4.

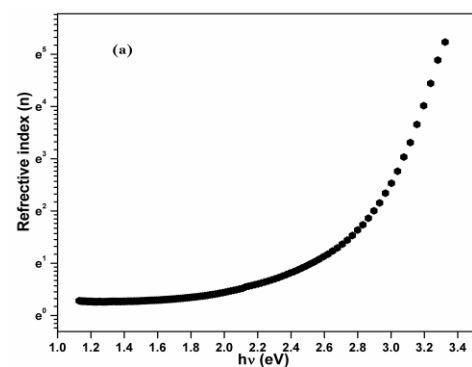


Figure: 5(a). Energy vs. Refractive index

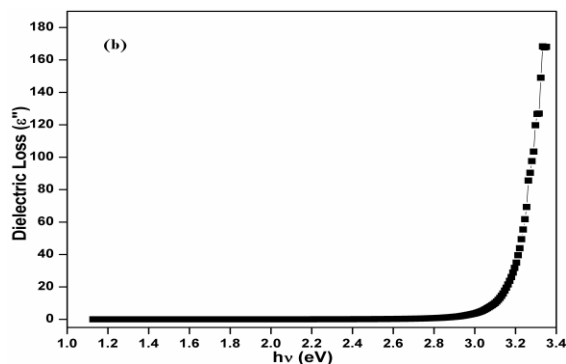


Figure:5(b). Energy vs. Dielectric loss

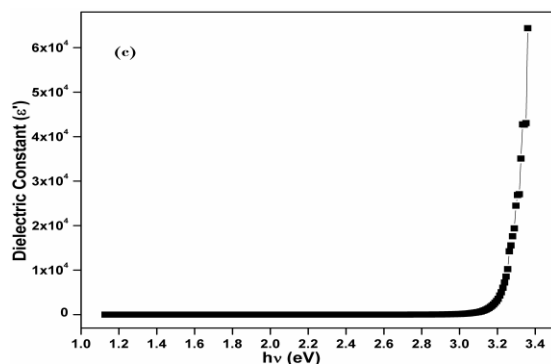


Figure: 5(c). Energy vs. dielectric constant.

SEM and XRD Studies:

SEM image of thin poly (3-methyl thiophene) film prepared on glass substrate is shown in figures 6. It is clear from the figure that the film has uniform morphology. From XRD spectra in figure 7, it is clear that the sample prepared is completely amorphous. This is due to the high cross-linking of the prepared polymer film. There are two amorphous humps observed in the diffraction pattern around 20.50, which represent poly (3-methyl thiophene) peaks from JCPDS data.

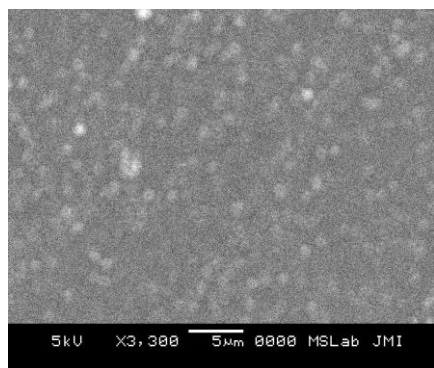


Figure: 6. SEM image of thin poly (3-methyl thiophene)

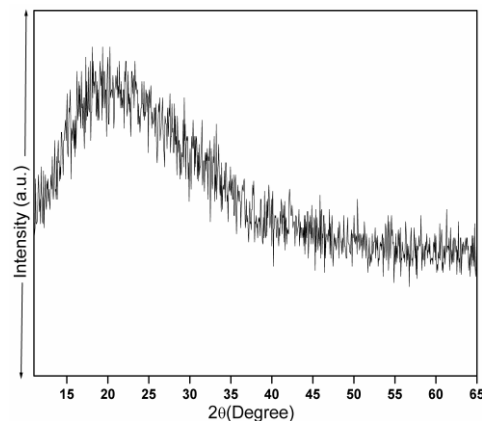


Figure: 7. XRD spectra of thin poly (3-methyl thiophene)

Conclusions:

Poly (3-methyl thiophene) thin films are successfully prepared by rf-plasma polymerization method without using any carrier gas. The film prepared has thickness 200nm and the deposition rate is estimated to be 3.33 nm / min. The amorphous nature of the sample is confirmed by XRD. The optical band gap of the polymer determined from UV-absorption spectra is 2.49 eV. The refractive index of the sample is 1.49 and optical dielectric constant is 2.24 in the visible region. The dielectric loss increases with increase in the photon energy in the visible region. The SEM image shows a uniform film.

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