Electrical and optical properties of plasma-polymerized \(N,N,3,5\)-tetramethylaniline thin films

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Abstract. Plasma polymerization is a versatile and important technique for depositing uniform, pinhole-free and flawless thin films of organic materials. So plasma-polymerized \(N,N,3,5\)-tetramethylaniline (PPTMA) thin films were deposited onto glass substrates at room temperature by a capacitively coupled plasma polymerization system using TMA as a precursor. Infrared spectroscopy, elemental analysis and UV–visible (UV–vis) spectroscopy reveal that there are conjugations in the matrix of the PPTMA thin films. From UV–vis spectroscopy it is found that indirect energy gap varies from 1.49 to 1.86 eV with film thickness. Current density–voltage characteristics indicate that the conduction mechanism in PPTMA thin films is space charge-limited conduction (SCLC). The activation energies in the SCLC region are 0.21 ± 0.05 and 0.93 ± 0.08 eV at lower and higher temperature regions respectively. Electrical and optical measurements suggest that the top of valance band and the bottom of the conduction band may have gap states and the middle of the energy gap may be equal to the high-temperature activation energy.

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1. Introduction

Thin films of organic compounds have attracted a great deal of attention of the researchers for their applications in efficient electronic devices such as organic light emitting diodes, photovoltaic cells, photo detectors, lasers, thin film transitions, etc [1, 2]. Generally, the properties of thin films strongly depend on the precursor material and various methods of deposition such as plasma polymerization [3, 4], pulsed laser deposition [5], ion beam deposition [6, 7], chemical vapour deposition (CVD) [8, 9], radio frequency (rf)/microwave plasma CVD [10], etc. The plasma polymerization method is largely recommended because it enables the fabrication of very thin films and compounds that could not be obtained by any other methods.

The effects of the discharge conditions on the structure and conductivity of the plasma-polymerized polypyrrole (PPPy) films were investigated by Hosono et al [11]. They observed that some pyrrole rings remained in the PPPy films prepared at 10 and 20 W discharge powers and almost all pyrrole rings cleaved at 50 and 100 W and the three-dimensional cross-linked structure were formed. They also concluded that the conductivity of the film was not affected by discharge conditions. Bae et al [12] deposited organic polymer thin films onto glass and Si (1 0 0) substrates at room temperature by the plasma-enhanced CVD (PECVD) method. They compared the surface and optical properties of plasma-polymerized organic thin films prepared at various rf power. They found that the contact angle, refractive index, and the intensity of the main absorption peak of thin films were increased as the plasma power increased, while the optical transmittance was decreased, signifying that the plasma-polymerized organic films have lower surface energy with increasing rf power. Kim et al [13] studied polymer-like thin films deposited onto glass and silicon substrates at temperatures in the range 300–673 K by PECVD method using thiophene as a precursor. X-ray diffractometry and Fourier-transform IR spectroscopic studies revealed that the as-grown films at 373 K have highly oriented amorphous polymer structure. From current–voltage and capacitance–voltage characteristics, they observed that the relative dielectric constants increased from 2.96 to 4.0, when the rf power was increased.
up to 200 W. And the activation energy for polymer-like thin film calculated from the Arrhenius plot was $-6.9 \text{ KJ mol}^{-1}$, signifying that a diffusion control process was the rate-determining mechanism.

Mitu et al [14] deposited parylene-like thin films of di-para-xylylene by plasma decomposition instead of conventional thermal decomposition. Growth rates within the range 4–250 nm min$^{-1}$ were achieved with plasma polymerization, comparing favourably with the low deposition rates of 5–10 nm min$^{-1}$ for the conventional CVD process. Depending on the rf power and precursor mass flow values, thin films with various morphology and composition were obtained, ranging from rough semi-crystalline to smooth amorphous and from polymer-like to hydrogenated carbon-like films. The electrical properties of the thin films studied by means of dielectric spectroscopy and charge stability measurements were correlated to structural properties of the films. Films deposited under low applied power/mass flow rate conditions showed good charge stability, making plasma deposited films interesting for electrostatic microelectromechanical systems applications. Plasma-polymerized m-xylene (PPm-X) thin films were studied by Shah Jalal et al [15]. The optical band gap allowed direct transition energy gap and indirect transition energy gap were determined for as deposited, heat-treated and aged PPm-X. Dc and ac electrical properties were investigated for thermally evaporated ZnPc thin films with aluminium (Al)/gold electrical contacts by Saleh et al [16]. The current density–voltage ($J$–$V$) measurements at room temperature indicated that an ohmic conduction was dominant at lower applied voltages, while at higher applied voltages, a space charge-limited conduction (SCLC) was observed.

Recently, several researchers [17, 18] investigated various properties of polyaniline thin films prepared using different techniques. Polyaniline thin films were deposited using an rf plasma polymerization technique by Saravanan et al [19]. Dielectric constant and ac conductivity were measured in the frequency range 100 Hz to 1 MHz and the temperature range 300–375 K. These films exhibited low dielectric constant values, which were stable over a wide range of frequencies. Thus, these films may be a probable candidate for low dielectric constant applications. The chemical analysis by IR spectroscopy and UV–vis spectroscopy of plasma-polymerized $N,N,3,5$-tetramethylaniline (PPTMA) thin films have been reported by Akther and Bhuiyan [20]. The PPTMA thin films have a slightly different structure from that of the monomer. The allowed direct transition and indirect transition energy gaps are determined to be 2.8 and 1.56 eV respectively. This paper reports the results of the optical and electrical investigations of PPTMA thin films. The relation between the optical band gap and activation energy of conduction in the SCLC region is also discussed.

2. Experimental details

2.1. The monomer and substrate

$N,N,3,5$-tetramethylaniline (TMA) was used as a organic precursor (Aldrich–Chemie D-7924, Steinheim, Germany). Glass (Clear Glass, Sail Brand, China) was used as substrates. Before deposition, the substrate was cleaned using concentrated nitric acid, sodium hydroxide solution, potassium dichromate solution and carbon tetrachloride. Finally, the cleaned substrates were rinsed with distilled water. Then the substrates were dried in a vacuum oven for 10 min at 453 K and were preserved in a desiccator.

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2.2. Preparation and chemical characterization

Details about the plasma polymerization system used in this work have been discussed in an earlier publication [20]. Glow discharge plasma was generated around the substrates, which were kept on the lower electrode, using a step up transformer connected to the electrodes with a power of about 40 W at line frequency (50 Hz) at a chamber pressure of about $1 \times 10^{-1}$ Torr. TMA vapour was injected into the glow discharge reactor through a flowmeter (Glass Precision Engineering Ltd., Meterate, UK) at the flow rate of about 20 cm$^3$ min$^{-1}$.

IR spectra of TMA and PPTMA thin films were recorded at room temperature using an IR spectrometer Shimadzu-IR 470 (Shimadzu Corporation, Tokyo, Japan) in the wavenumber region 4000–400 cm$^{-1}$. The C, H and N contents of PPTMA films were determined by ‘Dynamic Flash Combustion’ method using an Elemental Analyzer EA 1180 (Carlo Erba Instruments, TYCHN, Milan, Italy). UV–vis spectra of TMA and PPTMA were obtained with a spectrophotometer Shimadzu UV-160A (Shimadzu Corporation, Tokyo, Japan) in the wavelength range 200–800 nm at room temperature.

2.3. Electrical measurements

The $J$–$V$ characteristics were studied in sandwich structure configuration Al/PPTMA/Al with an effective area of $10^{-4}$ m$^2$ in the voltage range 0.2–13.0 V at room temperature. The lower and upper Al electrodes were deposited onto the glass substrate and sample respectively using an Edwards coating unit (Model: 306, Edwards, UK) at a pressure of the about $10^{-5}$ Torr. The thickness of the deposited films was measured by a multiple beam interferometry method.

The current across the Al/PPTMA/Al thin film structures of different thicknesses was measured by a high impedance electrometer (Model: 614, Keithley Instruments Inc., USA) and the dc voltage was supplied by a stabilized dc power supply (Model: E 3610A, Hewlett-Packard, UK). The measurements were carried out under dynamic vacuum of about $10^{-2}$ Torr pressure. Sample temperature was measured using a chromel–alumel thermocouple attached to a digital microvoltmeter (Model: 197A, Keithley Instruments Inc., USA).

3. Results and discussion

3.1. IR spectroscopic analyses

More details of IR studies about TMA and PPTMA thin films have been reported in a previous article [20]. The absorption peaks in the PPTMA thin films are not sharp compared to those of the TMA but most of the IR absorption features of the TMA are noticeable in the spectrum of PPTMA thin films with shifts in wave numbers. Finally, the observations reveal that the PPTMA thin films contain more conjugated bonds than TMA and NC and CH side groups in an aromatic ring structure.

3.2. Elemental analysis (EA)

The percentages (wt) of carbon, hydrogen and nitrogen in PPTMA detected by EA are presented in table 1. It is seen that the amount of C and H are decreased and that of N is increased in PPTMA relative to the amount of constituent elements in the monomer TMA. The percentage of oxygen...
Table 1. The percentages (wt) of C, H, N and O in PPTMA thin films.

| Sample    | C   | H   | N   | O   | Formula       | Empirical formula |
|-----------|-----|-----|-----|-----|---------------|-------------------|
| TMA (monomer) |     |     |     |     | C_{10}H_{15}N |                   |
| PPTMA     | 62.10 | 6.88 | 7.47 | 23.55 | C_{7.70}H_{10.30}N_{1.50}O_{0.80} |       |

Figure 1. Variation of absorbance (ABS) with wavelength, λ, for PPTMA thin films of different thicknesses (inset monomer).

(non-constituent) content was calculated on subtraction from the results of other elements [21], which is shown in table 1.

The incorporation of oxygen and nitrogen in PPTMA may be due to the post-deposition reaction of the PPTMA after exposure to air owing to reactions with radical species and dangling bonds in the structure and/or from the glow discharge chamber during polymerization. The deficiency of carbon and hydrogen contents in PPTMA may be due to the breakdown of bonds owing to the complex reaction during plasma polymerization. The complex reaction may be due to an oxidization reaction between the carbon and hydrogen with some residual gases forming CO, CO₂ or H₂O.

3.3. UV–vis spectroscopy

The spectral behaviour of absorbance in the wavelength range 200–800 nm of PPTMA thin films of thicknesses 300, 400 and 500 nm are shown in figure 1. In the absorption process, a photon excites an electron from a lower to a higher energy state, which is called an absorption edge. Absorption edge shifts to the higher wavelength compared to the liquid monomer (inset of figure 1). The $\pi-\pi^*$ transition in PPTMA thin film may demonstrate the presence of an increased
Figure 2. The \((\alpha h\nu)^{1/2}\) versus energy plots of different thickness PPTMA thin films.

Table 2. Values of allowed indirect transition energy gaps, \(E_{qi}\) (eV) and activation energy (eV), for various PPTMA thin films.

| Sample thickness d (nm) | Allowed indirect transition energy gap, \(E_{qi}\) (eV) | Activation energy, \(\Delta E\) (eV) |
|------------------------|---------------------------------|----------------------------------|
|                        |                                 | Temperature regions               |
|                        |                                 | Low | High |
| 300                    | 1.86                            | 0.17 | 0.91 |
| 400                    | 1.56                            | 0.22 | 0.98 |
| 500                    | 1.49                            | 0.26 | 0.91 |

degree of conjugation in the resulting films. The absorption co-efficient was obtained from the absorbance spectra of the PPTMA thin films.

The relationship between absorption coefficient, \(\alpha\), and optical band gap is expressed to calculate band gap of the PPTMA films by the following relationship [22]

\[
\alpha h\nu = B(E_{\text{opt}} - h\nu)^n,
\]

where \(B\) is an energy-independent constant and \(E_{\text{opt}}\) is the optical band gap and \(n\) is a constant which determines type of optical transition (\(n = 1/2\) for allowed direct transition and \(n = 2\) for allowed indirect transition). The experimental results show that the dominant transition is the indirect one proposed by Tauc [22]. Thus the plots of \((\alpha h\nu)^{1/2}\) versus \(h\nu\) were plotted to obtain the indirect optical band gaps, \(E_{qi}\) of the thin films, as shown in figure 2. Indirect gap was determined from the linear portions as shown in figures and the values are given in table 2. It is noticed that
$E_{q_t}$ gradually decreases with increasing thickness. This means that the thickness affects the optical band gap due to the change of some of the bonds. The band gap change may also arise from the photon–lattice interaction.

3.4. Electrical behaviour

Conduction processes were investigated for PPTMA thin films of different thicknesses (300, 400 and 500 nm) by measuring the $J$–$V$ characteristics of these thin films in the voltage range 0.2–13.0 V. The observed $J$–$V$ characteristics of the PPTMA thin films at room temperature are presented in figure 3. Each characteristic implies two different conduction processes, according to the power law of the form $J \propto V^n$ with different slopes in the lower and higher voltage regions, where $n$ is a power index. At lower voltage slopes of $0.80 < n < 1.26$, indicate approximate ohmic conduction, whereas at higher voltages the slopes of $1.70 < n < 2.20$ represent the non-ohmic conduction. The voltage dependence of current density for samples of different thicknesses at the higher voltage region suggests that the current may be due to SCLC, Schottky or Poole–Frenkel (PF) conduction mechanisms in PPTMA thin films [23]. According to SCLC theory, the thickness, $d$, dependence of the space charge limited current follows the relation of $J \propto d^{-l}$ where $l$ is a parameter depending upon the trap distribution as shown in figure 4. A slope $l < 3$ suggests the possibility of Schottky or PF mechanism and $l \geq 3$ reveals the possibility of SCLC mechanism. The linear slope derived from these data has a value of about $-3.5$, which is much higher than that corresponding to Schottky and PF conduction mechanism. Thus, the type of conduction mechanism in PPTMA is most probably SCLC.

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Figure 3. Plots of current density against applied voltage for PPTMA thin films of different thicknesses recorded at room temperature.
Figure 4. Thickness dependence of the current density, $J$, for PPTMA thin films at room temperature (applied voltage = 10 V).

Figure 5. Plots of current density against inverse of absolute temperature for PPTMA thin film in the SCLC region (applied voltage = 10 V).

3.5. Effect of temperature on the optical band gap of the thin film

Figure 5 shows the dependence of $J$ on inverse absolute temperature, $1/T$, for PPTMA thin films of different thicknesses (300, 400 and 500 nm) in the SCLC region with an applied voltage, 10 V. Each of the curves has two different slopes in the lower and higher temperature regions. The activation energies ($\Delta E$) calculated from the slopes for all the samples are recorded in table 2. The activation energies are about $0.21 \pm 0.05$ eV at the lower temperature and $0.93 \pm 0.08$ eV at...
the higher temperature regions. The $\Delta E$ values of lower and higher temperature regions suggest that there may be a transition of the conduction process from a hopping regime to a regime dominated by distinct energy levels. The low temperature activation energy is too high to draw a correlation with conventional hopping behaviour having activation energy of a few meV, although a decrease in $\Delta E$ with decreasing temperature may indicate a gradual transition to the hopping regime.

The band gap between the valence and conduction band can be explained in terms of the observed SCLC and optical absorption results. PPTMA thin films deposited using identical conditions have an indirect optical band gap of 1.86 eV and activation energy for conduction of 0.93 eV. It is seen that the activation energy is about half of the indirect band gap. It may be imagined that the energy gap may be filled up partially from top of the valence band and bottom of the conduction band where the Fermi level may be situated at the middle of the gap. Similar results have been reported by Silva and Amaratunga [24] for diamond-like carbon and for disorder solids [25].

4. Conclusions

IR spectroscopy, EA and UV–vis spectroscopy indicate that PPTMA contains more conjugation as compared to the monomer. The $\pi-\pi^*$ transition in PPTMA thin film demonstrates the presence of an increased degree of conjugation in the resulting films for different thicknesses. The indirect band gaps are found to be 1.49–1.86 eV. SCLC is observed in PPTMA thin films at higher (10 V) applied voltage. The activation energies in the SCLC region are $0.21 \pm 0.05$ and $0.93 \pm 0.08$ eV at lower and higher temperature regions respectively. The activation energy is about half of the indirect band gap. Thus it may be inferred that the energy gap contains gap states around the bottom of the conduction band and the top of the valence band and the middle of the gap may be free of gap states. Thus the free gap is equal to the observed high temperature activation energy.

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