

PREPARATION AND CHEMICAL ANALYSIS OF PLASMA POLYMERIZED N,N,3,5 TETRAMETHYLANILINE THIN FILM

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ABSTRACT

The plasma-assisted methods are now becoming one of the fastest growing areas in the field of direct deposition of entirely new kinds of polymeric materials. Plasma polymerized N,N,3,5 tetramethylaniline (PPTMA) thin films were deposited at room temperature by a parallel plate capacitively coupled glow discharge reactor. The as deposited PPTMA films of about 400 nm thick were characterized by scanning electron microscopy, elemental analysis (EA), infrared (IR), and x-ray photo electron spectroscopy (XPS). The surface of the PPTMA thin films was observed to be smooth and pinhole free. IR and EA reveal that there is a conjugation in the matrix of the PPTMA thin films. The XPS analyses show that C, N, and O were present on the surface of the thin film and possible groups C-H, C=C, C-N, and C=O are found in the PPTMA structure.

Keywords: N,N,3,5 Tetramethylaniline , Plasma Polymerization, Organic Material.

1. INTRODUCTION

The use of plasma polymerization for synthesis of novel thin film materials has become attractive and has been an active area of research in the recent past. Plasma polymerization is an efficient method for organic thin film deposition and surface modification. Plasma polymerization is a versatile and important technique for depositing uniform, pinhole-free and flawless thin films of organic materials [1-4]. Bhadra et al. [5] reviewed the synthesis, processing and applications of polyaniline (PANI). These paper provided of the different methods used for the synthesis of PANI along with a number of special methods used to obtain a nano structured PANI. They observed PANI can be applied in different areas such as electrical, electronic, thermoelectric, chemical, membrane, sensors, and so on because of its some special properties such as conductive in nature, the increase of viscosity in solution when under an electric field, its change in electrical conductivity or color when exposed to acidic, basic and some neutral vapors or liquids, its easy variation of oxidation states, very high capacitance values, volume changes at different oxidation state and its ability to emit color under various excitation.

Chowdhury et al. [6] studied on the chemical analysis of the plasma-polymerized diphenyl (PPDP) thin films. The PPDP films were characterized by SEM, elemental analysis (EA), IR spectroscopy, Auger electron microscopy (AES) and X-ray photoelectron spectroscopy (XPS). The SEM micrograph shows that there are clear grain boundaries of irregular shapes and

the surface morphology of the PPDP film is observed to be pinhole and fracture free. The elemental analysis reveals that PPDP film is mainly composed carbon, hydrogen and oxygen atoms with a small amount of nitrogen atom. The bulk atomic concentration determined from elemental analysis is different in comparison to that obtained by XPS and AES analyses of the film surface. Gong et al. [7] synthesized PANI thin films of various chemical compositions by rf plasma-polymerization technique and they showed a correlation between the C/N ratio and their different properties. The plasma-polyaniline films have been characterized by UV-Vis spectroscopy, FTIR spectroscopy, electron spin resonance, XPS, SEM and contact angle measurements, which indicated that the contents of quinoid sequences and aliphatic cross linking moieties increase with increasing plasma power input and discharge duration.

Polyaniline, has interesting combination of properties that make them very attractive in the area of electrical and electronic application. The structural property of polyaniline may be modified by adding electron donor groups like $-N(CH_3)_2$ in the aniline structure. The quantum mechanical investigations have been carried out by Mhin and Park [8] to examine the effects of constituents on structural deformations and electronic properties. They also predicted that the substitution of electron donor groups like $-N(CH_3)_2$ in aniline might affect the electronic property. N,N,3,5 tetramethylaniline

is proposed that the properties may be modified by adding electron donor groups like $-N(CH_3)_2$ in the aniline structure. From the point of view, N,N,3,5 tetramethylaniline is selected as a monomer for the preparation of thin film by plasma polymerization technique and to study its structural properties.

2. EXPERIMENTAL DETAIL

The plasma polymerization system is a bell-jar type capacitively coupled system, which consists of two stainless steel parallel plate electrodes of diameter and thickness 0.09 and 0.001 m respectively, placed 0.035 m apart. N,N,3,5 tetramethylaniline (TMA) was used as an organic precursor (Aldrich-Chemie D-7924, Steinheim, Germany). Fig. 1 shows the monomer TMA chemical structure. Transparent light yellow colored plasma polymerized N, N, 3, 5 tetramethylaniline (PPTMA) thin films of about 400 nm thick were deposited onto the glass substrates. The SEM was performed by a scanning electron microscope (S-3400 N Hitachi, Japan). The PPTMA powder was collected from the monomer deposited substrates by scrapping process. The C, H and N contents of PPTMA films were determined by an elemental analyzer EA 1180 of Carlo Erba Instruments, TYCHN, Milan, Italy.

The IR spectra of the monomer liquid and plasma polymerized thin films were recorded at room temperature using a double-beam IR spectrometer Shimadzu-IR 470 (Shimadzu Corporation, Tokyo, Japan). The strength of an IR absorption spectrum is dependent on the number of molecules in the beam. Its wave number range is $4000-400\text{cm}^{-1}$. The XPS was equipped with UHV chamber a semispherical XPS analyzer (Omicron, Germany). For XPS measurements the MgK_{α} (1253.6 eV) sources was used. After degassing the MgK_{α} -X ray sources all the parameters can be controlled by using a PC running with Ph/PC explorer software.

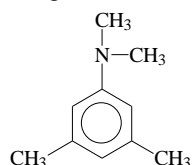


Fig.1 The structure of N,N,3,5 tetramethylaniline

3. RESULTS AND DISCUSSION

3.1 SEM micrographs of as deposited PPTMA thin film

The SEM micrographs of as deposited PPTMA thin films was recorded at magnifications $10k\times$ at accelerating voltage of 10 kV are shown in Fig 2. From the micrographs it can easily be visualized that the surface of the plasma polymerized thin films is smooth, flawless and pinhole free.

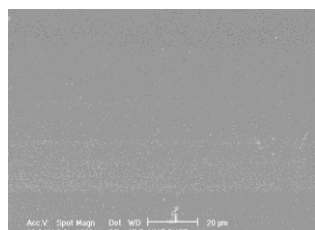


Fig. 2 SEM Micrograph of PPTMA thin film of 400 nm

thick.

3.2 Elemental Analysis

The chemical composition of PPTMA thin film was determined by elemental analysis, a useful technique for chemical investigation of organic inorganic materials. The weight percentages (wt%) of carbon (C), hydrogen (H) and nitrogen (N) in PPTMA detected by EA are presented in table 1.

Table 1 The weight percentages of C, H, N and O in TMA and PPTMA thin films

Sample	Elements detected (wt %)				Empirical formula
	C	H	N	O	
PPTM	62.1	6.8	7.4	23.5	$C_{7.70}H_{10.30}$
A	0	8	7	5	$N_{0.80}O_{1.50}$

It is seen that the amount of C, N, and H in PPTMA are decreased relative to the amount of constituent elements in the monomer TMA. The percentage of O content was calculated on subtraction from the wt (%) values of other elements [9]. From the EA the atomic ratio is found to be $N/C=0.12$ for PPTMA, which is just same to that of the monomer i.e. $N/C=0.12$. It is thus seen that there is no change of N/C ratio because N and C are decreased relative to the amount of constituent elements of TMA. The deficiency of C, N, and H contents in PPTMA may be due to the breakdown of bonds owing to the complex reaction during plasma polymerization. The incorporation of O and decrease in the amount of N 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.

3.3 IR spectroscopic analyses

The recorded IR spectra of monomer TMA and PPTMA depicted in Fig. 3 are represented by M and N, respectively. In the spectrum of TMA, N-H (asymmetric stretching - 3475cm^{-1} (A) and symmetric stretching - 3340 cm^{-1} (B)), C-H (stretching - 2935 (C) and 2793 cm^{-1} (D)), C=C (aromatic ring stretching vibration - 1680 to 1645 (E), 1485 and 1595cm^{-1} (F)), C-N (stretching - 1351 (G), 1307 (H), and 1223 to 1030 cm^{-1} (I)) bands are identified. The IR spectrum of PPTMA thin film does not resemble exactly to that of TMA and most of the peaks can be seen in the wide absorption envelope corresponding to the regions A (3475 cm^{-1}), C (2935 cm^{-1}), E (1680 to 1645 cm^{-1}), F (1485 and 1595cm^{-1}) and G (1351cm^{-1}) of TMA spectrum. The wide band around $1850-1603\text{ cm}^{-1}$ may also include the contribution due to C=O stretching vibration which is typical for plasma polymers. The formation of C=O may be attributed to the oxidation of the hydrocarbon part of the PPTMA after exposure to air. The IR studies indicate that PPTMA films contain an aromatic ring structure with NC and CH side groups.

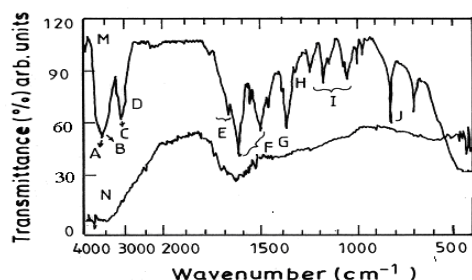


Fig. 3 The IR spectra of monomer N,N,3,5 tetramethylaniline (TMA), spectrum M; and PPTMA, spectrum N

3.4 X-ray photoelectron spectroscopic analyses

The XPS measurements were carried out to determine the relative amounts of C, N and O on the PPTMA thin film surface. The C1s XPS spectra of the PPTMA thin films are shown in Fig. 4. The envelopes of all the spectra were analyzed by fitting Gaussian peaks. It has been reported that the full width at half maximum (FWHM) for plasma polymers is expected to be relatively large, about 1.8 eV due to their random assemblies of molecular fragments [10]. The C1s spectrum in Fig. 4 contains peaks those represent the presence of C, N, and O. The C1s spectrum for these films consists of peaks those are not only close together but also relatively broad, thus yielding significant overlapping the peaks associated with N and O, which are at higher binding energies than the C-C and C-H peaks. The XPS data of PPTMA thin films revealed that besides C and N there is also significant amount of O in PPTMA films. The presence of O in the PPTMA thin films is expected in the plasma polymerized films owing to the existence of traces of oxygen and/or water vapour adsorbed on the walls of the reaction chamber, which would then be desorbed during the gas discharge. Another reason for the presence of oxygen is the reaction of long lived radicals in the deposited films with atmospheric oxygen and/or water after being exposed to the atmosphere. The C1s spectrum of PPTMA film can be deconvoluted into two component peaks as indicated in Fig. 4. The binding energies (BE's) for aromatic C-H (285.0 eV) and C=C, C-N, and C=O (287.02 eV) were assigned in the present material. The IR and EA analyses of PPTMA thin films showed the presence the same groups. The formation of carbonyl group was formed due to the oxidation of the hydrocarbon part of the PPTMA thin films. The asymmetric region in the high BE side of the C1s spectrum could be attributed to the presence of the shake-up $\pi - \pi^*$ structure arising from the transition in the aromatic rings in PPTMA thin film. This feature was also observed in PPTMA by the UV-Vis spectroscopic investigations [11].

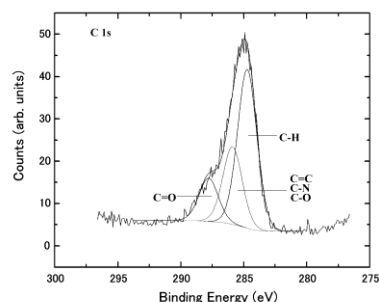


Fig. 4 The C 1s spectrum of PPTMA thin film

The composition of the PPTMA thin films could be estimated from the XPS spectra. A generalized expression for the determination of the atomic fraction C_x of any contribution in a sample, utilizing peak area and sensitivity, can be written as

Atomic fraction,

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x / \rho_x}{\sum I_i / \rho_i} \quad (1)$$

where n is the number of atoms of an element, I is the area of the photoelectric peak and ρ is the corresponding photoionization cross-section. The necessary photoionization cross-sections have been obtained from the article of Scofield [12]. The nitrogen-to-carbon atomic ratio, calculated using the Eq.(1), is found to be 0.20 for PPTMA thin films. From the XPS investigation, it is seen that plasma polymer of TMA prepared by glow discharge technique is elementally different from the monomer. The atomic concentration determined from elemental analysis is 0.12, which differs from value estimated by XPS analysis. It is suggested that on the film surface some carbon-nitrogen bonds in PPTMA were replaced by carbon-oxygen bonds. From the above observations, it is seen that there is quantitative variation in the surface and bulk compositions in the PPTMA thin films. On the surface of this film an increase of nitrogen content is observed with a drop of carbon concentration.

4. CONCLUSIONS

Plasma polymerization technique was successfully used to prepare good and reproducible thin films of desired thickness from TMA. The surfaces of the as deposited PPTMA thin films are observed to be smooth and pinhole free. The empirical formula of the PPTMA film was determined to be $C_{7.70}H_{10.30}N_{0.80}O_{1.50}$ from the EA data. It is found that the N/C ratio is 0.12 for as deposited PPTMA, which is very close to N/C of TMA. Non-monomeric oxygen was incorporated into the PPTMA films due to the post-deposition reaction with radical species (dangling bonds) trapped in the structure and from the glow discharge chamber during polymerization. The IR investigation shows that the as deposited PPTMA is structurally different from monomer and the PPTMA may contain an aromatic ring structure with NC and CH side groups. The XPS analyses of PPTMA thin films also show the possible groups, C-H, C=C, C-N, C-O, C=O on PPTMA surface. The atomic ratio N/C of the PPTMA thin film bulk and surface are

found to be 0.12 and 0.20 by EA and XPS, respectively. It is suggested that on the film surface some carbon-nitrogen bonds in PPTMA were replaced by carbon-oxygen bonds. From the above observations, it is seen that there is quantitative variation in the surface and bulk compositions in the PPTMA thin films. On the surface of this film an increase of nitrogen content is observed with a drop of carbon concentration.

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6. REFERENCES

References of cited literature should be identified in the text in square brackets and grouped at the end of the paper in numerical order of appearance. References should be styled and punctuated according to the following examples: journal article [1], book [2], thesis [3], proceedings [4], and technical paper/report [5].

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NOMENCLATURE

d	Thickness
EA	Elemental Analysis
FTIR	Fourier Transform Infrared
IR	Infrared
PPPA	Plasma polymerized polyaniline
PPTMA	Plasma polymerized N,N,3,5 tetramethylaniline
PANI	Polyaniline
SEM	Scanning electron microscopy
TMA	N,N,3,5 tetramethylaniline
XPS	X-ray photoelectron spectroscopy

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