Glow discharge plasma polymerized nanostructured polyaniline thin film optical waveguide

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Abstract

In this work, glow discharge continuous wave plasma polymerization technique was used to deposit nanostructured polyaniline (PANI) thin film by varying input power. The radio frequency (RF) used for plasma polymerization was 13.56 MHz and working pressure was 0.15 mbar. It was found that, changes in the input power can be used to control the properties of the plasma polymerized PANI thin films. Highly cross-linked structure with an increase in chain length was observed from FTIR spectra with input RF power, whereas the film surface morphology was found to be highly uniform, densely packed and smooth from FE-SEM images. The surface roughness of the film was found to increase with RF power. The refractive index and adhesion of the film was found to be increased while the optical band gap and surface energy decreased with input RF power. The plasma polymerized PANI film showed outstanding optical transmission loss properties and proved itself as excellent optical waveguide. Copyright © 2016 VBRI Press.

Keywords: Polyaniline, plasma polymerization, optical waveguide.

Introduction

Integrated optics is the heart of communication system, wherein a large number of optical components have been used for different functions. These optical components require a wide range of material system for its fabrication on a single substrate, which makes the technology complicated and uneconomic. Nowadays, the scientific community has focused their interest on the development of a single material, which can be used commonly for the development of all optical components on a single substrate.

In the last decade modification and inventions of new polymers have acquired more focus, which is due to the spectacular properties of conducting polymers and their wide use in numerous applications [**1–5**]. Among the series of conducting polymers, Polyaniline (PANI) is a unique and one of the most technologically promising conducting polymers because of its ease of preparation, low cost, high environmental stability and relatively stable electrical conductivity as well as thermal stability [**6–9**]. It has been previously reported as sensors [**10**], light emitting diode [**11**], electrochromic properties [**12**], anticorrosive material [**13**], surface modification [**14**], EMI shielding [**15**] etc. PANI can be prepared in different oxidation states, in different colors and different conducting states depending on its synthesis methods [**16-17**]. Such a versatile nature of PANI makes it a highly promising material for development of different optical component in integrated optics. Hence, we propose here to study PANI for optical waveguide application.

Various deposition methods have been reported earlier for PANI thin films viz. chemical method [**18**], vacuum evaporation method [**19**] and SILAR (Successive Ionic Layer Adsorption and Reaction) method [**20**], Autocatalytic Method [**21**] etc. Glow discharge plasma polymerization method allows the deposition of ultrathin and highly smooth surface film than the other methods. The plasma polymerization technique has been established as a versatile technique and having merits like; being cost effective, gives a product with less contamination and excellent stability, reproducibility and the material can be deposited on any kind of substrate. Plasma initiation corresponds to the ionization of gaseous monomer molecules through electronic impacts which forms radical cations that are responsible for the formation of the polymer chain [**22-23**]. Also, plasma generated ultraviolet radiation has a strong influence in oxidation as well as structural modeling of the deposited material [**24-25**]. To the author's knowledge, there are very few reports available on plasma polymerized polyaniline thin film [**26-29**]. In these reports, the polyaniline thin film was synthesized by plasma polymerization method, but have not used for optical waveguiding application. There are also few reports available on polyaniline thin film for optical waveguiding application [**30-32**] but, synthesis of polyaniline thin film was done by other than plasma polymerization viz. vacuum evaporation and chemical method. In our work, the polyaniline thin film is synthesized by plasma polymerization method and used as an optical waveguide.

Experimental

Substrate cleaning

Glass slides of dimensions 2.5 cm x 7.5 cm were used as substrate, which were cleaned initially with deionized water, then with soap solution and again by deionized water. These cleaned glass slides were rinsed with chromic acid and acetone and finally ultrasonically cleaned with deionized water before the deposition [**33**].

Preparation of thin film

The plasma polymerization process has been carried out in a glass reactor of diameter 30 cm. The schematic of the glow discharge plasma polymerization set up is shown in **Fig. 1**. The reactor consists of a pair of stainless steel plates, which on both sides to close the ends. Capacitively coupled circular electrodes were fixed at the center of the reactor with the separation of 10 cm from each other.

To remove the contamination, the system was evacuated at 0.15 mbar working pressure with a continuous flow of argon gas and again it was etched by plasma at 6 watt. Cleaned glass substrates were positioned horizontally over the bottom electrode. The deposition was started initially by tuning vacuum at 0.1 mbar and thereafter aniline monomer was inserted through the needle valve. Aniline (AR grade, SD fine – Chem Ltd.) was used without further purification.

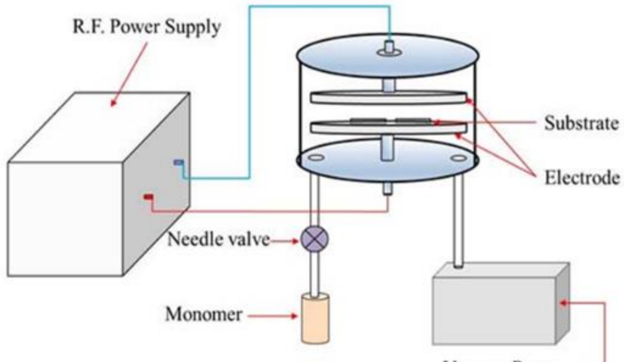

Fig. 1. Schematic of glow discharge plasma polymerization set up.

The flow rate of the monomer was adjusted in such a way that working pressure remained constant at 0.15 mbar. The monomer vapors were allowed to pass for a few seconds and after that RF power was applied. The pink colored plasma turned in to Violet, which indicated fragmentation and excitation of aniline molecules in the plasma state. The intensity of the plasma was adjusted with the help of matching unit and deposition was carried out with different powers for 15 minutes.

Growth mechanism

Chemical reactions that occur under plasma conditions are generally very complex and nonspecific in nature. Glow discharge polymerization of organic compounds seems to proceed by the free radical mechanism [**34-35**] and the extent of ionization is small. The schematic of growth of glow discharge plasma polymerized thin film has been shown in **Fig. 2**. When RF power is applied to the monomer vapors, fragmentation of monomer molecules takes place, which are known as radicals. These fragmented radicals sites on a solid surface and initiates a classic chain growth polymerization. In this polymerization process, monomer M gets continuously added to molecule P to form the polymer [**36**]. Free radical terminations (recombination) dominate the ending of chain growth. Disproportionation and radical transfer are also responsible for termination process **[37]**. This type of termination needs collision which again depends on pressure. In this case, R.F. power used is continuous wave (CW) which produce cross-linked polymer structure.

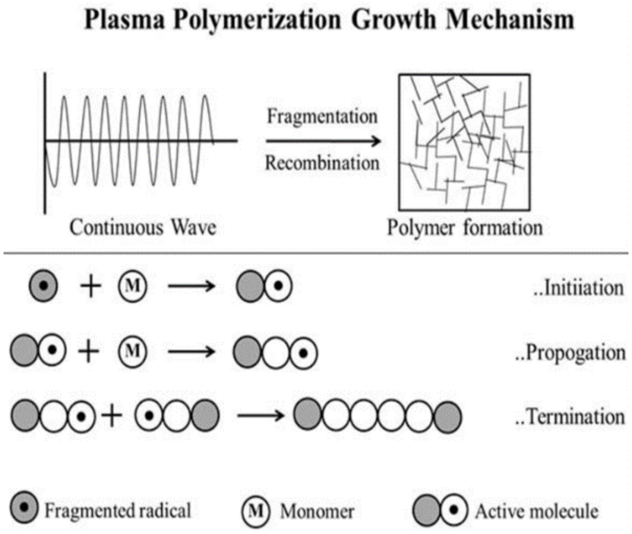

Fig. 2. Schematic of glow discharge plasma polymerization growth mechanism.

Characterization

Field Enhanced Scanning Electron Spectroscopy (FESEM) [Carl Zeiss, Supra 40 VP] was used to study surface morphology, while Atomic Force Microscopy (AFM) [Bruker Nano] was used in non-contact mode for roughness and three dimensional morphology studies. FTIR spectroscopy [Bruker, ALPHA 100508] was used in the ATR mode for functional group determination. The adhesion between film and substrate was measured by direct pull off method. Optical absorption and electronic transitions were studied by UV-Visible spectroscopy [Shimadzu] and the data obtained by this technique was further used to calculate refractive index and optical band gap. The optical transmission loss was measured by the prism coupling method.

Results and discussion

Surface morphology

The surface morphology of Glow discharge plasma polymerized thin films with power variation is shown in **Fig. 3**. The SEM images are shown by **3(a), 3(b), 3(c)** and AFM images by **3(a1), 3(b1), and 3(c1)** with RF power variation from high to low value. SEM images of plasma polymerized PANI thin film revealed highly smooth and very compactly nanostructured surface. No observable change in surface morphology was observed with power variation, except the film '**3(b1)**' shows morphology with some clusters scattered on its surface. This is may be due to the sample handling during the measurement. The AFM images also show similar morphological changes as in SEM images. The roughness values obtained from AFM images have decreased with RF power **(Table 1)**.

Table 1. Roughness, surface energy, adhesion, refractive index, optical band gap and optical transmission loss of plasma polymerized polyaniline thin films.

Sr. No.	Power (watt)	Roughness (nm)	Surface Energy (mJ/m^2)	Adhesion (N/m^2)×10^4	Refractive Index	Optical Band Gap (eV)	Optical Transmission Loss (dB/cm)
1	2.4	0.206	37.45	103.88	1.750	3.5	8.89
2	4	0.296	35.16	173.14	1.777	3.3	9.07
3	6	0.377	32.76	207.77	1.829	3.2	9.95

The degree of polymerization in plasma polymerization technique is dependent on applied RF power. At high RF power, the degree of polymerization is high, which increases the growth rate and obviously the roughness of the film. As the power decreases the growth rate also decreases, which gives enough time for the polymerization and settling the polymer chain on the substrate surface, which causes to decrease in surface roughness.

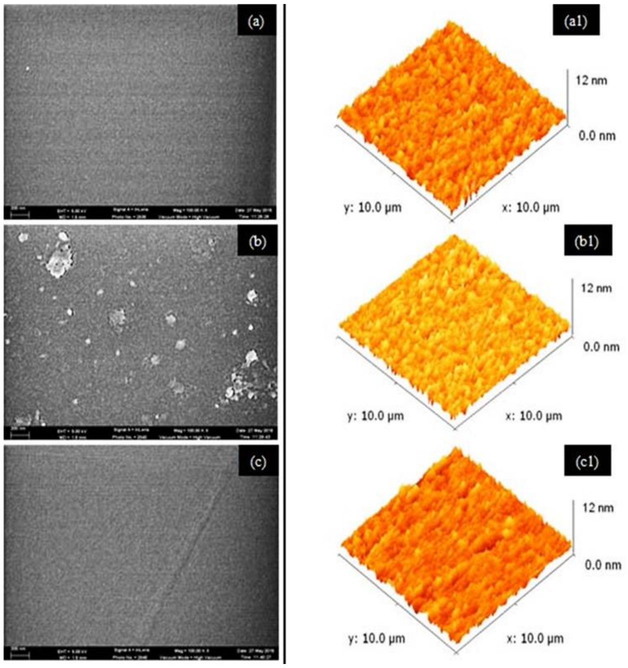

Fig. 3. FE-SEM (a, b and c) and AFM (a1, b1 and c1) images of plasma polymerized polyaniline thin film for 6 watt, 4 watt and 2.4 watt input power respectively.

In our previous report, we have reported the similar effect of growth rate on the film surface morphology, wherein chopping technique was used for the attenuation of the growth rate [**19, 38**]. The surface morphology of polyaniline thin films deposited by vacuum deposition technique showed long fibril and porous structure with some small granular particles scattered on the surface, which was became smooth and compact in vapor chopped film [**19**]. The film deposited by chemical route was observed as porous morphology with some irregularly arranged granules accumulated on the surface [**18**]. All these irregularities have been removed and the deposition is highly smooth having a compact surface structure in the glow discharge plasma polymerization technique.

FT-IR spectroscopy

The FTIR-ATR spectra of the polyaniline thin film are shown in **Fig. 4**. Spectra revealed the vibrating and stretching modes of those functional groups, which are present in the film. It is clear that, all peaks are found at the same position for all input RF powers and the only change is found in their intensity. The peak at 692 cm^{-1} is assigned to out of plane C=C bending vibrations [**39**]. The presence of this strong peak is attributed for 1, 3 di-substituted aromatic ring (meta), which is due to cross-linked structure of PANI [**40**]. The spectra clearly indicate that, the intensity of that peak also increases with increase in input RF power, which indicates that the cross linking in the film increases with input RF power. The peak at 745 cm^{-1} is the characteristic peak of out of plane C=C and C-H ring bending vibrations [**39**], whose intensity is found to increase with input RF power. The peak at 866 cm^{-1} is quite broad and corresponds to NH_2 wag. C-N stretching bonds were found at 1250 cm^{-1} and 1307 cm^{-1} and also found to increase with the input power. The peak observed at 1493 cm^{-1} corresponds to benzoid ring vibration [**41**] and the peak at 1597 cm^{-1} is attributed to quinoid ring vibration [**40**].

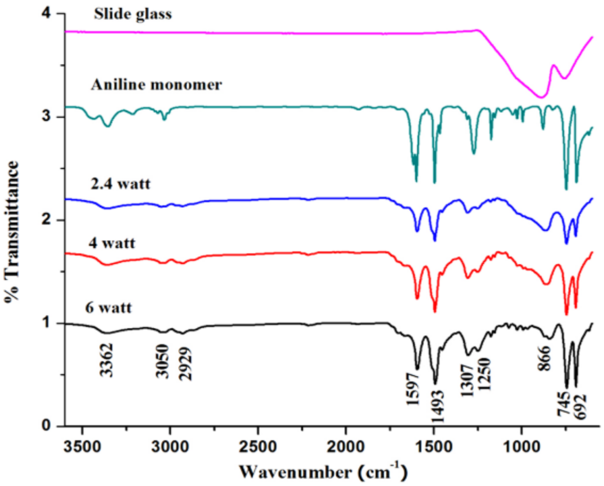

Fig. 4. FT-IR spectra of plasma polymerized polyaniline thin film for different powers.

The increase in chain length is confirmed with RF power in both benzoid and quinoid peaks, which are found to increase in intensity. The peak at 2929 cm^{-1} is assigned to stretching of C-H bond, which is the function of aromaticity in the plasma polymerized thin film [**42**] and shows more aromaticity loss at higher power. The retention of the aromatic structure is observed clearly from the FTIR spectra, as the doublet of aromatic C-H stretching appeared at 3052 and 3028 cm^{-1} [**43**]. Secondary amino group N-H is confirmed by 3362 cm^{-1}. All peaks show an increase in intensity, but this is the only peak, which is neutral to variation in input power.

Adhesion

Direct Pull Off method [**44**] is used to compute the adhesion between the substrate surface and the film, which has an importance as it can affect the performance of the device. The method consists of a pair of chucks in which film has to be fixed. A force F required to detach the film from substrate is applied by a pulling mechanism and can be measured by spring balance. This force is utilized to calculate the adhesion by the formula,

$$\sigma = \frac{(g \times F)}{A} \tag{a}$$

where, σ – Adhesion, g - gravitational force, F - load in Kg., A - Area of stud.

The calculated values of adhesion have been tabulated in **Table 1**. From table 1 it is observed that all films have good adhesion and shows slight decrease with decrease in power. From the results obtained by this method, it may be concluded that, high power increases cross linking in the film, which is responsible for enhancing bonding between film and substrate.

UV-vis-NIR Spectroscopy

UV-vis-NIR spectra of plasma polymerized polyaniline thin film with power variation are presented in **Fig. 5**. Spectra shows a single peak for all power variations, which corresponds to π-π* transition and then curve approaches to zero exponentially. In case of low power it is found at about 322 nm and shifts to about 338 nm for maximum power. It is known that the increase in the extent of conjugation lead to a bathochromic shift, where the UV–vis absorbance band shifts to higher wavelength [**45**]. The Figure shows that peak undergo a bathochromic shift which confirms increase in the extent of conjugation in terms of cross linking with respect to power. The extension in the peak in FTIR also confirms the same. High power films were found to absorb more light as compared to those deposited at low power.

Refractive index

Spectrophotometric method is used to calculate the refractive indices of plasma polymerized thin films. This method is based on the spectrometric results, by measuring the simultaneous absorption and transmittance of thin film at 621 nm wavelength [**44**]. The reflectance has been calculated by using the relation,

Transmittance + Absorption+ Reflectance = 1 (b)

and the refractive index (n) of thin films has been calculated by using the following formula,

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

where, n- refractive index of the film, n_s– refractive index of the substrate, T_f – transmittance and R_f – Reflectance.

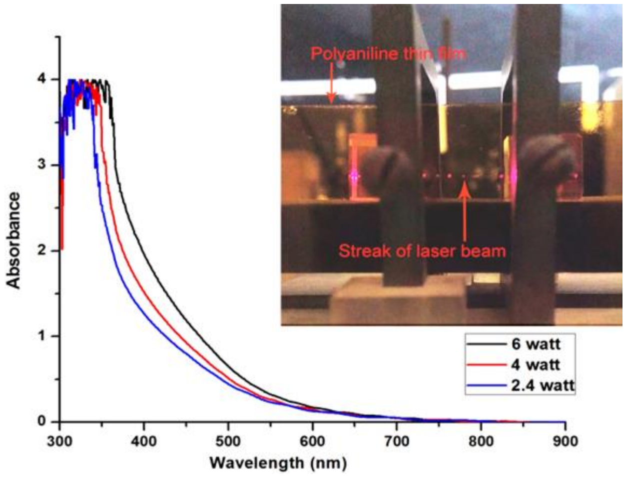

Fig. 5. UV-vis-NIR spectra of plasma polymerized polyaniline thin film for different powers, inset Figure – Photograph of Polyaniline thin film optical waveguide.

The calculated values of refractive indices have been tabulated in table 1, which made clear that there is a decrease in refractive index with decreasing RF power. High cross linked surface may enhance internal scattering and as explained in a UV visible study it absorbs more light, therefore there is an increase in refractive index. In case of less power it observed to approach lower value.

We have previously reported that, as the difference between the wavelength of absorption peak and wavelength at which the refractive index measured increases, the refractive index decreases [**19**]. The UV-VIS absorption spectra shown in Figure also reveal the similar results.

Optical band gap

The optical band gap has been calculated using the formula [**26**],

$$\alpha = \left[\frac{\alpha_0 \left(h\nu - E_g\right)^n}{h\nu} \right] \tag{d}$$

where, 'E_g' is an optical band gap, 'α' is absorption of thin film, 'α_0' is absorption coefficient, 'h' is the photon energy and 'n' is a constant. The obtained optical band-gap values are presented in table 1. Though polyaniline is basically a conducting polymer, its optical band gap by glow discharge plasma polymerization technique is observed to be higher. It is found to increase from 3.2 eV to 3.5 eV with decreasing power. It means cross linking enhances conductivity of the film.

Optical transmission loss

Prism coupling method was used to calculate optical transmission loss. It provides a convenient and efficient method for launching a laser beam into a thin film's structure. A streak of light observed in the thin film waveguide is shown in the inset of **Fig. 5**.

The optical transmission loss was calculated by the formula,

A = 10 log [Input intensity /output intensity] ….dB/cm. (e)

By measuring the output and input intensity, the values of optical transmission loss were obtained and presented in table 1 which made clear that optical transmission loss decreased with decreasing power. It is reported that, high input power creates high plasma density and high cross linking [**46**]. This cross linking may responsible to absorb more light. The result obtained from this study also supports UV-vis, refractive index, optical band gap and roughness studies.

Conclusion

The Polyaniline thin film has been deposited on glass by glow discharge plasma polymerization method and shows excellent optical waveguiding property. Input power strongly affects the surface, structural and optical properties of polyaniline thin film. Highly smooth and cross-linked structure can be obtained by this method. Input power can be tuned to control the desired properties. The optical waveguide with low power film shows better results. At low power, optical band gap is maximum which reduces absorption of the signal, refractive index is less means it enhances the transmission speed of signal through the material, surface roughness is less which reduces internal scattering and overall performance makes it a better optical waveguide.

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