



# Structural and thickness-dependent optical parameters of plasma polymerized 2-vinylpyridine thin films

POMPI MOJUMDER<sup>1</sup>, MOHAMMAD JELLUR RAHMAN<sup>2,\*</sup> , MD ABU HASHAN BHUIYAN<sup>2,3</sup> and SHAMIMA CHOUDHURY<sup>1</sup>

<sup>1</sup>Department of Physics, University of Dhaka, Dhaka 1000, Bangladesh

<sup>2</sup>Department of Physics, Bangladesh University of Engineering and Technology (BUET), Dhaka 1000, Bangladesh

<sup>3</sup>University of Information Technology and Sciences (UITS), Dhaka 1212, Bangladesh

\*Author for correspondence (mjrahman@phy.buet.ac.bd)

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**Abstract.** Plasma polymerized 2-vinylpyridine (PP2VP) thin films have been synthesized under glow discharge using a capacitively coupled system. In the scanning electron microscope images, surface morphology of the PP2VP thin films is observed to be very smooth and crack free. Fourier transform infrared spectra of the thin films clearly indicate that structural change occurs during the polymerization process. The information about the electronic structure and the existence of both direct and indirect optical transitions in the PP2VP thin films have been ascertained by the ultraviolet–visible spectroscopic studies. The bandgaps for the allowed indirect and direct transitions of the as-deposited PP2VP thin films are obtained as  $1.82 \pm 0.10$  and  $3.30 \pm 0.03$  eV, respectively. To understand the optical response of the PP2VP thin films elaborately, different optical parameters, such as extinction coefficient, Urbach energy, refractive index, steepness parameter, optical conductivity, etc., are estimated.

**Keywords.** Plasma polymerization; thin films; FTIR; UV–Vis spectroscopy.

## 1. Introduction

Polymer thin films play a very significant role in designing and operating innumerable optical systems and become very interesting area of research for the material scientists and engineers now-a-days. High-quality coating materials with proper and reproducible properties are necessary for the industrialization of such thin films. Although materials science and coating industries have been advanced remarkably during the last few decades, the number of suitable materials is unfortunately still restricted [1]. Organic thin films have importance in effective electronic devices like photovoltaic cells, light emitting diodes, photodetectors, thin film transistors, lasers, etc. [2]. Thin films grown on sensitive substrates are reported suitable for photonic devices [3]. Optimization of the optical and lasing properties of plasma nanocomposite thin films can be used as active components in optoelectronic devices [4]. Plasma polymerized (PP) photonic thin films became very interesting because of their interesting tunable optical properties [5]. When more than one monomer is used to obtain composite thin films, their optical properties can also be manipulated with the composition of the monomers, i.e., the monomer feed ratios [6]. To prevent corrosion, dielectric optical coatings obtained from plasma polymers become promising. Therefore, development and investigation of

high-quality plasma polymer thin films are of great importance to realize their different industrial applications [1,7]. Hence, researches on the structural and optical properties of plasma polymers from organic monomers received special consideration of the material scientists in the past years [7–15].

Thin films obtained by plasma-assisted method become interesting and growing very fast, because this method can produce thin films from almost any type of organic precursors, which are scarcely possible by the conventional polymerization methods. For the polymerization of organic and organometallic compounds, the use of glow discharges is very promising [7–10]. Plasma polymerization is advantageous for the deposition of chemically and physically durable ultra-thin films having good adhesion to nearly any substrate materials [16,17]. Because no solvent is used in this method, it is possible to handle complex geometries in a single step. Cross-linked and branched solid network of macromolecules are formed on the substrates exposed to the discharge, when volatile organic molecules are introduced in the plasma reactor [2,9,18,19]. During the polymerization, generally the structure of the polymers become changed from that of the monomers. Therefore, in order to incorporate well-defined chemical functionalities, the fragmentation processes of a precursor molecule are reduced carrying the deposition under mild conditions. The

synthesis parameters like chamber pressure, time of polymerization, flow rate of the monomer, etc. can be varied to alter the properties of the thin films. [12,20,21].

In this study, plasma polymerization technique is used to produce organic thin films under optimum condition. This method already confirmed the formation of smooth, flawless thin films having more conjugation as compared to that of the monomer [10,22–25]. The direct and/or indirect band-gap energy of such thin films are reported to vary with their thickness [8–10,22–25]. Cross-linked fragments of the monomer as well as intact molecules participated to form the thin films, which determine the optical properties observed in these materials [26]. To integrate these thin films as a photonic component of different applications, their microstructural and optical characteristics are very important.

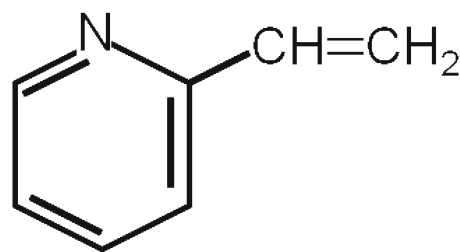
In this study 2-vinylpyridine (2VP) is used as monomer, because it can form simple reactive polymers having a great deal of industrial importance and most of the cases used in the production of a latex terpolymer for tire-cord binder [13]. In the chemical, dye, pharmaceutical and photovoltaic industries, 2VP is used as an intermediate and a precursor to specialty polymers [13,27,28]. Though several researchers investigated the thin films of 2VP [27–33], only a few used the plasma polymerization method [27], and reported as reversibly responsive coatings to control the surface wettability and swelling towards external stimuli [32]. Thus, it could be interesting to study plasma polymerized 2-vinylpyridine (PP2VP) thin films optimizing the electro-optic process parameters, which is essential for their use in desired potential applications.

Here, the PP2VP thin films are synthesized at optimized conditions by a capacitively coupled parallel plate glow discharge plasma system, and the morphology, chemical structure, absorption co-efficient, optical energy gaps, etc. are investigated. This study is expected to play a significant role in the fabrication and operation of different optical systems, especially to design single layer or multilayers of metals and dielectrics. This study will give an insight view of the optical properties of the PP2VP thin films to understand the electronic transition and formation of localized states between the energy bandgaps. To the best of our knowledge, this is not studied before for the PP2VP thin films produced by capacitively coupled system.

## 2. Experimental

### 2.1 Sample preparation

The monomer 2VP (Sigma-Aldrich Chemicals Ltd., England) is a heterocyclic aromatic amine having the chemical formula  $\text{CH}_2\text{CHC}_5\text{H}_4\text{N}$  and is a derivative of pyridine. It is a clear liquid having a vinyl group in the 2-position, next to the nitrogen as shown in figure 1. To deposit the PP2VP thin films, glass slides (Sail Brand, China) are used as



**Figure 1.** Chemical structure of the 2-vinylpyridine.

substrate. Prior to the film deposition the substrates are cleaned by acetone, thoroughly rinsed with distilled water, and dried in hot air. To deposit the thin films, the glow discharge plasma is produced inside a reactor ( $0.15 \text{ m}\phi \times 0.18 \text{ m}$ ) made of Pyrex glass using a capacitively coupled system, details of which are described elsewhere [34]. Inside the reactor, two circular stainless-steel plates each of diameter 0.09 m and thickness of 0.001 m are connected to high voltage copper connectors. During the film deposition, the inter-electrode separation is kept 4 cm and the substrates are placed on the lower electrode. The plasma chamber is evacuated to  $10^{-2}$  Torr using a rotary pump and to generate the glow discharge between the electrode plates. An ac power of 40 W is applied for deposition of the films. To introduce the monomer into the plasma chamber, a needle valve is used and a flowmeter (Glass Precision Engineering Ltd, Meterate, England) is attached between the needle valve and the monomer container to control the monomer flow rate. When the monomer vapor enters into the chamber, which can be noticed through the change in plasma colour, the chamber pressure is maintained at  $\sim 10^{-1}$  Torr and the deposition continues for 45–90 min to get PP2VP thin films of various thicknesses. Multiple-beam interferometry technique is used to measure the thickness of the PP2VP thin films [35].

### 2.2 Scanning electron microscopy

The surface morphology of the PP2VP thin films is examined by an Inspect F50 scanning electron microscope (EFI Company, Japan), where the images are taken at an operating voltage of 20 kV.

### 2.3 Fourier transform infrared spectroscopy

A double-beam Fourier transform infrared (FTIR) spectrophotometer (SHIMADZU, FTIR-8900, Japan) has been used to obtain the spectra of the PP2VP at room temperature in the transmittance mode and in the wavenumber range of  $400\text{--}4000 \text{ cm}^{-1}$ . For this, sample powder is collected from the upper surface of the lower electrode of the reactor and is used for FTIR analysis without any treatment or modification. It is believed that the structure of the powder would be

the same as the thin film on the substrate, because the powder is collected from the space close to the substrate.

#### 2.4 UV-visible spectroscopy

The UV-visible (UV-Vis) spectrum of the monomer (2VP) and the as-deposited PP2VP thin films are taken at room temperature by a SHIMADZU UV-1601 dual beam UV-Vis spectrophotometer in the wavelength range of 320–1100 nm. For measuring the optical absorption of the PP2VP films, a reference blank substrate is used.

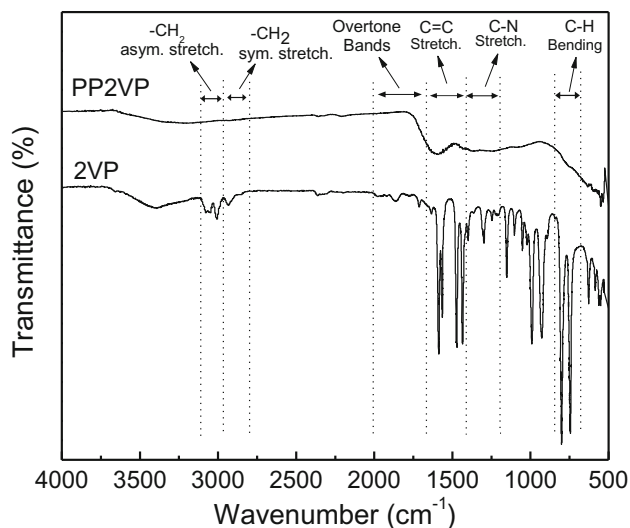
### 3. Results and discussion

#### 3.1 Surface morphology

Scanning electron microscope images of the as-deposited PP2VP thin films at two different magnifications are presented in figure 2. It is noticed that surface morphology of the PP2VP thin films is smooth and fracture free, but when the films are observed at a higher magnification there is some water wave-like structure on the surfaces, which indicates that some parts of the films may be aggregated. Usually when films are thicker (more than 200 nm), the clustering/aggregation is observed to occur, which was also observed in several PP thin films deposited [9,36,37]. The clustering occurred due to crosslinking during the polymerization for longer time duration [36].

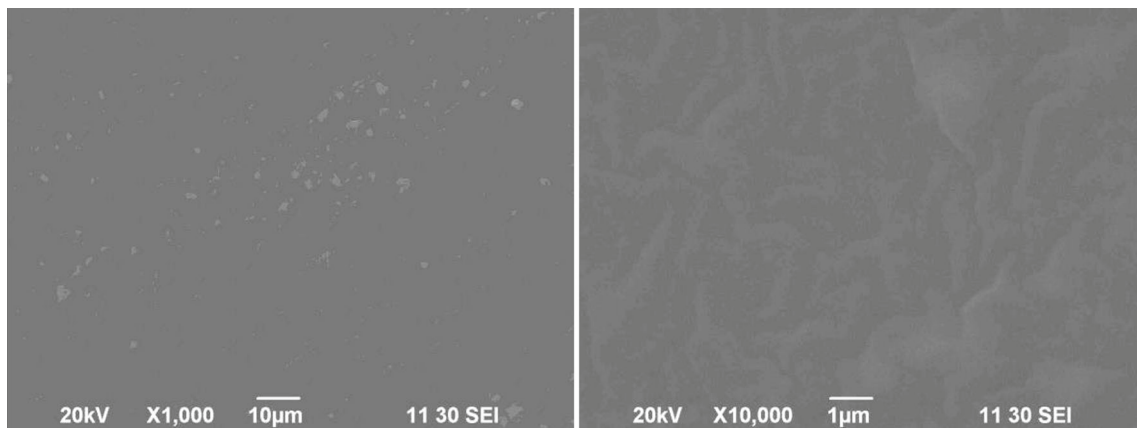
#### 3.2 Structural properties

FTIR spectra of PP2VP is observed to deviate clearly from that of the 2VP monomer, as shown in figure 3. The significant decrease of the relative intensity of the absorption bands of PP2VP with respect to that of 2VP indicate the fragmentation of the monomer structure during the plasma



**Figure 3.** FTIR spectra of the 2VP and as-deposited PP2VP thin films (curves are linearly shifted).

polymerization. The information regarding band assignments is presented in table 1. The appearance of a wide band at around  $3400\text{ cm}^{-1}$  in the spectrum of PP2VP indicate the existence of  $-\text{OH}$  stretching bonds [38], which may conjecture due to the oxidation of the monomer during its exposure to the atmosphere. In the spectrum of 2VP, aromatic  $\text{C}-\text{H}$  stretching bands are observed around  $3100\text{--}3000\text{ cm}^{-1}$  [38]. These bands are merged to broad bands in the spectrum of PP2VP and are not clearly observed due to the decrease in intensity. The  $-\text{CH}_2$  backbone stretching bands are observed at  $2950$  and  $2865\text{ cm}^{-1}$ . The absorption band in the range  $1650\text{--}1400\text{ cm}^{-1}$  indicates the  $\text{C}=\text{C}$  stretching vibrations in the skeleton of benzene derivatives [39]. It is also observed that some of the bands observed in the spectrum of 2VP are completely absent in the spectrum of PP2VP, which confirms the monomer fragmentation in the plasma polymers.



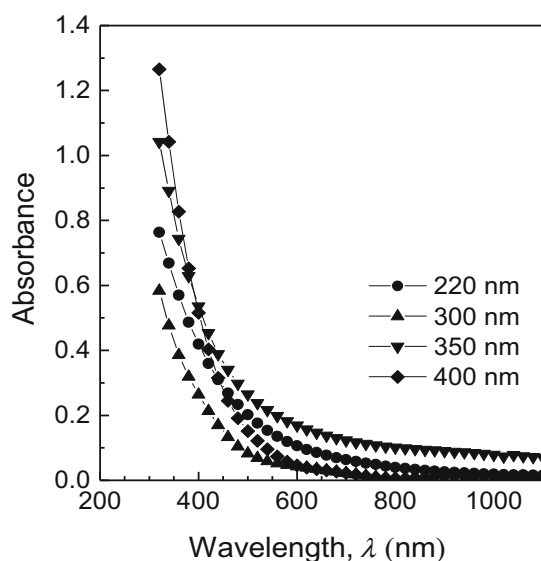
**Figure 2.** Scanning electron microscope micrographs of the as-deposited PP2VP thin film of thickness 220 nm at two different magnifications.

**Table 1.** Assignments of FTIR absorption bands for 2VP and PP2VP.

Assignments	Wavenumber (cm <sup>-1</sup> )	
	2VP monomer	As-deposited PP2VP thin films
-OH stretching	3500–3000	3500–3000
Aromatic (sp <sup>2</sup> ) = C–H	3100–3000	Merged in broad band 3100–3000
CH <sub>2</sub> asymmetric stretching	2950	2940
CH <sub>2</sub> symmetric stretching	2865	Merged in broad band 2865
CO <sub>2</sub> in atmosphere	2354	2340
Overtone	2000–1700	
C=C stretching (vinyl group) or C=N stretching	1630	1591
C–C stretching	1650–1400	Merged in broad band 1650–1400
C–N stretch	1350–1250	Weak
C–C–C skeletal stretch	1035–1005	Merged in broad band 1035–1005
-C=C–H out-of-plane bend	980–700	Merged in broad band 980–700
Aromatic ring out-of-plane bend	870–670	613
C–H wagging vibration	744	Weak

### 3.3 Optical properties

Plasma polymers have received much attention for their potential applications as light guide material, optical fibres, photovoltaic energy converters, photodiodes, optical coatings to inhibit corrosion, etc. [7]. To realize these applications, PP thin films need vast optical investigations. The PP organic thin films are usually amorphous and their electronic properties depend on the localized electronic states created in the band energy gap [9,10,14]. Optical investigations are done taking the UV–Vis absorbance spectra of the as-deposited PP2VP thin film of various thicknesses at room temperature (300 K), which is shown in figure 4. It is

**Figure 4.** Absorbance as a function of wavelength for the PP2VP thin films of different thicknesses.

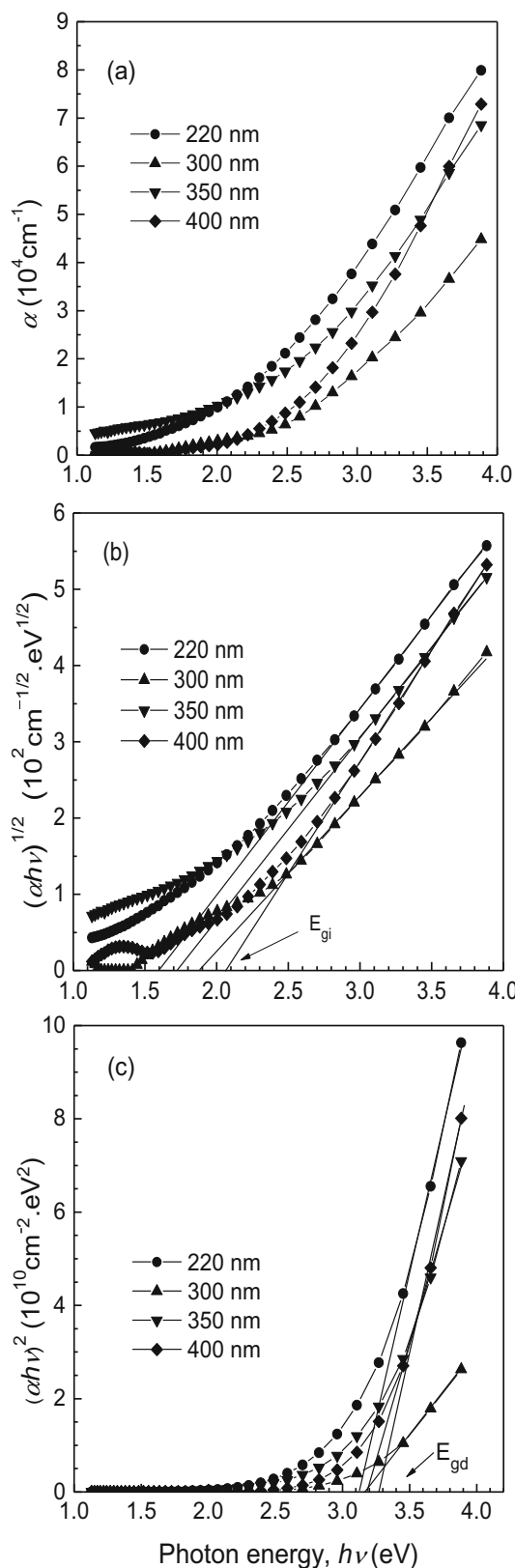
observed that for all the samples the absorbance attains its maximum value at  $\sim 320$  nm. The absorption coefficient,  $\alpha$ , of the PP2VP thin films is calculated using the below formula [23],

$$\alpha = 2.303 \frac{A}{t}, \quad (1)$$

where  $A$  is the absorbance,  $t$  the film thickness and the change of  $\alpha$  with the photon energy,  $h\nu$ , for the as-deposited PP2VP, as shown in figure 5a. It is observed that the values of  $\alpha$  begin to increase from around 1.6 eV and from  $\sim 2.5$  eV this increase is very rapid. These curves can be characterized by different slopes representing the existence of different optical transitions in the PP2VP thin films [9], and the exponential edge indicates the presence of defects or lack of long-range order in the PP2VP thin films. The optical band gap,  $E_{\text{opt}}$ , of an amorphous material can be expressed by the Tauc relation [40]

$$\alpha h\nu = B(h\nu - E_{\text{opt}})^{\beta}, \quad (2)$$

where  $B$  is a constant independent of the photon energy and the index  $\beta$  depends on the nature of optical transition.  $\beta$  equals  $\frac{1}{2}$  and 2, respectively, for the allowed direct and indirect optical transitions. The indirect bandgap energy ( $E_{\text{gi}}$ ) therefore can be obtained from the intersect point of extrapolation of the linear fit of the linear portion of the  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  plot to zero as shown in figure 5b. Similarly, the direct bandgap energy ( $E_{\text{gd}}$ ) can be obtained from the  $(\alpha h\nu)^2$  vs.  $h\nu$  curve, as shown in figure 5c. The obtained values of  $E_{\text{gi}}$  and  $E_{\text{gd}}$  for the as-deposited PP2VP thin films of various thicknesses are listed in table 1. The values of  $E_{\text{gi}}$  and  $E_{\text{gd}}$  are observed to be increased with the film thickness. However, average values of the  $E_{\text{gi}}$  and  $E_{\text{gd}}$  for the as-deposited PP2VP thin films are  $1.82 \pm 0.10$  and



**Figure 5.** (a) Plot for absorption co-efficient with photon energy, (b)  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  curves and (c)  $(\alpha h\nu)^2$  vs.  $h\nu$  curves for the as-deposited PP2VP thin films of different thicknesses.

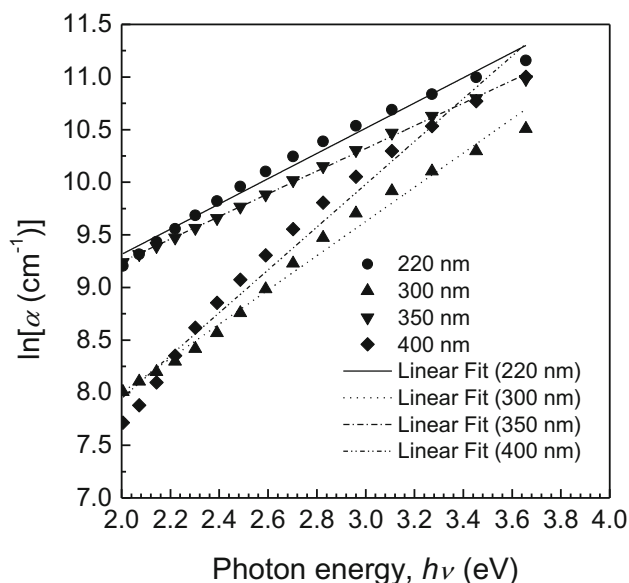
$3.18 \pm 0.03$  eV, respectively, which confirms the amorphous nature of the PP2VP thin films [9]. The small peak around 1.4 eV for the thin film of thickness 400 nm, as shown in figure 5b, indicates the creation of energy states within the gap due to charged or structural defects, which may contribute in the conduction [10].

When electron near the valence band edge absorbs photons, it is excited near to the bottom of the conduction band. During this transition, for amorphous system the electron may experience disorders caused by defect centres and/or thermal vibrations, which create density of states tailing into the forbidden energy gap [9]. The width of this tail, called Urbach tail, is an indicator of the presence of defect levels in the forbidden gap between the valence and conduction bands. The energy associated with this tail is referred to as the Urbach energy ( $E_u$ ), indicating the width of the localized states and is calculated by the relation [41]:

$$\alpha = \alpha_0 e^{h\nu/E_u}, \tag{3}$$

where  $\alpha_0$  is a constant. The values of  $E_u$ , obtained from the gradient of the plot  $\ln\alpha$  against  $h\nu$  as shown in figure 6, are listed in table 2 for the PP2VP films of different thicknesses. It is observed that the values of  $E_u$  show decreasing trend as the thickness of the PP2VP thin films increases, and this is conjectured due to the decrease of the disorder or defect states in the PP2VP thin films [10,25,42].

Another optical parameter called the steepness parameter,  $\sigma_s$ , arises from the electron/exciton–phonon interaction



**Figure 6.** The Urbach plots of PP2VP thin films of various thicknesses.

**Table 2.** Different optical parameters of the PP2VP thin films of different thicknesses.

Thickness, $d$ (nm) $\pm$ 5%	Indirect bandgap, $E_{gi}$	Direct bandgap, $E_{gd}$ (eV)	Urbach energy, $E_u$ (eV)	Steepness parameter, $\sigma_s$
220	1.60	3.12	0.83	0.031
300	1.88	3.16	0.61	0.042
350	1.73	3.18	0.53	0.048
400	2.06	3.27	0.49	0.052

indicating the absorption edge broadening and is estimated by the expression [42,43]:

$$\sigma_s = \frac{k_B T}{E_u}, \quad (4)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature (here  $\sim 298$  K). The calculated values of  $\sigma_s$  are noted in table 2 and are observed to increase with the thickness of the PP2VP thin films, which may attribute to the increase in the electron–phonon interaction [43].

The extinction coefficient,  $k$ , represents how strongly a material absorbs incident light at a given wavelength and can be estimated by the formula [10],

$$k = \frac{\alpha \lambda}{4\pi}. \quad (5)$$

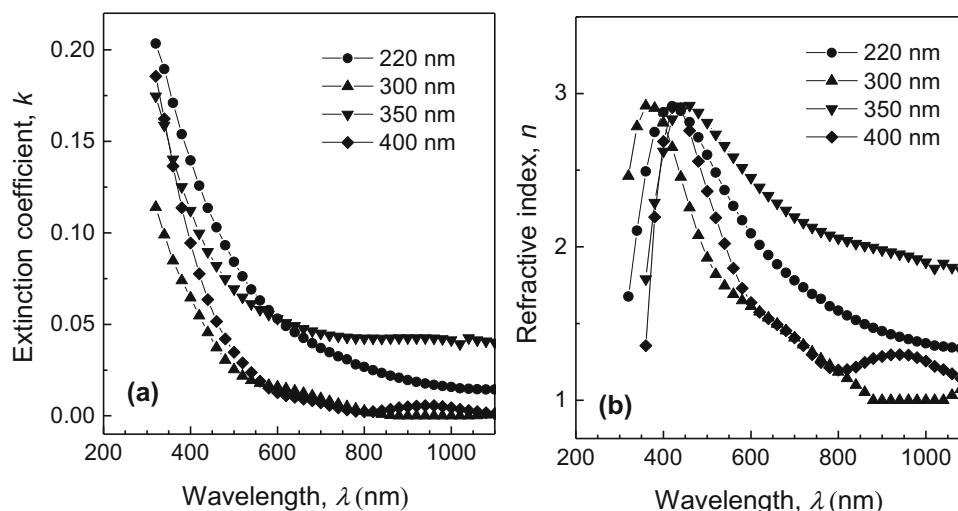
The variation of  $k$  with  $\lambda$  for the PP2VP thin films is shown in figure 7a. It is observed that the value of  $k$  increases with the increase in photon energy, which indicated the transfer of the electron across the mobility gap [10].

To understand the propagation of light through the material, refractive index,  $n$ , of the thin films is studied. It also plays a vital role to find materials having enhanced optical properties and in designing optical communicating

devices [10]. For amorphous system like PP2VP thin films,  $k^2 \ll n^2$ , and  $n$  is calculated by the Fresnel's formula [44],

$$n = \left( \frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}, \quad (6)$$

where  $R$  is the reflectance. It is revealed from figure 7b that the values of  $n$  for the as-deposited PP2VP thin films in the UV region increases with  $\lambda$ , but decreases in the visible region for all the films. The variation of  $n$  with thickness does not follow regular trend, however, the increase of  $n$  in some of the thin films of higher thickness may be attributed to the formation of cross-linking in the films [8,45]. A high cross-link density affects the ‘closeness’ between chains and the particles in the thin films pose considerable obstacles, thus reducing the speed of the traversing light radiation. Thus the  $n$  becomes directly related to crosslink density [46]. Introduction of extra absorption close to the fundamental inter-band absorption increases the  $n$  value in the visible spectral range according to the Kramers–Kronig relation [47]. When films of higher thickness are formed, by operating the plasma for a longer period, post-heating effect may be introduced, which may be responsible for the decrease of the defects in the thin films and eventually the value of  $n$  decrease [47].



**Figure 7.** The change of (a) extinction coefficient and (b) refractive index with  $\lambda$  for the PP2VP thin films of different thicknesses.

In this study, the variations of  $n$  and  $k$  with thickness of the PP2VP thin films does not show any regular pattern, however those are calculated to measure other optical parameters and to understand the correlation among the other properties. Higher values of  $n$  and  $k$  in the lower wavelength region indicate the absorption of surface plasmon in the PP2VP thin films [48]. On the other hand, lower value of  $n$  may be indicating the relaxation in the thin films, because the number and sharpness of the extrema depend on the film thickness. Thus,  $n$  may be regarded as an adjustable parameter for regulating the sharpness of the extrema for thin films of various thicknesses [48].

Complex dielectric constant,  $\epsilon (= \epsilon_r + i\epsilon_i)$ , where  $\epsilon_r$  and  $\epsilon_i$  are, respectively, the real and imaginary parts, is studied for the PP2VP thin films to know the electronic structure and the charge polarizability in the films. When an electromagnetic wave propagates through a lossy material like PP2VP thin films, it experiences attenuation, that is, it loses its energy due to the generation of phonons, scattering, free-carrier absorption, etc. [49]. For these type of materials, the complex refractive index is defined as,  $\hat{n}(= n - ik)$ , with  $n$  the real part of the refractive index. For nonmagnetic substances,  $\hat{n}$  is related to  $\hat{\epsilon}$  by the relation,  $\hat{n} = \sqrt{\hat{\epsilon}} = \sqrt{\epsilon_r - i\epsilon_i}$  [10]. Therefore, the  $\epsilon_r$  and  $\epsilon_i$  of PP2VP thin films can be assessed by the following equations [10,39]:

$$\epsilon_r = n^2 - k^2 \tag{7}$$

$$\epsilon_i = 2nk \tag{8}$$

The values of  $\epsilon_r$  and  $\epsilon_i$  of the PP2VP thin films against  $\lambda$  are shown in figure 8a and b, respectively. It is observed that both the value of  $\epsilon_r$  and  $\epsilon_i$  decreases rapidly up to 600 nm, and thereafter, the decrease is very slow with the change in wavelength, which may be conjectured due to the electronic polarizability for the dielectrics [50]. Also, the values of  $\epsilon_r$  at higher wavelength approaches towards zero, indicating the insulating nature of the films [10]. It is also noted that, the change of  $\epsilon_r$  and  $\epsilon_i$  follows identical pattern and the values of  $\epsilon_r$  are always higher than that of  $\epsilon_i$ . The dissipation factor,  $\tan\delta$ , for the PP2VP thin films are calculated using the below relation [41] and are depicted in figure 8c,

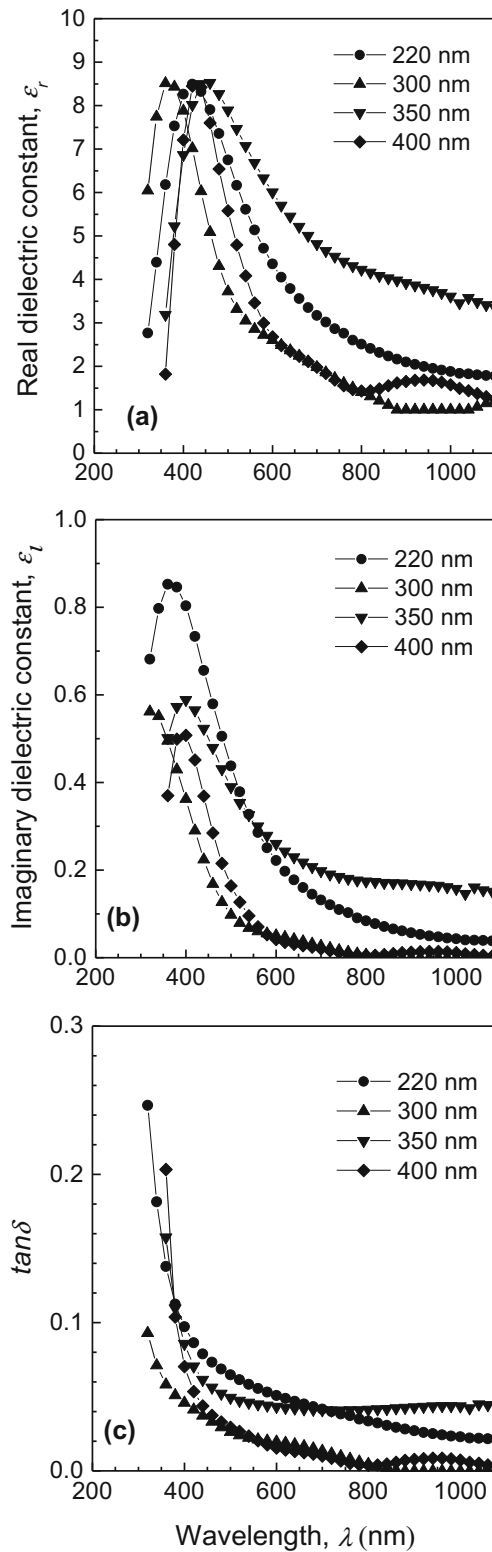
$$\tan\delta = \frac{\epsilon_i}{\epsilon_r} \tag{9}$$

It showed that the dielectric loss becomes very low for the radiation of wavelength more than 500 nm.

Optical conductivity,  $\sigma_{opt}$ , is considered to be a powerful parameter to realize the optical response and electronic state of the PP2VP thin films and is evaluated by the equation [51],

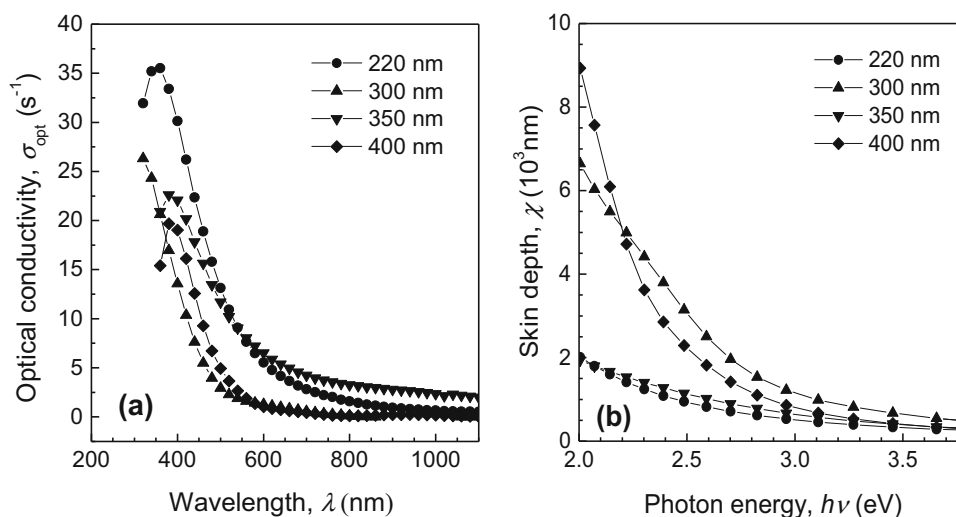
$$\sigma_{opt} = \frac{\alpha nc}{4\pi} \tag{10}$$

where  $c$  is the speed of light used. A sharp reduction of the  $\sigma_{opt}$  values up to 550 nm is noted for PP2VP thin films, above which it becomes almost steady approaching zero, as



**Figure 8.** The variation of (a) real dielectric constant, (b) imaginary dielectric constant and (c) dissipation factor,  $\tan\delta$ , with wavelength for the PP2VP thin films of different thicknesses.

shown in figure 9a, and this may be considered owing to the higher absorption of radiation by the PP2VP thin films. Besides, electrons get excited by the photon energy when



**Figure 9.** The variation of (a) optical conductivity,  $\sigma_{\text{opt}}$ , and (b) skin depth,  $\chi$ , as a function of wavelength,  $\lambda$ , for the PP2VP thin films of different thicknesses.

they interact with the incident photon [52]. It is also observed that most of the cases  $\sigma_{\text{opt}}$  rises for the film of higher thickness, which is conjectured due to the formation of localized states by the defect sites in the PP2VP thin films [43,53]. Incident photon interacts with the electrons and the degree of interaction can be estimated by the skin depth,  $\chi$ , defined as [51],

$$\chi = \frac{\lambda}{2\pi k}. \quad (11)$$

Change of  $\chi$  against  $h\nu$  for the PP2VP thin films is presented in figure 9b. In the lower energy range the value of  $\chi$  is observed to be large and deviates with the film thickness, which indicates the increase of collisions among the electrons [54]. However, at the higher energy range it becomes very low and almost independent of the film thickness.

#### 4. Conclusions

The PP2VP thin films showed smooth and fracture-free surface. The significant reduction of intensities of the absorption bands in the FTIR spectra of the PP2VP thin films compared to that of the monomer spectrum specifies monomer fragmentation during the plasma polymerization. The appearance of some new absorption peaks in the polymer films confirmed the change of the chemical structure of the PP2VP thin films from its monomer. The slow increase of the absorption coefficient around the photon energy 1.6 eV along with the rapid increase from 2.2 eV in the UV–Vis spectra of the PP2VP thin films revealed the presence of both indirect and direct optical transition in the thin films of various thicknesses. The energy gaps for these two transitions,  $E_{\text{gi}}$  and  $E_{\text{gd}}$ , vary around  $1.82 \pm 0.10$  and  $3.30 \pm 0.03$  eV, respectively, where their values are observed to increase with the film thickness. The calculated

values of  $E_{\text{u}}$  for the PP2VP thin film are observed to vary from 0.49 to 0.83 eV depending on the film thickness, indicating the reduction of localized states in the bandgap. The value of  $\sigma_{\text{s}}$  for the PP2VP thin films are observed to increase from 0.031 to 0.052 with the film thicknesses, indicating the reduction of electron–photon interaction and the broadening of the absorption edge.

The values of  $\sigma_{\text{opt}}$  decreases sharply with the increase in wavelength, indicating higher absorption of radiation by the thin films, and the rise of  $\sigma_{\text{opt}}$  with film thickness indicates the formation of localized states by the defect sites in the PP2VP thin films. In the lower energy range, the large value of  $\chi$  deviates with the film thickness indicating the increase of collisions among the electrons. However, at the higher energy range it becomes very low and almost independent of the film thickness.

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