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Characterization of Plasma Polymerized Polyaniline Thin Films

Ozkan Bayram (Corresponding author)
Bayburt University, Department of Material Science and Nanotechnology Engineering,
Engineering Faculty, TR-69100 Bayburt, Turkey
E-mail: obayram@bayburt.edu.tr

Onder Simsek
Ataturk University, Department of Physics Education,
Kazım Karabekir Education Faculty, TR-25240, Erzurum, Turkey
E-mail: osimsek@atauni.edu.tr

Marefat Feizi Khanghah
Ataturk University, Graduate School of Natural and Applied Sciences,
Department Nanoscience and Nanoengineering, TR-25240 Erzurum, Turkey
E-mail: m.feizi@atauni.edu.tr

Mustafa Tolga Yurtcan
Ataturk University, Department of Physics Education,
Kazim Karabekir Education Faculty, TR-25240, Erzurum, Turkey
E-mail: yurtcan@atauni.edu.tr

Abstract

In this study, it is aimed to obtain polymeric thin films derived from Aniline, which is an organic compound. The glass substrates were placed in the vacuum chamber after washing and cleaning in organic solvent, hot distilled water, and ultrasonic bath respectively. After depressurizing the vacuum chamber to 100 mTorr by means of vacuum pump, vacuum chamber pressure was fixed and power of RF source designed as 20 Watt whilst thin films were obtained. Molecular structure, amorphous phase, optical and surface morphology characteristics of obtained thin films were researched by using respectively FTIR, XRD, UV-VIS spectroscopes and SEM. It was revealed that thin films, obtained as a result of the process of characterization, have highly cross linked, amorphous structured and semiconducting properties. The thickness of the films was found to be 240 nm by Ellipsometry. The deposition rate was found to be 4 nm/min. It is believed that, obtained thin films have the potential of being used in semiconducting tools industry considering the energy-gap.

Keywords: Conducting polymers, Plasma polymerization, Polyaniline, Organic thin film, FTIR

1. Introduction

Occurrence of new technologies in the field of electronic applications, particularly in the bioelectronics and organic electronics, has significantly increased the interest to produce and develop polymeric thin films, which are obtained from organic sources. Therefore; recently lots of studies have been made on the subject of growing and researching organic thin films (Bae et al. 2001, Srinivas et al. 2012, Abdulla et al., 2012). When these studies are examined, it is seen that the researchers concentrate on the optical and electrical characteristics of nanoscale thin films, which are obtained from organic sources. And, is understood from these studies; polyaniline is one of the most important conducting polymers (Srinivas et al. 2012, Biederman et al. 2011, Friedrich et al. 2011, Pal et al. 2011, Barman et al. 2012, Ghani et al. 2010). One of the most common applications for surface coating of organic molecules such as Aniline is the polymerization of organic molecules on the surface. Polymerization can be in the form of condensation or addition polymerization in terms of process mechanisms. Condensation polymers are obtained through composition of micro molecules as a result of reacting similar or different structured monomers. Such polymers are called condensation polymerization (step-growth polymerization). This method is so stepwise that it is not economical. Monomers grow the polymer chain by joining the active center one by one in the addition polymerization. Monomers directly join the polymer molecules by the chain reactions. Another name of this method is chain-growth polymerization. Every organic molecule is not possible to be polymerized with these two methods, which have low reactivity and also are not biodegradable. The other way to polymerize organic molecules is “Plasma Polymerization” technique. This method, notwithstanding the molecule structure, makes possible to polymerize every organic molecule (Quillard et al 1994). This condition has been an important factor to designate our study design.

When the organic molecules are present in the plasma media, radicals are composed as a result of hemolytic decomposition of intra-molecular bonds (covalent bonds). Radical, is the common name of the atoms or molecules, which have unpaired electrons. Because of the radicals tend to pair their unpaired electrons, they are chemically active and they may cause a chain reaction. As a result of chain reaction, polymer formation may occur. In the case organic molecules are emitted to plasma media; these molecules become polymerized and form a thin film on a substrate. This technique is named as “Plasma Polymerization” (Goktas et al. 2013).

In this study, polymeric thin films were obtained by using plasma polymerization of aniline, an organic compound. It was researched molecular structures of the produced thin films by FTIR Spectroscopy, their surface morphology by SEM analysis, structures of the films by XRD, and their electrical and optical properties by UV-Visible spectroscopy. The results of characterization reveals that organic Polyaniline thin films, which are low – cost and environmentally friendly, have the potential of being preferred in emerging technologies such as growing electronic and biomedical industries.

2. Experimental

Aniline organic compound, which was used as a monomer material in this study, was supplied by procurement from the company, Sigma Aldrich. Plasma polymerization was employed in order to obtain polyaniline (PANI) thin films on glass quartz substrates. The schematic diagram of experimental set up used in this study is shown in Figure 1. Plasma polymerization set up consists of a chamber coupled to a vacuum system, RF amplifier and a monomer holder. In this study, approximately 10 mL of aniline used as monomer was placed into the holder. Glass substrates, before placed in plasma polymerization system, were subjected to surface cleaning process in two stages as dry and wet. Firstly, substrates were cleaned with ethanol for wet cleaning to purify from organic impurity, afterwards they were washed with hot distilled water and then they were dried by cleaning in ultrasonic bath. Dried substrates were placed in vacuum chamber, then dry surface cleaning process was applied to purify their surfaces from oxygen and other impurities. In this process, cleaning of the substrate surfaces in the vacuum chamber was carried out with argon plasma obtained through RF – PECVD technique by using argon gas. Upon completion of the cleaning process of the substrate surface, base pressure of the vacuum chamber was depressurized to 100 mTorr by means of vacuum pump, and then aniline monomer was emitted to vacuum media from monomer tank retainer in the gas form gradually by means of a valve. RF energy, one of the significant parameters of this study, was obtained by applying voltage between electrodes. Coating parameters designed for this study were selected considering the current studies in literature (Biederman et al. 2011, Friedrich et al. 2011, Tamirisa et al. 2004, Lakshmi et al. 2009). RF energy (at a frequency of 13.56 MHz) was delivered to the deposition chamber via copper electrodes separated by 10 cm. 20 W RF power was applied for about 60 minutes. The vacuum maintained during the process was of 2×10^{-1} to 4×10^{-1} mTorr. The film obtained was of 0.24 μm thick yielding a deposition rate of 4 nm/min. The prepared films were characterized by FTIR, XRD, UV–visible absorption- reflection and SEM. FTIR, UV–visible Spectroscopy, XRD and SEM were carried out by using NEXUS-670 FTIR spectrometer, Hitachi U-3300 UV–visible Spectrometer, Bruker AXS, D-8 Advance X-ray diffractometer, JEOL JSM- 6380 scanning electron microscope, respectively.

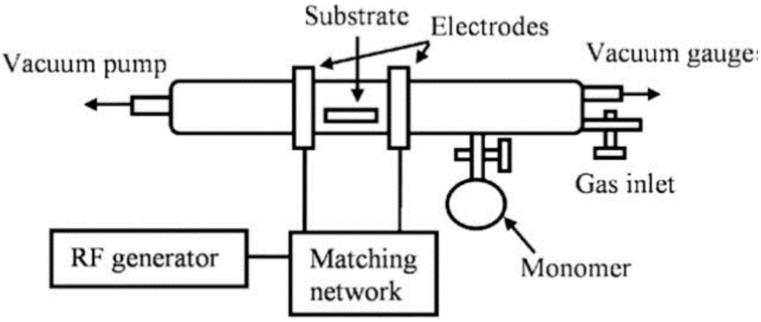


Figure 1. The RF-plasma polymerization set up (Easton et al., 2013).

3. Results and discussion

3.1 Analysis of chemical structure

Molecular structure was determined for PANI thin films by using “Spectrum One” brand spectroscopy of Perkin Elmer Company. It was aimed to compare the literature by identifying the functional groups of polymeric thin films by determining molecular structure. FTIR spectrum of Polyaniline thin film was examined based on the number of wavebands at 4000-400 cm^{-1}. And band distance of this spectrum is shown in Figure 2. Upon examination of the FTIR spectrum of PANI thin film, it is seen that the band close to 3746 cm^{-1} value resulted from OH stretch of the absorbed water. Pal et al. (2011) found in their study that OH stretch is in between 3448– 3855 cm^{-1} range The 3363 cm^{-1} peak point belongs to N-H stretch of the secondary amino group of PANI (Tamirisa et al. 2004). Meanwhile, Lakshmi et al. (2009) observed the stretch of secondary amino group at 3325 cm^{-1} band. Barman and Pal (2012) found out that unsaturated C-H stretch is in between 3052-3028 cm^{-1} range; the unsaturated (aromatic and alkene) C-H stretch was determined in between 3052 cm^{-1} and 3027 cm^{-1} peaks in our study. In another study by Tamirisa et al. (2004), it was observed that C-H stretch of aromatic ring was at 3024 cm^{-1} band. Furthermore, the peaks in between 2927-2864 cm^{-1} resulted from saturated C-H stretch (Pal et al. 2011). On the other hand, Barman et al. (2012) determined this property in between 2949–2921 cm^{-1} band. The band at 2220 cm^{-1} corresponds to nitrile vibration; and its relation to chain termination is also possible. Moreover, Tamirisa et al. implied that the bands close to 1871 cm^{-1}, correspond to out of plane C=H deformations in aromatic rings. In our study on the other hand, this property was observed at 1866 cm^{-1}. Finally the bands observed around 1191 cm^{-1} reveals the aromatic C-H resulting from the in-plane bending (In plane bending vibration) (Lakshmi et al. 2009).

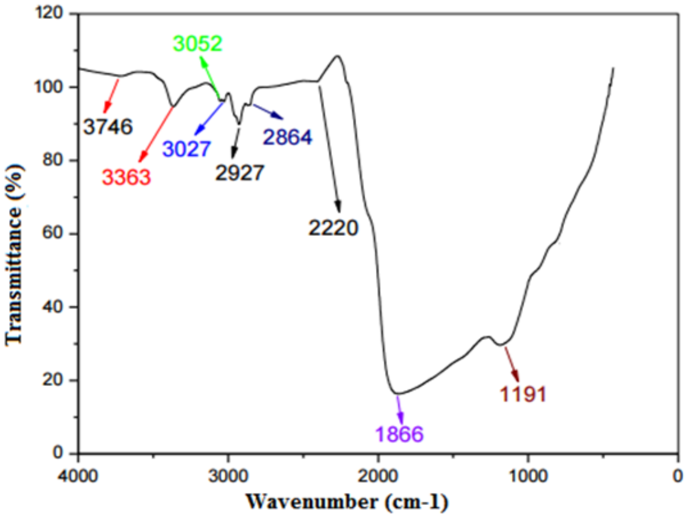


Figure 2. FTIR spectrum of PANI thin film

3.2 Surface Morphology and Structural Analysis

Surface imaging process with SEM was performed by a FEI brand and Inspect S50 model Scanning Electron Microscope in Chemistry Laboratory in Faculty of Sciences of Ataturk University. SEM has analyzed the surface morphology of coatings and macro-granular structures on the coated polymer surface. In the studies by Abdullah and Abbo (2012), they observed that the surfaces of the films are not smooth but it has macro-granular structures formed through the aggregation of small global structures. SEM analysis shown in Figure 3 based on the PANI thin films obtained in this study supports the above-mentioned study. In other words, surfaces of PANI thin films have a rough structure and are comprised of macro-granular structures. Besides, these structures are like cauliflowers for their shapes. Abdullah and Abbo (2012) emphasized that these structures have an amorphous morphology. Therewithal, Tamirisa et al. (2004) observed the same property in Polyaniline films they synthesized (Pal et al. 2011) and reported that presence of these lines on the surface of PANI increases the conductivity.

Examination phases composed as a result of coating process was performed by means of using an X-Ray Diffraction (XRD) device. In XRD analyses, Cu Kα ray of 1.54 nm wavelength was used. X-Ray Diffraction was employed to characterize the PANI thin film structure obtained via plasma polymerization technique. As seen in Figure 4, wide peaks in between 2θ = 20°-28° introduce that Polyaniline is in the amorphous form (Abdolahi et al., 2012). Lakshmi et al. (2009) reported that PANI is a cross-linked polymer and these films have an amorphous form because of a constant spectrum in XRD analysis. Ghani and Young (2010) stressed that the peaks in between 2θ = 38° - 44.7° band have arisen from characteristic peaks of PANI, the same as in the studies of Mexiang Wan et al (1994) and Abdulla and Abbo, (2012). Besides, this condition was observed in the study by Vilela et al. (2007). Furthermore, the peaks in between 5°-10° arose from polymeric chains, which cause conductivity (Vilela et al. 2007).

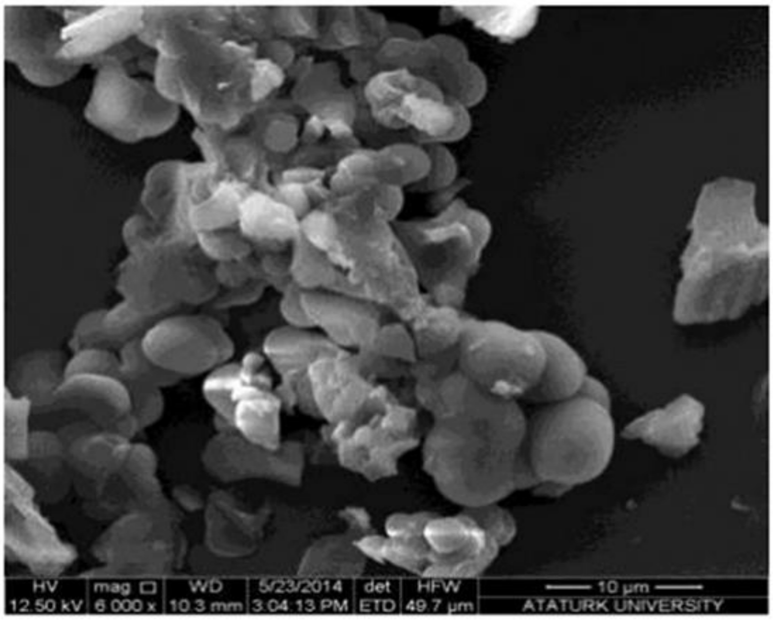


Figure 3. SEM image of synthesized PANI thin film.

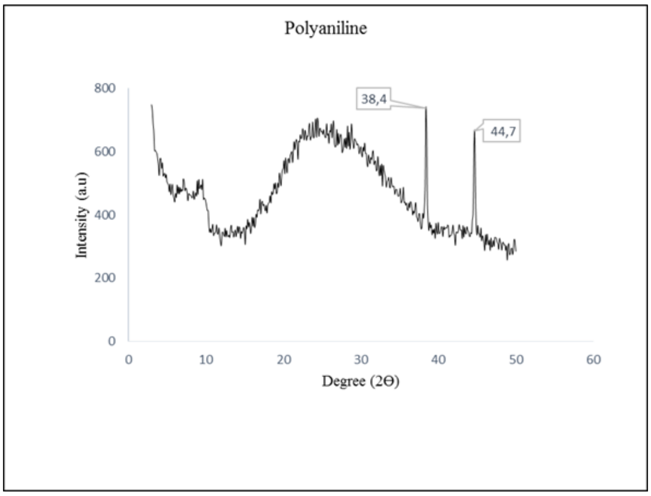


Figure 4. X-Ray diffraction (XRD) spectrum of PANI thin film.

3.3 UV-Visible Analyze

For the purpose of determining energy band gap and some optical properties of obtained films; Lambda-2s brand UV–Visible spectroscopy, a production of Perkin-Elmer Company, was preferred. Wavelength-Absorption of the Polymeric thin film was drawn in curves in a graphic drawing program based on the data of Energy - absorption coefficient, and squared coefficient of Energy - absorption. UV visible Spectroscopy results, we used for investigating the electronic and optical properties of obtained thin films, are given in Figure 5 and Figure 6, respectively. Figure 5 shows absorption has great values at ultraviolet or smaller wavelengths such as visible regions. Particularly, in between 320 nm and 400 nm range, absorption gives the biggest value. This results from transition of the electron in electronic orbital of the film to the next level in ultraviolet and visible region (Goktas et al. 2013). In Figure 6, the spectrum was drawn according to the energy instead of the wavelength in order to ensure that absorption is independent of thickness and other parameters (Tuzemen et al. 2006). The optical band gap was determined from the absorption spectrum according to Tauc's relation;

$$\alpha h\vartheta = \left(h\vartheta - E_g\right)^n \quad \text{n=1,2,3} \tag{1}$$

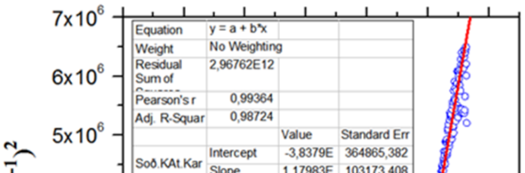
The present system obeys the rule of indirect transition with n = 2. α is calculated using the relation,

$$\alpha = \frac{O_d}{t} \tag{2}$$

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

$$k = \alpha\lambda \,/\, 4\pi \tag{3}$$

where λ is wavelength of incident photon. The value of $(\alpha h\nu)^{1/2}$ with incident photon energy hν is plotted in Fig. 6, and the value of Eg is determined to be 3.25 eV, by taking the intercept of hν on the x-axis.



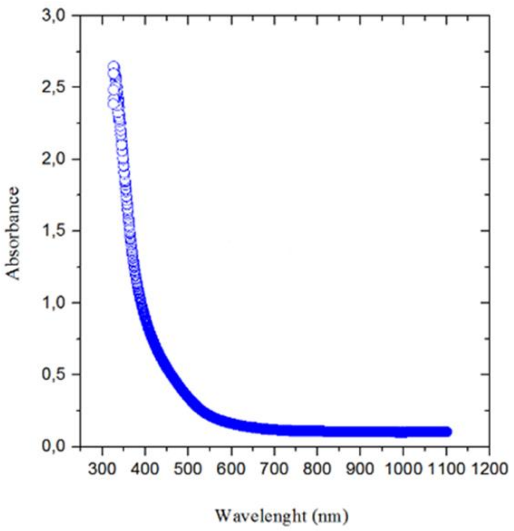


Figure 5. UV-Vis absorption spectrum.

Figure 6. Absorption coefficient as a function of wavelength of film deposited at 20 W

4. Conclusion

PANI thin films were successfully deposited on glass substrates by using radio frequency plasma enhanced chemical vapor deposition technique. The film prepared has a thickness of 240 nm and the deposition rate is estimated to be 4 nm/min. FTIR spectroscopy results were examined to identify the characterization of obtained thin films. In examination of the bands in FTIR spectrum, it was introduced that thin films have cross-linked structures after determining the functional groups of PANI. SEM was employed to determine surface geometry and morphology of the created thin films. In the images taken with SEM, it was observed that thin films have aggregated structures with small granules. On the purpose of determining the structure of thin films XRD spectroscopy was used and as a result of the analysis conducted, it was determined that polymeric thin films have an amorphous structure and bear characteristic peaks of PANI. UV- visible spectroscopy as employed to determine electronic and optical properties of created thin films. It was observed that absorption values of the obtained thin films correspond to visible region in UV-Visible spectrums. Band gap was calculated as 3.25 eV. This result shows that Polyaniline thin films have the potential of being preferred in semiconducting industry, particularly in production of FET transistors.

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