Thin Solid Films 587 (2015) 66–70

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Conductive polythiophene-like thin film synthesized using controlled plasma processes

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ARTICLE INFO

Available online 19 December 2014

Keywords:
Aromatic ring structure
Plasma polymerization
Polythiophene-like
Conductivity

ABSTRACT

Transparent conductive polythiophene-like thin films were synthesized by a plasma polymerization technique using a middle range frequency (40 kHz). The effects of the variation of power and pressure on the chemical structure of the deposited film were investigated along with the effect of doping with iodine vapors on the conductivity of the films. Plasma polymerization is a low temperature process, provides deposition of thin polymer films on a wide variety of substrates, and has advantages due to non-involvement of any solvents. The chemical structure of the films was characterized using Fourier Transform Infrared Spectroscopy. The wetting properties of the films were studied using water contact angle measurements. The fragmentation of the thiophene monomer structure increased with increasing discharge power, implying that at low discharge power, the plasma phase was energy-deficient. The lower fragmentation of the monomer led to high retention of the monomer structure in the deposited films. Under various pressure conditions, the retention of the monomer structure was found to be similar as that of the deposited films. After doping with iodine vapor, a large conductivity enhancement, from 3.52×10^{-6} to 2.3×10^{-3} s/cm was observed. The results showed the retention of a monomer structure having conjugated bonds in the films, responsible for the enhanced conductivities.

1. Introduction

Polymers are one of the most commonly used materials in the modern world, finding their use and applications ranging from containers to clothing. Polymers are known to have good insulating properties and are therefore used to coat metal wires to prevent electric shocks. MacDiarmid et al. [1] discovered that polymers can be made electrically conductive, and for this discovery they were awarded the Chemistry Nobel Prize in 2000. Such polymers were then seen as a possible substitute for metallic conductors and semiconductors. The unique property of these polymers is that they have conjugated double bonds along their backbone. The conjugation bond contains alternately a strong chemical bond (the "sigma" (σ) bond) and a weak chemical bond (the "pi" (π) bond). However, most polymers having conjugation bonds are semiconducting, but become conductors in a charged or "doped" state.

Recently, conductive polymers are being developed for many applications, such as electronic sensors [2], organic field effect transistors [3], light emitting diodes [4] and solar cells [5]. For these applications, conventional methods such as chemical, electrochemical, spin casting and screen printing [3,5–9] are generally used. However, conventional methods have their limitations because of the contamination due to presence of dangerous solvents in the film [10].

Another promising method of synthesizing conducting polymers is plasma polymerization. The main advantage of this method is non-involvement of solvents or oxidants, which reduces the possibility of contamination during the synthesis. Other advantages are direct low temperature synthesis on different types of substrates, the possibility of using a wide range of monomers, and a less-time consuming process [11–13]. Due to these advantages, plasma polymerization has been applied to prepare conducting polymer films, finding applications in different fields, such as fuel cells [14], tissue regeneration (biomaterial–cell interfacial interaction) [15], strain sensors [16], and photovoltaic coatings [17]. In plasma polymerization, plasma-reactive species are formed by collisions of energetic electrons with monomer molecules. These

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http://dx.doi.org/10.1016/j.tsf.2014.12.030
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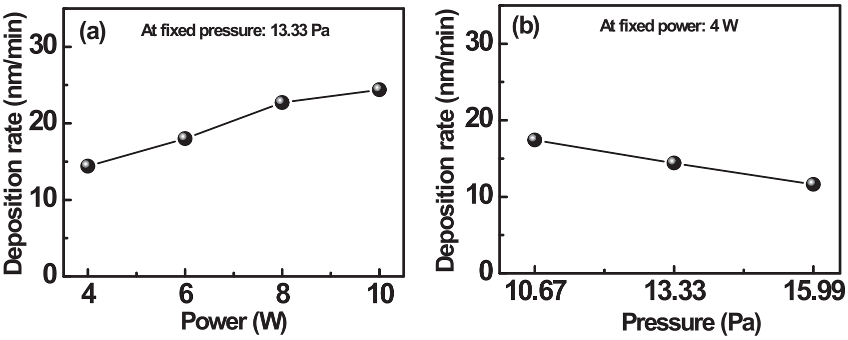

Fig. 1. Deposition rate of polythiophene-like film: (a) as a function of power at a constant pressure and (b) as a function of pressure at a constant power.

collisions result in the excitation, fragmentation, and ionization of the discharge gas, producing excited molecules, free radicals and ions. Also, plasma generated by ultraviolet radiation has a strong influence on oxidation and enhances the cross-linking of the deposited material [13,18]. Barman et al. [12] reported the retention of a monomer structure having a highlighted conjugation bond. The retention of the aromatic structure in deposited films is an important feature regarding conductivity in polymers. Low power and appropriate pressure were applied to reduce the excessive fragmentation and enhance the retention of the thiophene monomer [19,20]. In organic chemistry, an aromatic hydrocarbon is a hydrocarbon with alternating single and double bonds between adjacent carbon atoms, which causes ring formation. An aromatic ring structure is made of aromatic organic compounds that are arranged in a conjugated planar ring system. Simple aromatic rings can be heterocyclic if they contain non-carbon ring atoms such as oxygen, nitrogen, and sulfur. Typical simple aromatic compounds include benzene, furan, pyrrole, and thiophene. Polythiophene, a conductive polymer that is stable in air, has a low cost, can be processed easily, and has a precursor with a high vapor pressure. Additionally, with a plasma polymerization method, it is not necessary to heat the source during processing.

In this study, plasma polymerization process is presented for the preparation of polythiophene-like thin films along with the effect of power and pressure in obtaining high conductivity. The possible influence of the doping by iodine vapors on the film was investigated. Also, optical properties of the un-doped and doped films are presented as a function of plasma parameters. The possible mechanism for enhanced electrical conductivity is presented based on the retaining of the monomer structure during plasma polymerization.

2. Experimental detail

Plasma polymer thin films were deposited using the plasma-enhanced chemical vapor deposition (PECVD) method. Polythiophene-like films were synthesized through middle frequency (MF, 40 kHz) power using a thiophene (C_4H_4S) precursor. Additionally, 50 sccm of argon gas was used as a carrier gas. The reaction chamber consisted of two cylindrical electrodes that were 8 in. in diameter. Before the process, the substrates (except KBr) were washed with acetone and alcohol to remove contamination. The cleaned substrates (glass, KBr, wafer) were placed on the center of the bottom electrode. During the experiment, the base pressure was ~2.67 Pa. During the process, the thiophene precursor and argon gas were allowed to flow through the top electrode (shower head). The distance between the top electrode and bottom electrode was 70 mm. We tried to keep the film thicknesses to be same, around 200 nm, by controlling the deposition time. The typical conditions of the PECVD process applied in this study for film deposition were 4, 6, 8, and 10 W MF power and 10.67, 13.33, and 15.99 Pa pressure.

Plasma polymerization was carried out in a stainless steel PECVD cylindrical chamber with dimensions as 450 mm in length and 390 mm in diameter. The thiophene was purchased from Aldrich Chemicals. The chemical structures of polythiophene-like thin films were observed using a Fourier Transform Infrared Spectroscopy (FT-IR), of model Bruker Optik, Vertex 70. The spectra were obtained between 4000 and 600 cm^{-1} at a spectral resolution of 4 cm^{-1} using transmission mode. The number of scans was 64.

UV–vis spectra were obtained using a UV-1800 ENG 240 V, SOFT spectrometer in the wavelength range of 200–1000 nm. The thickness of the film was measured using α-step profilometer (KLA Tencor Alpha-step IQ). A metal-tipped pen was used to scribe a thin line in the films deposited on glass substrates, after which the film thickness was determined using the profilometer. The thickness of a given film was measured at five different positions for each sample, and averaged for determining the deposition rates at the end of the deposition.

Contact angle measurement is the fastest and simplest method for investigating surface wetting properties [21,22]. Distilled water was used as the test liquid and a 4-μL drop of liquid was placed on the surface of the test substrate material. Contact angles were measured more than five times for each sample and the mean value was used. The experiments were carried out at atmospheric pressure.

Resistance was measured using a resistance meter (ANSI/ESD Model 152). Doping was accomplished by a chemical method of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase. In the gaseous doping process, polythiophene-like thin films were exposed to iodine vapor in a sealed chamber.

3. Results and discussion

We synthesized polythiophene-like thin films with good conductivity at low power and working pressures. The resulting films were first analyzed using α-step. Fig. 1 shows the variation of deposition rate as a function of power and pressure. Fig. 1(a) shows the deposition rate of the polymer films as a function of the input power varying from 4 to 10 W at fixed pressure (13.33 Pa). With increasing input power, the deposition rate increased steadily. The increase of the deposition rate with increasing power can be explained simply in terms of the increase in electron temperature [23], resulting in the greater fragmentation and dissociation of the thiophene monomer precursor. A decrease in deposition rate was observed with increasing pressure at fixed power (4 W), as shown in Fig. 1(b). The reason behind this can be understood by the fact that at the lower power conditions, an increase in pressure leads to a shortened mean free path, which leads to the loss of energy of the produced reactive species and subsequent neutralization on the way to the substrate location due to higher collision frequency [24]. Thus, a decrease in deposition flux at the substrate is in agreement with the behavior reported in the literature [24].

Fig. 2(a) shows the FT-IR spectra of the polythiophene-like thin films as a function of pressure conditions. Absorption bands at 3025 and 2930 cm^{-1} are due to the aromatic C–H stretch and aliphatic C–H stretch, respectively. The absorption bands at 1667, 1601, 1447, and