



## Effect of distance from discharge to substrate on plasma-polymerized polythiophenes



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### ABSTRACT

Plasma-polymerized polythiophenes were deposited as thin films utilizing plasma of mid-range frequency (40 kHz) and low power (4 W). The thin films were prepared by changing the distance from the top electrode to the substrates, and the resulting films were compared. Conductivity increased with distance up to 110 mm, and then decreased with further increase in distance. FT-IR and XPS analysis showed that the thin films had similar molecular structures regardless of the distance. However, as the distance increased, surface roughness increased from 0.54 to 5.53 nm, which suggested gas-phase nucleation and molecular packing.

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### 1. Introduction

Conducting polymers have been the subject of much research in various fields such as organic electronics, optoelectronics, sensors, actuators, etc. [1–5], since their development by Chiang et al., Fincher et al., and Park et al. [6–8]. Most conducting polymers have conjugated  $\pi$ -bonds throughout their backbones, which are responsible for their unique properties. Due to extended  $\pi$ -conjugation, most polymers are semiconducting at their neutral or “undoped” state, but become conducting at charged or “doped” state. Conducting polymers can be prepared by chemical or electrochemical oxidation of monomers such as thiophenes, pyrroles, anilines, and other relatively electron-rich aromatics [9–15]. Recently, conjugated (conducting) polymers with elaborated chemical structures have been also prepared by metal-catalyzed carbon–carbon bond forming reactions [16,17]. Typical examples of such class of polymers are regioregular poly(3-hexylthiophene)s (rr-P3HTs) [18] and poly(thienothiophene-benzodithiophene)s (PTB series), which are the key active materials in organic photovoltaics [19]. By either oxidative polymerization or metal-catalyzed polycondensation, conducting polymers all show extended  $\pi$ -conjugation, especially in the “undoped” state.

Plasma polymerization is another method of synthesizing conducting polymers. In a plasma phase, high energy electrons and ions can activate monomer molecules to facilitate polymerization and concomitant deposition in substrates. Plasma polymerization is a “dry” process since it does not use any solvents and does not require purification steps. In addition, plasma-polymerized films can be deposited on any type of substrate regardless of shape, and the resulting films are generally smooth and pinhole-free. Due to such advantages, plasma polymerization has been applied to prepare conducting polymers. However, general complexity and uncontrollable nature of the plasma phase can render the synthesized polymers virtually insulating, presumably due to the excessive fragmentation of the monomer molecules. Thus plasma conditions have been controlled to minimize the fragmentation but promote polymerization with highly extended structures of  $\pi$ -conjugation [20,21].

Herein, we report the synthesis of plasma-polymerized polythiophene at plasma conditions of mid-range frequency (40 kHz) and low power (4 W), which were applied to reduce the excessive fragmentation of the thiophene monomer, and we then characterize them. The thin films of plasma-polymerized polythiophene were very smooth and pinhole-free, containing large portions of extended  $\pi$ -conjugation, revealed by FT-IR. The films were conductive after iodine doping ( $10^{-3}$ – $10^{-4}$  S/cm). The distance from the substrate to the glow-discharge electrode significantly affected the conductivity and morphology. As the distance increased (far away from the glow-discharge), the deposition rate decreased but the synthesized

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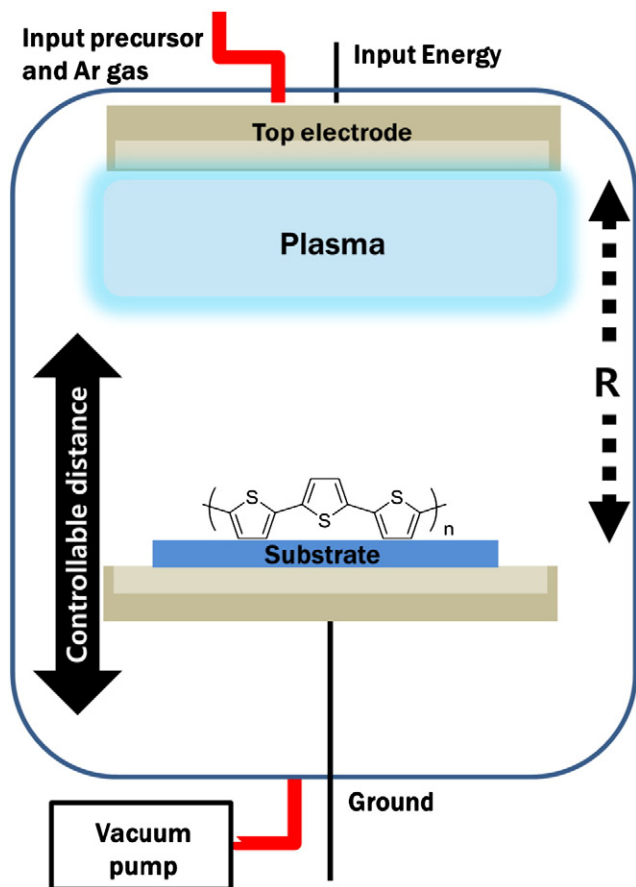


Fig. 1. Schematic representation of a plasma-enhanced chemical vapor deposition (PE-CVD) chamber using a thiophene monomer.

polymers had higher conductivity and increased roughness, which can be explained by the balance between deposition and gas-phase recombination.

## 2. Experimental

### 2.1. Materials and instruments

The thiophene was purchased from Aldrich. Chemical bonding of plasma-polymerized films on sodium bromide crystals was examined with FT-IR spectrometry (Bruker Optik, Vertex70). The surface morphology of the plasma polymerized films was observed by a contact mode AFM (SPA-300HV, SII Nano Technology, Inc., Tokyo, Japan) and field emission scanning electron microscopy (FE-SEM,

JEOL JSM 7000F). UV-Vis spectra were obtained using a UV-1800 ENG 240V, SOFT spectrometer. Film thickness was measured by  $\alpha$ -step profilometer (KLA Tencor Alpha-step IQ). X-ray photoelectron spectra (XPS) were measured on a silicon wafer using an ESCA2000 (VG microtech:UK) photoelectronic spectrometer with AlK $\alpha$  (1,486.6 eV)/MgK $\alpha$  (1253.6 eV) as X-ray source. Resistance was measured by Resistance Meter (ANSI/ESD Model 152).

### 2.2. Plasma polymerization

Plasma-polymerized films were synthesized by middle frequency (40 kHz) plasma-enhanced chemical vapor deposition using a thiophene (C<sub>4</sub>H<sub>4</sub>S) precursor with Ar carrier gas. The deposition chamber consisted of two electrodes, 8 in. in diameter, in a cylinder. The substrates ranged from slide glass to silicon wafer to KBr pellets. Before deposited, the substrates (except KBr) were cleaned using acetone and alcohol to remove contamination. After cleaning the samples, the substrates were placed on the bottom electrode. During film deposition, the base pressure was approximately  $1 \times 10^{-3}$  Torr and the working pressure was 0.1 Torr (Fig. 1).

## 3. Results and discussion

### 3.1. Plasma polymerization of thiophene

We conducted plasma polymerization for various distances ( $r$ ) from the powered electrode to the grounded electrode where the substrates were placed. As shown in the scanning electron microscopy (SEM) images (Fig. 2), plasma polymerization of the thiophene monomer resulted in pinhole-free polymer thin films with high degree of homogeneity, regardless of the distance  $r$ . Plasma-polymerized polythiophenes could be deposited on various substrates such as glass, silicon wafer, and plastics, showing the significant merit of plasma polymerization. However, the rate of film deposition decreased as the substrate distance  $r$  increased. At  $r = 30$  mm, the film deposition rate was 25 nm per min, but at  $r = 130$  mm, it reduced to 12 nm per min. We suspect that “active ingredients” for polymerization exist in large amounts near the powered electrode. Molecules of thiophene monomer collide with ions, radicals or high-energy electrons from the plasma phase to produce “active ingredients”, which are probably fragmented species with dangling bonds [21–23]. Those species may react with each other to polymerize on substrates. When the distance ( $r$ ) increases, these fragmented species will start to recombine in the gas phase, decreasing the concentration of “active ingredients”.

### 3.2. Conductivity measurements

The conductivity of plasma-polymerized polythiophenes was dependent on the distance  $r$  from the powered electrode. The conductivities of the thin films were in the range of around  $10^{-7}$  S/cm to  $10^{-6}$  S/cm,

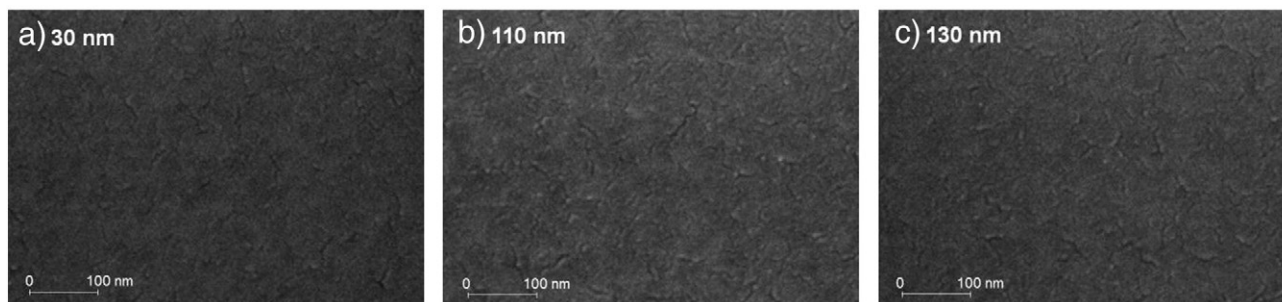


Fig. 2. Comparison of SEM images of thin films of plasma-polymerized polythiophenes with different distances from the top electrode, 30 mm (a), 110 mm (b), and 130 mm (c). Scale bar = 100 nm.

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