Preparation and Characterization of Thin Films of the Poly(p-phenylene vinylene) Semiconducting Polymer

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ABSTRACT: Conjugated polymers have been the subject of many studies because of their widespread applications in electronic and optoelectronic devices. Poly(p-phenylene vinylene) is a leading semiconducting polymer in optical applications. This work is focused on the development of thin films of poly(p-phenylene vinylene) by spin coating and their characterization with Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy to understand their changes. An empirical model has been developed to show the effect of the variables—the spin speed, polymer concentration, and spin time—on the film thickness. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1917–1922, 2009

Key words: conjugated polymers; spin coating; thin films

INTRODUCTION

Conjugated polymers, being electroluminescent, have received a great deal of attention because of their applications in electronic and optoelectronic devices such as light-emitting diodes,[1] thin-film transistors,[2] photovoltaic cells,[3] chemical, physical, and biological sensors, nonlinear optical and molecular devices,[4,5] and electrochemical cells.[6] Conjugated polymers have the advantages of versatile multicolor emission and easy fabrication of small- and large-area active layers.[1] These semiconducting polymers consist of at least one backbone chain of alternating double and single bonds. Poly(p-phenylene vinylene) (PPV), because of its high yield emission, is popular among semiconducting polymers, especially for optical applications.[1,7] The conjugated π-electron system of PPV is responsible for its outstanding nonlinear optical and electrical properties.[8,9] The electrical and optical properties of light-emitting diodes on flexible substrates determine their lifetime, turn-on voltage, and operating voltage.

Thin films of PPV can be formed either by wet-processing methods such as the Langmuir–Blodgett film method, spin coating, dip coating, and solution casting or by dry-processing methods such as physical and chemical vapor deposition.[10,11] Spin coating is a widely accepted method for coating a thin (0.5–2-μm), uniform, adherent, and homogeneous film over the surface of a silicon wafer.[12] Optical and electrical properties of film-coated optoelectronic devices are controlled by the polymer morphology, which in turn is affected by treatment conditions such as a variety of solvents, differing concentrations of polymer solutions, and various spin-coating conditions.[13,14] It becomes essential to study the effects of such process variables on the nature of the film deposited by spin coating and optimize them. The statistical design of experiments allows us to establish the relationship between process variables and response. Factorial design requires the execution of a relatively small number of different experiments and is more efficient than one-factor-at-a-time experiments.[15] Cecchi et al.[16] applied an experimental methodology design to optimize polymer light-emitting diode film coatings and reported that the polymer film thickness and film nonuniformity depended on the polymer concentration and spin speed and were not influenced by ramp acceleration.[16]

This work focuses on the preparation of spin-coated PPV thin films on glass substrates having a thin layer of indium tin oxide (ITO). The films were characterized with X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). A mathematical model was also developed to quantify the effects of process variables such as the spin speed, concentration, and spin time on the film thickness.

EXPERIMENTAL

ITO film preparation

Before the polymer was applied, an ITO film was deposited on a glass substrate (1″ × 1″) with a commercial sputtering system. To deposit the ITO film,

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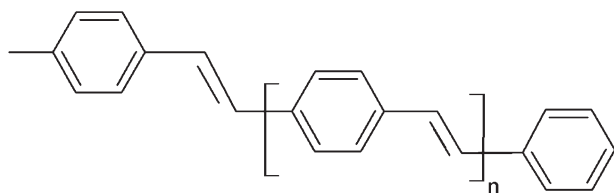
Figure 1 Basic structure of PPV.

an indium–tin (90 : 10) alloy target with a purity of 99.99% was loaded at the holder provided in the sputtering system at a fixed distance of 40 mm from the substrate. The vacuum chamber was evacuated to a pressure of 2×10^{-5} mbar before deposition. Then, argon gas was introduced until the preset pressure reached 8×10^{-4} mbar. The film was deposited with 50-W power for 30 min.

Spin coating

In this experiment, PPV with a molecular weight of 5234 (its basic structure is shown in Fig. 1), procured from Sigma–Aldrich (St. Louis, MO, USA), was used. PPV was coated onto the ITO substrate through the spin-coating process. Because we were aiming to optimize the spin-coating process parameters to obtain a desired PPV film thickness, ranges of spin speeds, solution concentrations, and spin times were chosen for experimentation (Table I). These conditions were chosen on the basis of previous studies and limitations of the spin coater.[16]

Initially, PPV was dissolved in toluene at three different concentrations (1, 3, and 5 mg/mL) and stirred for 3 h. The filtered solutions were then spin-coated onto the ITO substrate in a nitrogen atmosphere with an SCU 2005 spin coater made by Apex Instruments (Kolkata, India). The whole coating process was performed in three stages. During the first stage of static dispensing, a small puddle of the PPV solution (ca. 1 cc) was dropped at the center of the substrate loaded in the spin coater. Then, the coating was accelerated to 1000, 3000, and 5000 rpm to get a solution of the desired thickness. During the last stage, the coated film was dried in a vacuum oven at 40–45°C for 1 h for complete removal of the solvents.

Characterization

The PPV film thickness was measured with a Taylor/Hobson precision (Leicester, England) NCS profilometer. The XRD pattern was obtained for the ITO substrate before and after the coating of PPV with a Philips X'Pert-PRO X-ray diffractometer (Eindhoven, Netherlands). The FTIR spectra of PPV thin film samples were recorded with a ThermoNicolet Nexus 870 FTIR spectrophotometer (Madison, WI). Topographical imaging of thin films was obtained with a JEOL JSM-5800 (Tokyo, Japan) scanning electron microscope.

Process optimization

Optimizing device performance entails determining the effects of several process parameters. In this experiment, ranges of spin speeds, solution concentrations, and spin times were chosen at two levels for optimization (Table I). A three-factor, two-level, full factorial experiment was run to estimate the factor effects. The experimental design matrix was generated (Table II) and responses were analyzed with MINITAB (version 13.1) statistical software from Minitab, Inc. (PA, United States). The individual combinations in the design matrix were run in a random order to avoid the influence of the experimental setup. Subsequently, the response data were fitted into a factorial model, and main and interaction effects were analyzed through analysis of variance and factorial plots.

RESULTS

Characterization

XRD analysis

XRD studies were carried out on the ITO substrate and PPV by high-resolution XRD at a low angle ($<2°$) with a Cd X-ray source to study the nature of the phase. The XRD pattern of the ITO film [presented in Fig. 2(a)] showed a very strong diffraction peak at 35°, which confirmed the crystalline nature of the ITO film. No sharp diffraction peak was observed from the XRD patterns of PPV films coated at room temperature, as shown in Figure 2(b), which depicts the amorphous nature of the PPV polymer. A similar XRD pattern for the amorphous nature of

TABLE I
Range of Coating Parameters for the Design of the Experiments

Sample	Parameter	Unit	Minimum	Center	Maximum
1	Spin speed	rpm	1000	3000	5000
2	Concentration	mg/mL	1	3	5
3	Spin time	s	20	30	40

TABLE II
Film Thicknesses for Different Combinations of the Spin Speed, Solution Concentration, and Spin Time

Sample	Design matrix			Spin speed (rpm)	Concentration (mg/mL)	Spin time (s)	Film thickness (Å)
1	+	+	+	5000	5	40	560
2	+	+	−	5000	5	20	490
3	+	−	+	5000	1	40	110
4	+	−	−	5000	1	20	100
5	−	+	+	1000	5	40	1175
6	−	+	−	1000	5	20	1496
7	−	−	+	1000	1	40	245
8	−	−	−	1000	1	20	310
9	0	0	0	3000	3	30	400
10	0	0	0	3000	3	30	420
11	0	0	0	3000	3	30	405
12	0	0	0	3000	3	30	397

pure poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] was reported by Kazim et al.[17]

FTIR spectroscopy

FTIR was used to study the structural behavior of the spin-coated polymer under various conditions. The chemical structure of PPV is explained by the absorption bands of the IR active vibration in the spectral range of 4000–500 cm^{-1} in Figure 3. The absorption bands appearing at approximately 951 and 3016 cm^{-1} were assigned to the *trans*-vinylene C—H out-of-plane bending and *trans*-vinylene C—H stretching vibration, respectively.[18] The band at 2949 cm^{-1} was due to C—H stretching from remnant saturated aliphatic groups, as reported by Saramas et al.[19] The peaks corresponding to the aromatic in-plane C—H deformation vibration (at 1273, 1250, 1192, 1041, and 1019 cm^{-1}) were observed in the range of 1290–1000 cm^{-1}. The band at 837 cm^{-1} was due to phenylene ring C—H out-of-plane bending. Ring carbon–carbon stretching vibrations occurring in the region of 1625–1430 cm^{-1} were observed at 1572, 1484, and 1424 cm^{-1}. The conjugated aromatic C=C stretching vibration was confirmed by the absorption band appearing at 1580 cm^{-1}.[20] Furthermore, these studies indicated no structural difference present in thin film samples at various spin speeds.

SEM

The effect of the spin speed on the surface morphology was studied at a constant solution concentration and a constant spin time of 5 mg/L and 40 min,
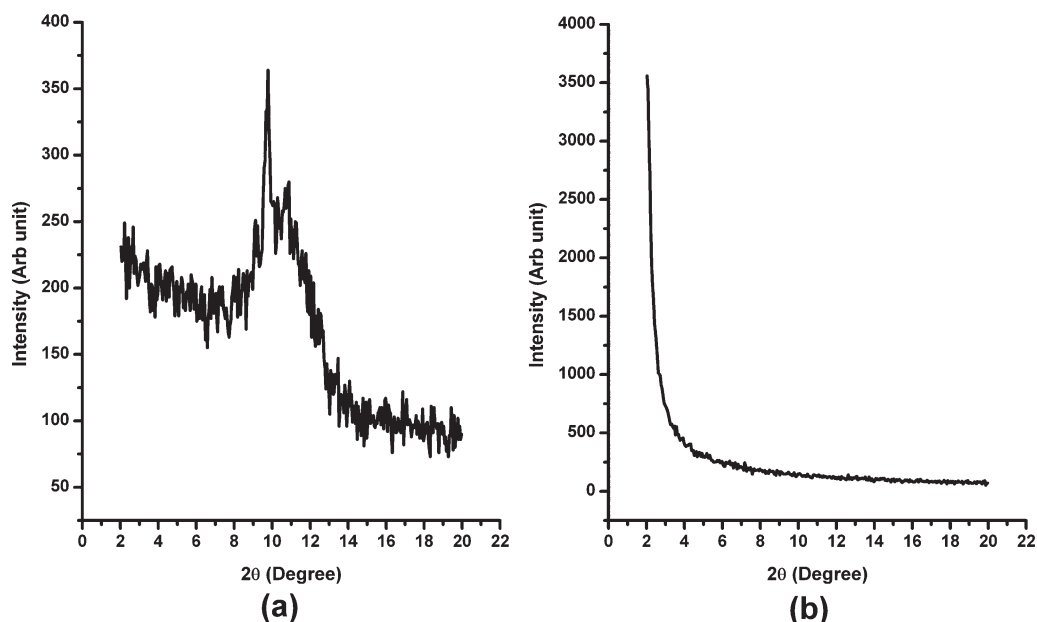

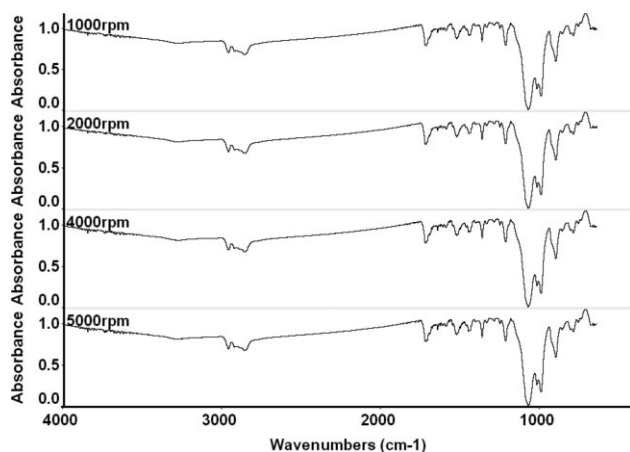**Figure 2** XRD patterns of (a) the ITO film and (b) the PPV film.

Figure 3 FTIR spectra of PPV films coated at 5 mg/L for 40 s at speeds of 1000, 2000, 4000, and 5000 rpm.
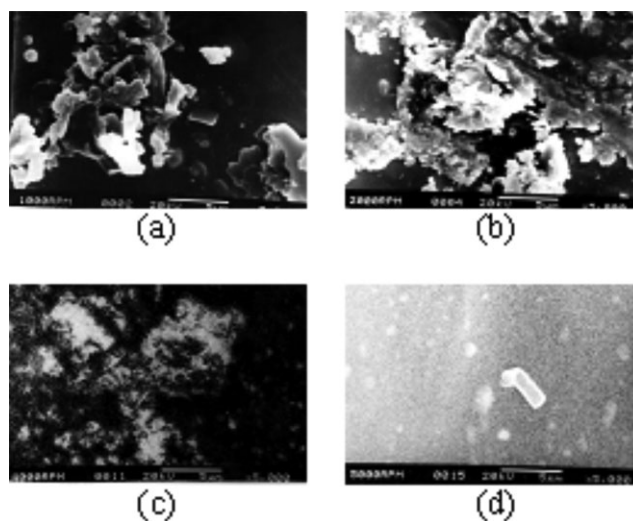

Figure 4 SEM views of PPV thin films on ITO-coated glass substrates at 5 mg/L for 40 s at speeds of (a) 1000, (b) 2000, (c) 4000, and (d) 5000 rpm.

respectively. The SEM picture, as shown in Figure 4, clearly indicates that as the spin speed increased, the polymer spread more uniformly over the substrate. The SEM analysis further indicates that the PPV films coated at a high spin speed had a more uniform and smoother surface. This may be due to shearing of the polymer by the greater force acting on it at higher speed levels.

Process optimization

An empirical model for film thickness was derived by multiple regression analysis based on an analysis of variance considering the main and interaction effects of the three factors:[16]

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1x_2x_3 + e \quad (1)$$

This model was used to determine the main effect of each of the three factors [the speed (x_1), concentration (x_2), and time (x_3)], the three two-way interactions (x_1x_2, x_1x_3, x_2x_3), and the one three way interaction ($x_1x_2x_3$) on the response (Y). b_1, b_2, b_3, b_4, b_5, b_6, and b_7 are regression coefficients, whereas b_0 and e are the intercept and error, respectively. The

analysis of variance results displayed in Table III reveal that all three factors (the spin speed, solution concentration, and spin time) had a significant influence on the film thickness ($P < 0.01$). The main effect plot displayed in Figure 5 reveals that the film thickness decreased with increasing spin speed and spin time but increased with increasing solution concentration. Furthermore, the analysis of variance indicated that all two-way and three-way interactions among the selected factors were significant ($P < 0.01$). The two-way interactions of the spin speed and solution concentration and the spin speed and spin time had a more significant influence on the film thickness than the interaction of the solution concentration and spin time, as shown in Figure 6 ($P < 0.01$). The solution concentration showed the largest effect among all the effects; it was extended farthest, as shown in the Pareto chart (Fig. 7), whereas time showed the least effect. Although concentration more significantly influenced the thickness, it had a smaller interaction effect when combined with time, unlike the interaction effect of the spin speed and spin time, which was larger.

TABLE III
Analysis of Variance of the Film Thickness

| Source	Degrees of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean square	F	P
Main effects	3	1,587,091	1,587,091	529,030	5,000	0.000
Two-way interactions	3	235,468	235,468	78,489	752.30	0.000
Three-way interactions	1	12,482	12,482	12,482	119.64	0.002
Curvature	1	64,274	64,274	64,274	616.04	0.000
Residual error	3	313	313	104	—	—
Pure error	3	313	313	104		
Total	11	1,899,628				
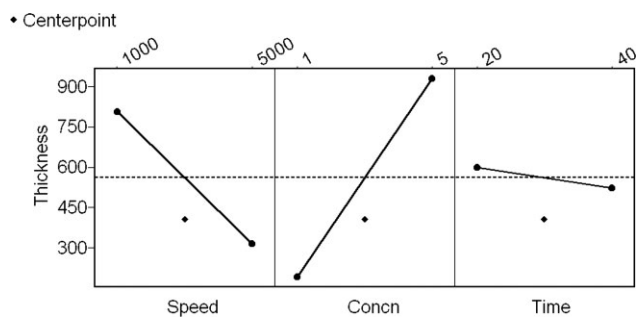
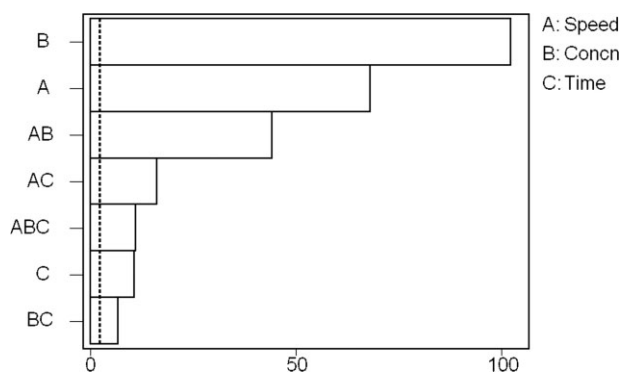**Figure 5** Main effect plot for thickness.

Figure 7 Pareto chart of standardized effects.

The empirical model was developed through linear multiple regression analysis based on main, two-way interaction, and three-way interaction effects of these factors. The empirical model of film thickness in coded units was obtained as follows:

$$F_t = 560.8 - 245.7(S_s) + 369.5(C) - 38.2(S_t)$$
$$- 159.5(S_s \times C) - 24.5(C \times S_t)$$
$$+ 58.2(S_s \times S_t) + 39.5(S_s \times C \times S_t) \qquad (2)$$

where F_t is the film thickness (Å), S_s is the spin speed (rpm), C is the concentration (mg/mL), and S_t is the spin time (s).

The accuracy of the model developed by factorial runs was checked by a comparison of the experimental and predicted film thickness values. A graphical plot showing the predicted film thickness versus the actual film thickness (Fig. 8) indicated that the statistical model was adequate because these values formed a straight line passing through the diagonal. The error percentage on average was about 9%, which was mainly due to the central runs.

CONCLUSIONS

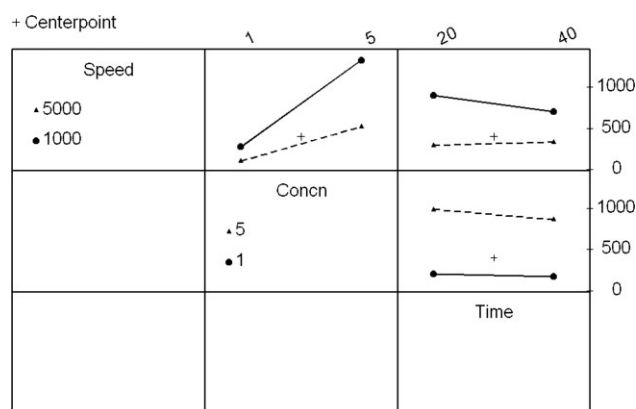A PPV thin film deposited by spin coating was characterized with different analytical techniques. XRD established that the coated polymer was amorphous in nature, and the FTIR spectra showed no structural difference in thin-film samples at selected spin speeds. The SEM pictures showed that as the spin speed increased, the polymer spread uniformly over the substrate. The experimental methodology design was applied to study the effects of the solution concentration, spin speed, and spin time. The spin speed, solution concentration, and spin time had a significant influence on the film thickness. An analysis of variance revealed that all three main, two-way interaction, and three-way interaction effects were highly significant ($P < 0.01$).

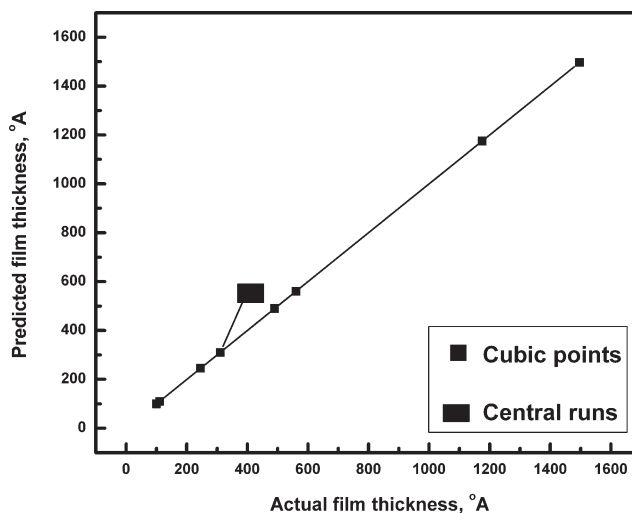**Figure 6** Interaction effect plot for thickness.

Figure 8 Predicted thickness versus the actual thickness.

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