Method to optimize polymer film spin coating for polymer LED displays

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Abstract

Research and development of displays and image sensors based on semiconducting polymers require design of new polymer materials and evaluation of film properties. Application of statistical methods can expedite process development. Optimizing device performance entails determining the effect of several process parameters, necessitates numerous samples, and may consume more scarce new material than desired. Uniform film thickness, with no voids, pinholes, inhomogeneities, or particulate contamination across the substrate can improve display efficiency and uniformity. After performing and analyzing a two-cubed full-factorial experiment with three replicated center points, this paper concludes that spin velocity and polymer concentration have statistically significant effects on film thickness, film uniformity, and device efficiency. Ramp acceleration does not. Analysis of variance methodology determines the effect of the three spin coating factors and their two-way interactions.

Keywords: Spin coating, Electroluminescence, Poly(phenylene vinylene) and derivatives.

1. Introduction

Semiconducting polymers blend several attractive material properties that enable inexpensive and unique applications, including the next generation of flat and flexible image sensors and multimedia displays [1-8]. The application of a homogeneous, uniform thin film with no imperfections is fundamental to the manufacture of flat-panel-displays [9]. To meet these stringent requirements, researchers and scientists may employ statistically designed experiments. "By the statistical design of experiment, we refer to the process of planning the experiment so that appropriate data will be collected, which may be analyzed by statistical methods resulting in valid and objective conclusion."[10]. Experimental design assists engineers and researchers in understanding the relationships between input factors and responses in the most efficient way; by building mathematical models to relate the response to the input factors.

2. Experimental Setup

This experiment considered the factors of polymer concentration, spin speed and ramp acceleration. The responses were coefficient of variation (CV) [11] for thickness also called film non-uniformity, film thickness, and device efficiency. A three factor, two-level, full factorial statistically designed experiment was run in order to estimate the desired factor effects. Figure 1 shows the design matrix.

Solutions of OC_1C_{10}-PPV were made in three concentrations of 7:3 mixtures of Toluene and THF [4, 5].

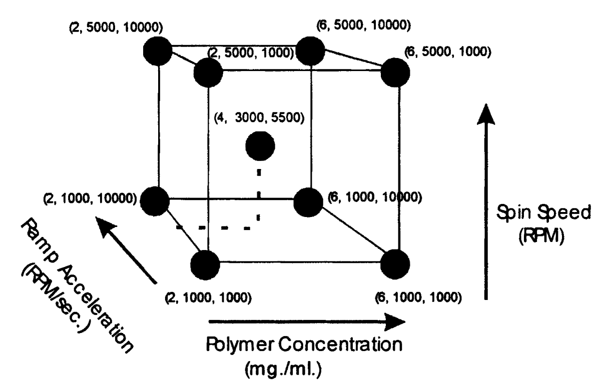

Figure 1. Design Matrix showing each combination of the factors: polymer concentration, spin speed, and ramp acceleration.
Example: At the center point (4, 3000, 5500) means (4 mg/ml, 3000 rpm, 5500 rpm/sec.)

Single layer devices were prepared on 30 mm x 30 mm glass substrates covered with patterned indium-tin oxide (ITO) electrodes using a previously reported technique [3]. The OC1C10-PPV polymer films were spin-coated from toluene/THF solutions with concentrations between 2 and 6 mg/ml. Spin speed between 1000 and 5000 rpm, and ramp acceleration between 1000 and 10000 rpm / sec. were used. Calcium contacts deposited on top of the polymer films by vacuum evaporation at pressures below $2x10^{-6}$ Torr yield active areas of 54 mm^2.

2. Results and Discussion

The following statistical model was developed to analyze this experiment [10, 11]:

$$y = \mu + \alpha + \beta + \gamma + \alpha\beta + \alpha\gamma + \beta\gamma + \varepsilon$$

This model allows the determination of the effect of each of the three factors (α, β, γ) plus the three two-way interactions ($\alpha\beta$, $\alpha\gamma$, $\beta\gamma$) on the response (y). Finally, all experiments include both experimental error, which is quantified by ε, and a constant μ.

Analysis of variance methods show that both polymer concentration and spin speed significantly influence CV (film non-uniformity). The corresponding p-values [11] are 0.019 and 0.003 respectively. Ramp acceleration does not effect CV, with a p-value >0.05. See Figure 2. There is no significant interaction between these factors, with p-value >0.05.

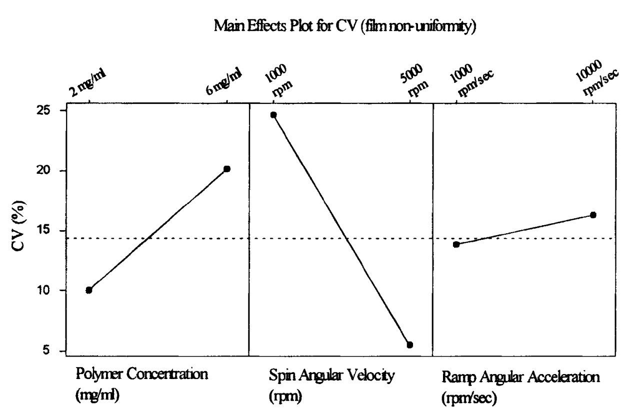

Figure 2. Mintab summary of the main effects for film non-uniformity. To minimize film non-uniformity, one may choose 2mg/ml polymer concentration and a 5000 rpm spin angular velocity.

Polymer concentration and spin speed significantly influence film thickness. Figure 3 shows a significant interaction between these two factors (p-value of 0.024). No statistically significant factor effects are found to influence device efficiency (all p-values exceeded 0.05).

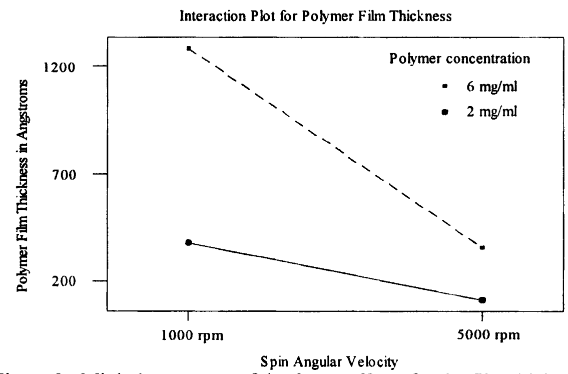

Figure 3. Minitab summary of the factor effects for the film thickness. There is a spin angular velocity effect, because the average thickness over both polymer concentration levels decreases as spin angular velocity increases from 1000 rpm to 5000 rpm. However the amount of decrease depends on the level of polymer concentration.

3. Conclusion

This work applies the Design of Experiment (DOE) methodology to optimize polymer LED film spin coating. The study analyzed the effect of polymer concentration, spin speed, and ramp acceleration on polymer film non-uniformity, thickness, and device efficiency. Rather than the 26 samples required by a One Variable at a Time (OVT) experimental approach, DOE provides an exhaustive study of the same design space with only 10 samples. Our experimental findings suggest that polymer film thickness and film non-uniformity depend on polymer concentration and spin speed. Ramp acceleration did not seem to be important.

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