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Effect of the P3HT Concentration in the Precursor Solution on the Crystallinity of Annealed P3HT Thin Films Prepared by Spin-Coating

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***Abstract*—Crystalline properties of annealed P3HT thin films deposited by spin-coating were studied by X-ray diffraction (XRD) and Raman spectroscopy. Three different P3HT concentrations of regio-regular P3HT powders dissolved in chlorobenzene were studied to determine the most appropriate precursor solution for depositing thin films on glass by a spin-coating process. When the "as-grown" films were annealed at 170 °C, they re-crystallize in the orthorhombic structure from an almost amorphous phase. Therefore, it was confirmed that this annealing process was an important step for obtaining good crystalline quality films. In addition, it was shown that 25 mg/ml P3HT concentration in the precursor solution provided the best crystallinity for the annealed films, as determined from XRD and Raman spectroscopy. Finally, the UV-vis diffuse reflection spectroscopy measurements allowed us to determine the annealed P3HT films bandgap to be around 1.9 eV.**

Keywords—p3ht, thin films, spin coating, x-ray diffraction

I. INTRODUCTION

Polymer based photovoltaic devices have shown promising potential because of their good optoelectronic properties achieved at low-cost from a solution deposition method. In this regard, a very important polymer property is a high charge mobility [1]; for this reason, one of the most studied organic polymers is Poly-3-hexylthiophene-2,5-diyl (P3HT). It exhibits advantages over other polymers, including high degree of crystallinity, high hole mobility in regio-regular state (10^{-4} to 10^{-1} cm^2/V-s), extended absorption in the red region (up to 650 nm), bandgap values from 1.9 to 2.0 eV, and environmental stability [2]-[3]. This affordable material is used as p-type semiconductor (hole transport layer) for optoelectronic devices [4]. P3HT presents two chemical conformations: Regio-regular and Regio-random, alkyl groups ordered or disordered placed throughout the polymer chain, respectively [5].

It is well known that solar energy converters based on silicon have achieved high photovoltaic performances, but the high production cost and sophisticated fabrication process have increased the researchers interest to investigate low cost and simple fabrication polymeric materials. In addition, polymer PV devices can provide properties such as long-term stability, durability, and mechanical flexibility. Nowadays, power conversion efficiency of P3HT based cells has reached 5.5%, but several efforts to reach higher efficiencies continue [6]-[9].

In the last two decades a lot of investigation work on P3HT has been done [9]. To obtain it, several deposition methods have been used. For instance, blade coating, convective coating, deep coating, drop casting, spray coating, inkjet printing, electrospray deposition (ESD) and spin coating method [10]-[14]. Spin coating is one of the most used methods to obtain P3HT layers. Spin coating is a simple and easy low-cost method to obtain thin films. Annealing effects (varying temperature and heat treatment time), deposition speed effects (from 1000 to 3000 rpm), spin coating volume solution effects (40 to 200 µl), thickness effect, dissolvent effect (toluene, dichlorobenzene and chlorobenzene), additive effect (1,8-octanedithiol), regio-regular and regio-random P3HT conformations effects, different long chain and molecular weight of P3HT effect, and different ratio of P3HT:PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) blends, P3HT doping effect, and enhanced charge transport on P3HT thin film properties have been studied by different researchers [15]-[23].

In this work, the effect of varying the concentration of P3HT in the solution for spin-coating deposition on the optical, morphological, and structural properties of P3HT thin films was studied. Three different concentrations were investigated. From the results, we analyze and choose the best P3HT concentration

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to be applied for obtaining high crystallinity thin films. P3HT layers were deposited by the spin-coating method using a regio-regular P3HT conformation due to the regularity influence on electronic properties such as the hole mobility [5]. The prepared films were annealed at 170 °C in order to improve their crystalline quality. This treatment temperature was selected taking in account previous research work, which showed that for lower temperatures their crystallinity does not improve and for temperatures above 200 °C these polymeric compounds might become unstable [17].

II. Experiments

Polymer with regio-regular conformation and chain length mol average Mw 50,000-100,000 of Poly (3-hexylthiophene-2,5-diyl) (P3HT) from Sigma Aldrich with purity ≥ 90 % was used to prepare the spin-coating precursor solution by dissolving it in 1 ml of chlorobenzene. This solution was stirred by 1 hour at room temperature. Solution concentration was varied using 17, 25 and 50 mg/ml of P3HT in chlorobenzene. A volume of 100 µl the precursor solution was deposited by spin-coating on a corning glass substrate at 1500 rpm for 15 seconds. The layers obtained were heat treated at 170 °C for 1 hour. All the process was carried out inside a glove box with a nitrogen environment and low relative humidity. The substrates were cleaned previously by sonicating in neutral detergent, followed by piranha solution (mixing of sulfuric acid and 30% of hydrogen peroxide) and degreasing with acetone and isopropyl alcohol, rinsing in deionized (DI) water in every step, and finally dried with nitrogen. Samples were identified according to their P3HT concentration as follows: H1 for 17 mg/ml, H2 for 25 mg/ml and H3 for 50 mg/ml.

Films morphology was characterized using a JEOL scanning electron microscope (SEM), model JSM-6360LV. The optical diffuse reflectance was measured using a Jasco UV-vis spectrophotometer model V-670. Structural characterizations were done with an X-Ray Rigaku equipment, model Smart Lab, using a Cu–Kα radiation source of 1.541862 A°, and a Raman NT-MDT Integra Spectra equipment with a green laser (wavelength of 530 nm) as excitation source. Thickness measurements were performed using a Bruker profilometer model DEKTAK XT.

III. Results

A. Morphology

A characteristic brown color was observed in all the P3HT layers and a strong adherence to the substrates were obtained. The SEM micrographs of the "as grown" and annealed (at 170 °C for 1 hour) P3HT thin films at different concentrations are shown in Fig. 1. The presence of pinholes and substrate areas without deposited material were minimal. A compact and homogeneous without roughness surface was observed in all samples.

B. X-ray diffraction

P3HT is a semi-crystalline polymer organic semiconductor, and so there will be both crystalline and amorphous within the deposited films. Although we use a regio-regular P3HT reactive

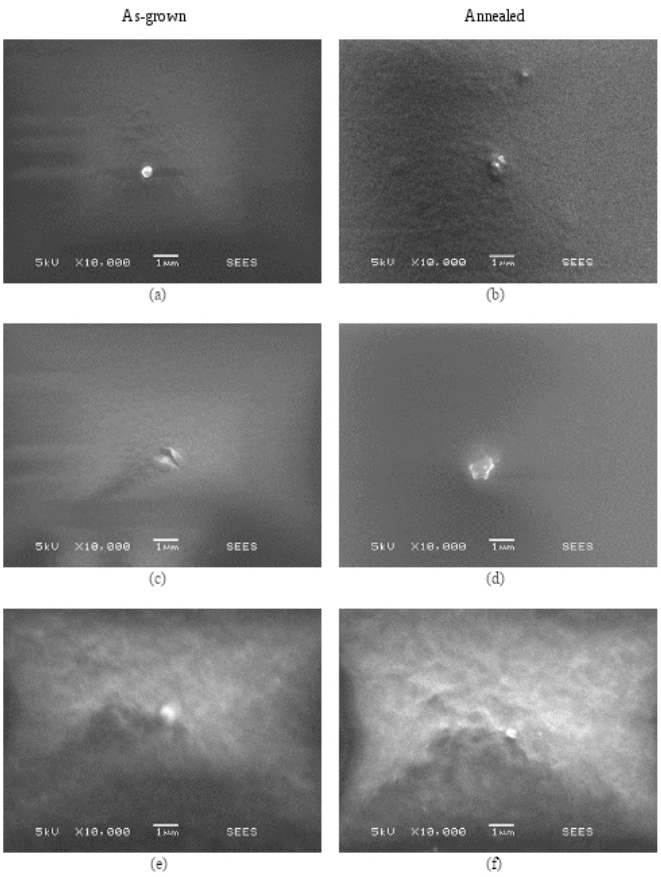

Fig. 1. SEM images for the P3HT films: a) and b) for H1, c) and d) for H2, and e) and f) for H3.

to obtain the films, there will be a fraction of amorphous compound P3HT [24]. In the present work, the crystal structure of P3HT thin films deposited by spin-coating at different P3HT concentrations were studied by X-ray diffraction. Their diffractograms are shown in Fig. 2. In all cases the diffractograms were normalized to 1.

It is already known that P3HT crystallize in an orthorhombic phase at room temperature. The 00-054-2080 PDF card was used to compare our results [25]-[26]. For all the films, the XRD pattern show two main peaks for 2-theta around 5.3° and 25°, which correspond to the (100) plane of the P3HT orthorhombic crystal structure and the amorphous-like phase, respectively. Notice that in the x-ray diffraction pattern for the 17 mg/ml concentration (H1 sample), there is a small relative increase for the crystalline (100) peak when the sample is annealed. For the 25 mg/ml P3HT concentration, the heat-treated sample (H2) shows a high crystallinity improvement, since the (100) orthorhombic peak intensity became the dominant one, and it is narrowed compared to the "as grown" thin film. In addition, two peaks at 2-theta at 10.7° and 16.1° appear, which correspond to the (200) and (300) orthorhombic planes, respectively. For the 50 mg/ml P3HT concentration, the heat-treated sample (H3) also show a crystallinity improvement, but not as high as in the case of the 25 mg/ml annealed films. The additional XRD peak observed at 2-theta 44.1° has been identified as due to the presence of P3HT oxidation.

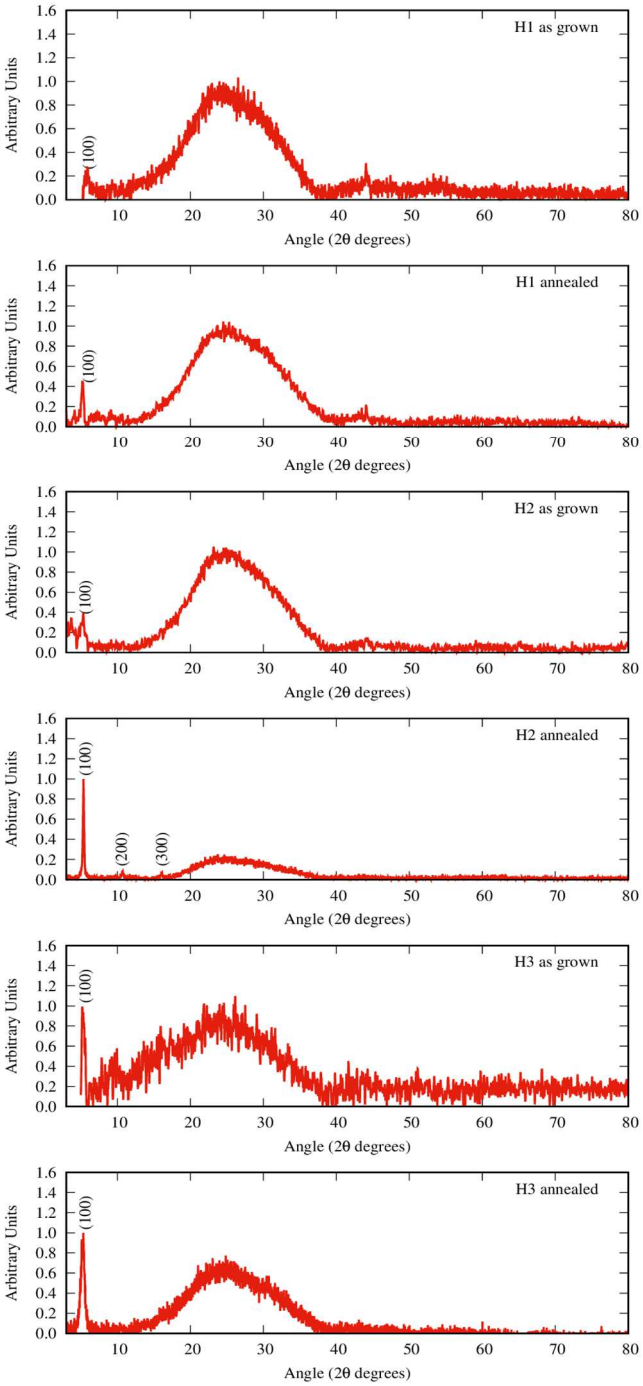

Fig. 2. XRD patterns from every P3HT sample.

The film crystallite sizes were estimated using the well-known Scherrer equation for the crystallites oriented in the orthorhombic (100) plane [27]. The values are shown in Table I. Sizes from 10 to 16 nm were determined for the "as grown" P3HT samples. An increase in the crystallite size was observed for the annealed films, except for the H3 samples (50 mg/ml concentration). This fact confirms that for this concentration, the crystallinity improvement by the heat treatment is not as high as for the 25 mg/ml case.

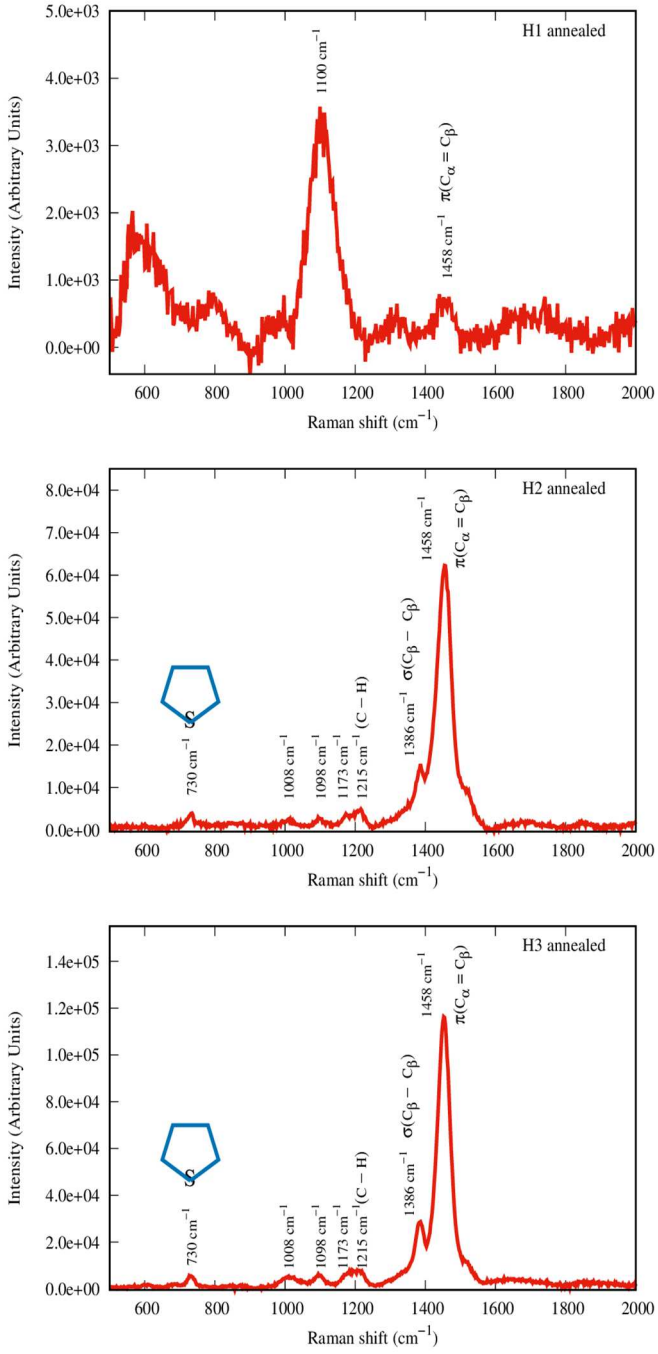

Fig. 3. Raman spectra from annealed P3HT samples.

C. *Raman spectroscopy*

In addition to XRD diffraction, the P3HT films structural properties were studied by Raman spectroscopy. The Raman spectra for the annealed samples with different P3HT concentrations in the precursor solution are presented in fig. 3.

The Raman spectra for the 17 mg/ml P3HT concentration sample show two Raman modes corresponding to P3HT, the C-H bending mode and a weak Raman mode located at 1100 cm^{-1} and 1458 cm^{-1} respectively. This Raman shift corresponds to the sigma C=C bond from the thiophene ring. Raman spectra for the

25 and 50 mg/ml P3HT concentrations (H2 and H3 samples), present vibrational modes at 730 cm^{-1}, which is related to the asymmetric stretching between C-S-C from the thiophene ring

The predominant modes are at 1386 cm^{-1} and 1454 cm^{-1}, which are related to (C_β-C_β) σ bond (the carbon-carbon single bond in the thiophene ring) and to (C_α=C_β) π bond (doble bond in the thiophene ring), respectively. Other less intense Raman bands can be observed at 1008, 1098, 1173 and 1215 cm^{-1}, which coincide with the C_β-C_{alkyl} (carbon from the thiophene ring to carbon from the hexyl radical), the C-H bending mode, the C_α-C_α symmetric stretching mode and a mix of the C_α-C_α and the C_β-H stretching modes respectively [28]-[30].

D. UV-Vis Diffuse refectance spectroscopy

Measurements of optical diffuse reflectance were made by UV-vis spectroscopy. From measured spectra, the bandgap was determined using Tauc like plots for the corresponding Kubelka Munk functions [31]. The Tauc plots are shown in fig.4, and the corresponding bandgap averages can be seen in Table I. The bandgap increases slightly when samples are heat treated. The bandgaps obtained for all the films are near 1.91 eV, and this value coincides with the bandgap reported in the literature for P3HT orthorhombic crystals [2].

The increase of the concentration in the precursor solution causes an increase in film thickness, as expected. Thickness of the different P3HT thin films is presented in Table I.

IV. DISCUSSION

From the SEM micrographs we can say that the spin-coating process produce very smooth films and the annealing treatment did not modify the surface roughness appreciably. On the other hand, the XRD results show that the obtained P3HT films are semicrystalline. We can see that the 17 mg/ml P3HT concentration was not enough to crystallize the layer, even when it is annealed. In contrast for the 50 mg/ml concentration the crystallinity of the annealed film was not as good as for the 25 mg/ml concentration. It is very likely that the higher P3HT concentration in the solution overpasses the solubility product, and it avoids a complete P3HT dissolution. The best XRD result was for the annealed sample H2 with 25 mg/ml P3HT concentration, because it shows the highest relative intensity and the narrower peak for the orthorhombic (100) plane orientation.

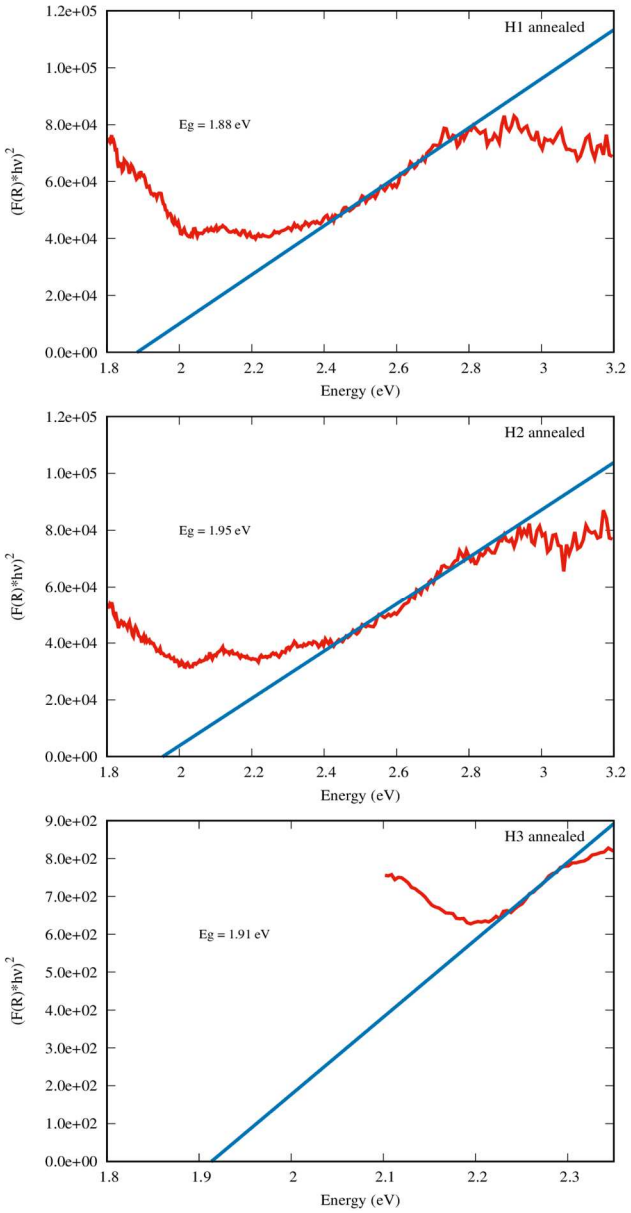

Fig. 4. Bandgap Eg for annealed P3HT films.

TABLE I. SUMMARY OF P3HT FILM PROPERTIES

Property	Sample – Concentration					
	H1 – 17 mg/ml		*H2 – 25 mg/ml*		*H3 – 50 mg/ml*	
	as grown	*annealed*	*as grown*	*annealed*	*as grown*	*annealed*
Thickness (nm)	60 ± 3	61 ± 3	98 ± 7	91 ± 7	238 ± 15	248 ± 15
Bandgap (eV)	1.84 ± 0.03	1.88 ± 0.03	1.91 ± 0.04	1.95 ± 0.04	1.86 ± 0.03	1.91 ± 0.03
Crystallite size (nm)	10 ± 1	23 ± 1	13 ± 1	42 ± 1	16 ± 1	15 ± 1

The crystallite sizes increased after the annealing process for the 17 and 25 mg/ml, with the 25 mg/ml concentration which causes the highest crystallite size increased. In contrast, for the 50 mg/ml concentration the heat treatment did not cause an increase of the crystallite size. This seems to confirm the fact that the best P3HT concentration in the precursor solution is the one that corresponds to 25 mg/ml. The Raman spectra for the 17 mg/ml P3HT concentration shows only a weak Raman mode corresponding to P3HT located at 1458 cm^{-1}, which corresponds to the sigma bond C=C from the thiophene ring is observed. The other vibrational modes obtained for the H1 thin films do not correspond to P3HT [32]-[33]. On the other hand, the Raman spectra for the 25 mg/ml and 50 mg/ml P3HT concentrations (H2 and H3 samples) show all the characteristic Raman shifts reported in earlier research for this semiconductor polymer. Both the XRD and Raman spectra, show that the heat treatment is an important step to improve the crystalline quality. The bandgaps are higher for the annealed as compared to the "as grown" samples, as consequence of the improved crystallinity. For the annealed films the bandgap is between 1.88 eV and 1.95 eV which agrees well with previously reported results.

V. CONCLUSIONS

In the present work, we prepared P3HT thin films at three different concentrations in the precursor solution by spin-coating, and subsequently annealed them. The obtained films had good adherence to the substrate, nanometric crystallite sizes and no pinholes. The 25 mg/ml P3HT concentration for the spin-coating solution achieved the best crystallinity for the annealed deposited films. Below this concentration, the films are highly non-crystalline, while above it the solubility in chlorobenzene seems to be above the limit causing inferior results than for the 25 mg/ml P3HT concentration in the solution. The thermal treatment is decisive to reduce the non-crystalline phase and increase the polycrystallinity of the P3HT films. The energy bandgap was confirmed to be around 1.9 eV (in average).

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