

Polymer Thin Film Preparation and Characterization for in-situ GISAXS Analysis

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September 07, 2022

Abstract

Polymer thin films possess incredible material properties which grab the attention of scientists. Due to their lightweight, flexible, biocompatible nature, polymers thin film have numerous applications in health and energy areas as organic electronic devices. Many organic electronic devices are based on metal-polymer composite structures. Since the demand and need for organic electronic devices increase, existing studies should focus on improving the metal-polymer composite systems. Therefore, understanding of interactions among metal and polymer thin film during fabrication paves the way for improved systems. In-situ analysis techniques offer great opportunities to reveal interactions between metals and polymers. GISAXS is a robust technique to collect and analyse in-situ and ex-situ data from the polymer-metal interface. Although GISAXS is a powerful tool for analysis, it also comes with some challenges. Since GISAXS provides averaged information, it requires homogenous polymer thin film for reliable data. Also, the thickness of the polymer thin film should be regulated strictly since it might make data analysis complicated. Therefore, this study focuses on the preparation and characterization of good-quality polymer thin films for GISAXS applications.

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1. Introduction

Polymer thin films are low-cost and versatile materials that grab the attention of numerous scientists working on different subjects. Polymer thin films can be utilized for different applications depending on the materials of the polymers. For instance, the optical properties of polymers can be utilized to prevent reflections [1], and therapeutic studies favour polymers thanks to their biocompatibility [2]. Additionally, polymer thin films play role in the production and working mechanism of several electronic and polymer-metal composite devices such as organic transistors, sensors for various applications, and organic photovoltaic devices [3]–[6]. Polymer-metal interactions and mechanisms during fabrication are major factors affecting the quality of the final composite device. Therefore, a better understanding of these mechanisms is required to improve the efficiency and effectiveness of polymer thin film-based organic devices.

Grazing-incidence Small Angle X-ray Scattering (GISAXS) is a powerful characterization technique based on the scattering of X-rays in grazing geometry. GISAXS technique provides the structural information about the measured sample[7], [8]. Gaining insight into the 3D structure and chain orientation of polymers carry importance since the electronic properties of the produced device are highly dependent on these features [9]. Unlike SEM and TEM, GISAXS contains average information of the sample [10]; therefore, GISAXS allows comprehensive analysis of the surface. Furthermore, GISAXS systems can be combined with different instruments to conduct in-situ experiments. In-situ analysis of metal deposition on polymer thin films reveals the interaction and important mechanisms which take place during the organic device fabrication. For example, Gensch and their colleagues report growth mechanisms of Ag and Al metals on different polymer thin films by analysing in-situ sputter deposition by GISAXS[4]-[6]. Performing such measurements comes with different challenges. One of the challenges is the production of macroscopically homogenous and roughness-free polymer films. Different artifacts and rough surfaces create noise and might affect the growth mechanism of metal, which dangers the reliability of the study. Additionally, high-intensity X-rays are destructive to soft materials. Thus, different parts of the polymer film must behave the same since in-situ GISAXS measurements are performed under y-scan mode which prevents the destruction of thin film and provides reliable data. As a result, one of the most crucial parts of GISAXS experiments is the fabrication of high-quality polymer-thin films.

In this study, different polymer thin films are prepared for substrate preparation part of a project which focuses on adhesive properties of sputtered coinage metals by high power impulse magnetron sputtering on polymer thin films. This project also aims to reveal the growth and adhesion mechanisms of metals on polymer thin films by using in-situ GISAXS analysis. Prepared thin films are characterized by spectroscopic ellipsometry, optical microscope, AFM, and GIUSAXS, and the quality of polymer thin films are discussed. *Figure 1* shows the flow of the project and the focus of this study is highlighted by the orange rectangle.



Figure 1 Summary of the whole project as a flowchart (rectangle represents the part of the project on which this study focuses)

2. Materials and Methods

2.1.Materials

(100) orientation silicon wafers are used as substrates for polymer thin film production. Silicon wafers are cut 12 mm x 15 mm. Several different polymers are used for this study. These are Poly(methyl methacrylate) (Mn= 64,500 Mw=77,000 PDI= 1.19), Polyvinyl alcohol (Mn= 53,000 Mw=95,000 PDI= 1.8), Polystyrene (Mn= 62,000 Mw=64,300 PDI= 1.04), Poly(3-hexylthiophene) (Mn= 17,400 Mw= 20,700 PDI: 1.19) and (M n = 10,500 M w = 13,000 PDI: 1.25), Poly(3-hexylthiophene)-b-styrene (Mn = 15,000-b-75,000 Mw/Mn: 3.3) and (Mn = 12,000-b-24000 Mw/Mn: 3.0), Poly(3-hexylthiophene)-b- Polymethylmethacrylate (M n = 15,000-b-85,000 Mw/Mn: 1.9) and (M n = 15,000-b-22000 Mw/Mn: 2.3). Ultra-pure water, toluene, chlorobenzene, chloroform are used for solution preparation depending on solubility of particular polymer into solvents. 0.2 μ L PTFE filters are used if the polymer solution contains precipitate to ensure the quality of polymer thin films.

2.2.Substrate Cleaning

Silicon wafers are cleaned before spin coating to remove any organic or inorganic contaminants that can lower the thin film quality. Firstly, wafers are sonicated in acetone for 10 minutes and rinsed with isopropanol and ultra-pure water respectively. Then, piranha solution (190 mL sulfuric acid (96%), 87.5 mL hydrogen peroxide (30%), and 37.5 mL ultraclean water) is prepared and heated up to 70 °C. After that, substrates are kept in the piranha solution for 15 minutes. After piranha cleaning substrate surface becomes extremely hydrophilic which increases thin film quality. Cleaned substrates are stored in ultra-pure water. Right before the spin coating, silicon wafers are washed with deionized water and dried with nitrogen gas.

2.3.Polymer Thin Film Production

It is aimed to produce macroscopically homogenous, smooth surface, 40 nm thick polymer thin films. There are optimized recipes for PVA, PMMA, and PS. The optimized recipe for PVA is 6000 rpm, step 9, 30 seconds for 100 μ L solution. The solution concentration of optimized PVA solution is 25 mg/mL in ultra-pure water. If the solution contains precipitates, the solution is heated at 65 °C while stirring. 13.75 mg/mL PMMA in toluene is the optimized

concentration. This solution is heat treated at 60 $^{\circ}$ C if the solution is not homogenous. The spin coat recipe for PMMA is 3600 rpm, step 9, 30 seconds 100 μ L solution. For PS, optimized concentration is 9 mg/mL in toluene. The optimized spin coat recipe for PS is 3600 rpm, step 9, 30 seconds 100 μ L solution.

There is no optimized recipe for P3HT, P3HT-b-PS, P3HT-b-PMMA. Thus, an optimization study is done for these polymers. Solutions of different concentrations with different solvents are prepared. Then, numerous different spin coating trials are done including longer spin coat time (up to 120 seconds) and different RPMs (ranging between 500-6000). All parameters can be found in attachments. Toluene, chloroform, and chlorobenzene are used as solvents for P3HT polymers and toluene is the main solvent for the DBCs.

2.4.Polymer Thin Film Characterization

Polymer thin films are characterized by using an optical microscope, spectroscopic ellipsometry (SE), atomic force microscope, and grazing incidence ultra-small angle X-ray scattering. To see one step further than bare eyes, Keyence VHX-600 optical microscope equipped with 250x-2500x digital objective is used to investigate the surface of polymer thin films. Optical microscope images are taken from the middle of the sample. Spectroscopic ellipsometry is used to get insight into the thickness of the films by analysing their optical properties. Measurements are done by using J.A. Woollam M2000 spectroscopic ellipsometry with focusing probes. 55°,60°, and 65° measurements are taken from the centre and edges of the polymer thin film with 10 seconds of exposure time each. Collected SE data is analysed with CompleateEASE6 software and a general oscillator, or B-spline models are developed for every polymer film because there is no optical data provided for polymer thin films. For AFM measurements NTEGRA AFM machine with Bruker semi-contact cantilevers (75 kHz) is used. Measurement parameters are $2x2 \ \mu m^{2}$, 1024x1024 pixels and 0.20 Hz frequency. Then, images are processed with Gwyddion software. GIUSAXS is performed at PETRA III P03 beamline of DESY. 0.1048 nm wavelength X-ray is used to analyse big repetitive structures of polymer films. The sample detector distance is 9505 mm and the grazing angle is 0.4. Then, detector images are analysed with DPDAK software. Firstly, line cuts are taken around the Yoneda region of silicon and polymer and line integration is performed on these areas. Then, the obtained graph is undergone function fitting operation. After that, structural information can be interpreted.

3. Results and Discussions

Each polymer has drastically different properties and the main goal of this study is to obtain polymer thin films with similar surface characteristics such as smooth and homogeneous surfaces. Each polymer has different side groups which create a different surface chemistry and induce different interactions with sputtered metals. This project investigates the effect of the chemical environment on the adsorption and growth mechanisms of metals on polymer thin film surfaces. Therefore, the effect of undesired physical features coming from the film production process should be eliminated such as roughness and sudden thickness change due to colloidal particles or dust. On the other hand, repetitive surface structures due to phase separation of DBCs such as lamella are desired because these kinds of structures originate from polymers themselves and create a different environment for sputtered metals.

3.1. Thin Films Produced by Using Optimized Recipes

PVA, PS, and PMMA homopolymer thin films are prepared based on optimized recipes mentioned in the previous section. Optical microscope and spectroscopic ellipsometry measurements are performed on these polymer thin films.



Figure 2 Image of PVA thin film as representative of homopolymer thin films

Figure 2 shows the image of PVA coated silicon wafer. It has darker coloured edges due to the characteristic property of spin-coated which is called edge beads. However, centre part has light brown-grey colour. This colour is common among PS, PVA, and PMMA films that are produced. The reason is that polymer thin films are really thin, which a thickness is around 40 nm this thickness is lower than the skin depth of the polymer and this causes interference of light and produces this colour for PS, PVA, and PMMA.



Figure 3 Optical microscope images of polymer thin films a, d, g) PMMA thin film 250x, 1000x, and 2000x respectively. b, e, h) PS thin film 250x, 1000x and 2000x respectively. c, f, i) PVA thin film 250x, 1000x and 2000x respectively.

Optical microscope images show more detailed features of polymer thin films. *Figure 3* shows the images taken from the middle of the polymer thin films. Although all films look homogeneous without any zoom, they all have small defects on the surface. These defects are seen as small black dots on the optical microscope images. These dots might be aggregated polymers or small dust particles. 2000x zoom images of PMMA and PS clearly show these defects, unlike PVA which has a relatively clean surface compared to others. However, there is a small black dot appears in every image which can be seen on PVA images. This is not a defect of polymer films, that is dirt from objective. Although all polymer films have defects, these defects are acceptable compared to defects caused by large dust particles. Since these

defects are not repetitive, they cannot be detected by GISAXS measurement. Additionally, their effect on the metal deposition process can be processed within the error limits.

Sample	MSE	Thickness (Å)	
SI_NTVE_CENTER	2.237	13.37	_
SI_NTVE_SHORT	2.247	13.59	
SI_NTVE_LONG	2.219	14.12	
ps_center	16.933	405.36	
ps_short	15.613	383.42	
ps_long	18.148	421.58	
pmma_center	5.532	593.3	
pmma_short	1.6	556.15	
pmma_long	1.721	557.73	
pva_center	4.628	736.02	
pva_short	4.498	728.87	
pva_long	13.875	866.66	

Table 1 Thickness results of polymer thin films obtained by spectroscopic ellipsometry

Ellipsometry is used to determine the thickness of polymer films. Unfortunately, optical data for polymer film does not exist. Thus, mathematical fitting tools are used for modelling. Since these tools do not depend on proven experimental data, there might be problems with fitting operations. Therefore, these thickness values cannot represent the exact thickness, these are more like approximations. Before polymer films are analysed, the native oxide layer on the silicon wafer surface is measured and analysed. This information increases the fitting rate of the model for polymer films. According to *Table 1*, the native oxide layer is an average of 13.5 Å, and thickness of native oxide layer is kept constant for polymer film models. According to the results, PS films show expected results around the 40 nm thickness. However, PMMA films seem higher than 40 nm, but it is not thick to produce oscillation peaks under GISAXS measurements. This means that PMMA films are within the acceptable range. Unfortunately, PVA films show too high thickness. Since these results are generated by a mathematical model, this high thickness value might come from the model. For further analysis, these samples should be undergone surface profilometer measurements or GISAXS to check the oscillations coming from thickness.

3.2.P3HT and P3HT Based DBC Polymer Thin Film Study

P3HT is a semiconductive polymer which has promising applications on organic electronic devices. Thus, it is important to understand the interactions between metals and P3HT polymers deeply. To reveal details of this, P3HT polymer films and P3HT-based DBC films are prepared. Two different molecular weight polymers are used for each polymer type. Naming details of the polymers can be found in the following table. This name convention is used throughout this section.

Table	2 N	Vaming	of low	and high	molecular	weight	polymers

Name	Properties
P3HT (i)	Mn= 17,400 Mw= 20,700 PDI: 1.19
P3HT (ii)	Mn = 10,500 M w = 13,000 PDI: 1.25
P3HT-b-PS (i)	Mn = 15,000-b-75,000 Mw/Mn: 3.3
P3HT-b-PS (ii)	Mn = 12,000-b-24000 Mw/Mn: 3.0
P3HT-b-PMMA (i)	Mn = 15,000-b-85,000 Mw/Mn: 1.9
P3HT-b-PMMA (ii)	Mn = 15,000-b-22000 Mw/Mn: 2.3

Since there is no optimized recipe for these polymers, the initial thought is that preparing optically similar thin films to PS, PVA and PMMA films. Meaning that aim is to have light brown-grey coloured films. The process starts with solution preparation. Different polymer solutions are prepared with different solvents and different concentrations. Chlorobenzene (CB) and toluene (T) are the solvents for solutions. P3HT solutions are prepared only using chlorobenzene and DBC solutions are prepared from both solvents. Firstly, 9, 10, 11 mg/mL solutions are tested. Then, lower concentration solutions like 4, 5, 6 mg/mL solutions are prepared and also 20 mg/mL solutions are tested.

Figure 4 demonstrates the images of some of the polymer films produced. The most common film colours are blue and gold-like brown. According to *Figure 4*a and 4c, colour of the polymer films turns into gold from blue as solution concentration increases. There is no light brown colour observed like PS and PMMA films. The main reason is that P3HT is a conductive polymer, unlike PS and PMMA. Conductivity induces different light-matter interactions which causes different colour. On the other hand, DBCs show brown-like colour due to the contribution of PMMA and PS parts (*Figure 4*d and 4f). *Figure 4*b shows the films of chlorobenzene solution which are blue again and *Figure 4*f presents the films of chloroform solutions.



Figure 4 İmages of P3HT based polymer films (3600 rpm, step 9, 30s) a) P3HT (ii) left to right 5, 10, 20 mg/mL in toluene samples. b) left to right P3HT (i) and P3HT (ii) 9 mg/mL in chlorobenzene. c) P3HT (i) left to right 5, 10, 20 mg/mL in toluene samples. d) left to right P3HT-b-PS (ii), P3HT-b-PMMA (i), P3HT-b-PMMA (ii) 11 mg/mL in toluene. e) left to right P3HT-b-PS (i), P3HT-b-PS (ii) 5 mg/mL in toluene and P3HT-b-PMMA (i), P3HT-b-PMMA (ii) 8 mg/mL in toluene. f) top left P3HT (i) 10 mg/mL, top right P3HT (ii) 10 mg/mL, P3HT (ii) 20 mg/mL in chloroform.

Optical microscope images show that P3HT-based polymer thin films have certainly similar surfaces to polymer thin films of PS, PVA, and PMMA. This means that similar quality optimized recipes can be obtained when colloid-free solutions are prepared for P3HT-based polymer thin films. *Figure 5* shows the optical micrographs of some polymer thin films. Similar to *Figure 3* images, all thin films include black dot-like defects. Thus, these defects are acceptable. The most prominent difference between P3HT thin films and optimized thin film images is the colour of the micrograph. Samples of *Figure 3* have gold-like yellow coloured optical microscope images while P3HT films have green-brown colour, which indicates the different interactions of light and P3HT films.



Figure 5 Optical microscope images of P3HT based thin films a, b, c) P3HT (i) 5 mg/mL in T 250x, 1000x and 2000x respectively. d, e, f) P3HT-b-PS (i) 5 mg/mL in T 250x, 1000x and 2000x respectively. g, h, i) P3HT-b-PS (ii) 5 mg/mL in T 250x, 1000x and 2000x respectively. j, k, l) P3HT-b-PMMA (i) 8 mg/mL in T 250x, 1000x and 2000x respectively. m, n, o) P3HT-b-PMMA (ii) 8 mg/mL in T 250x, 1000x and 2000x respectively.

Table 3 Ellipsometry analysis of some P3HT (i) polymers with different RPMs,concentrations, and solvents

Sample	MSE	Thickness (Å)
center_p3ht-i_10mg_cf_3600	24.928	1167.49
longside_p3ht-i_10mg_cf_3600	25.392	1153.96
shortside_p3ht-i_10mg_cf_3600	23.469	1117.52
center_p3ht-i_10mg_cf_6000	22.965	1105.26
longside_p3ht-i_10mg_cf_6000	22.725	1066.14
shortside_p3ht-i_10mg_cf_6000	23.281	1020.75
center_p3ht-i_20mg_cf_3600	51.482	2134.84
shortside_p3ht-i_20mg_cf_3600	59.252	2122.2
center_p3ht-i_5mg_t_3600	4.868	242.23
shortside_p3ht-i_5mg_t_3600	4.988	236.71
center_p3ht-i_10mg_t_3600	9.708	458.15
center_p3ht-i_10mg_t_3600	10.378	471.58
shortside_p3ht-i_10mg_t_3600	8.446	432.05
center_p3ht-i_20mg_t_3600	23.149	1121.15
longside_p3ht-i_20mg_t_3600	26.537	1064.02
shortside_p3ht-i_20mg_t_3600	21.735	1166.08

Table 4 Ellipsometry results of P3HT (ii) films with different concentrations and RPMs

Sample	MSE	Thickness (Å)
center_p3ht-ii_5mg_t_3600	4.235	222.96
longside_p3ht-ii_5mg_t_3600	4.346	225.32
shortside_p3ht-ii_5mg_t_3600	4.422	220.52
center_p3ht-ii_5mg_t_6000	3.511	265.56
longside_p3ht-ii_5mg_t_6000	3.591	266.41
shortside_p3ht-ii_5mg_t_6000	3.96	262.84
center_p3ht-ii_5mg_t_500	4.632	387.93
longside_p3ht-ii_5mg_t_500	44.195	482.66
shortside_p3ht-ii_5mg_t_500	16.297	353.08
center_p3ht-ii_20mg_t_3600	19.217	1287.59
longside_p3ht-ii_20mg_t_3600	20.05	1221.74
shortside_p3ht-ii_20mg_t_3600	60.463	1202.29
center_p3ht-ii_20mg_t_6000	24.586	1100.49
longside_p3ht-ii_20mg_t_6000	27.624	1062.03
shortside_p3ht-ii_20mg_t_6000	34.943	966.73
center_p3ht-ii_20mg_t_1500	28.691	1576.72

Spectroscopic ellipsometry results further prove the relation between thin film colour and thickness. *Table 3* and *Table 4* show the thickness values obtained by modelling operation. Similar to previous ellipsometry analyses, this modelling is done using a mathematical fitting tool and these results are approximations. When ellipsometry results and images from *Figure 4* are correlated, gold-like samples are more than 120 nm, which is way above than desired 40 nm thickness. Additionally, 5 mg/mL concentration samples are thinner than desired. According to the results, the most optimum concentration is 10 mg/mL in terms of thickness. Lower RPM samples with 5 mg/mL have a thickness of around 40 nm but the film homogeneity is not good enough at lower RPMs. Since P3HT has different properties compared to optimized samples and the error margin is high for ellipsometry, these samples should be checked for thickness oscillations under GISAXS measurements.



Figure 6 Yoneda region cut of GIUSAXS images a) P3HT (i) 5 mg/mL in toluene b) P3HT (i) 10 mg/mL in toluene c) P3HT (i) 20 mg/mL in toluene d) photos of measured samples.

Figure 6 shows the GIUSAXS images of P3HT (i) thin films with increasing concentration. The first image shows no oscillations due to thickness. Yoneda peaks of silicon (top) and polymer (bottom) are easy to distinguish. Although ellipsometry results suggest that 10 mg/mL is optimum for 40 nm thick polymer films, *Figure 6*b shows that 10 mg/mL polymer film also has oscillation due to the thickness. This does not mean that ellipsometry results are completely wrong. Since P3HT has conductive and different electronic properties than PS and PMMA, that might cause the thickness oscillations to occur for thinner films than insulator polymers. Additionally, the 20 mg/mL sample has several oscillations. GIUSAXS results show that the suitable samples are thin samples with light blue colour. This outcome is considered while sample preparation for further studies. The following table summarizes the suitable samples based on GIUSAXS thickness analysis:

 Table 5 Samples without thickness oscillation under GIUSAXS

Name	Parameters
P3HT (i)	5 mg/mL in T – 3600 rpm, 9 mg in CB and CF- 3600rpm
P3HT (ii)	5 mg/mL in T – 3600 rpm
P3HT-b-PS (i)	5 mg/mL in T – 3600 rpm, 5 mg/mL in T – 1500 rpm
P3HT-b-PS (ii)	5 mg/mL in T – 3600 rpm, 5 mg/mL in T – 1500 rpm
P3HT-b-PMMA (i)	8 mg/mL in T – 3600 rpm, 9 mg/mL in CB – 3600 rpm,
P3HT-b-PMMA (ii)	8 mg/mL in T – 3600 rpm,

GIUSAXS reveals the micrometre range repetitive structure of the thin films. To get an insight into the structure of the polymer, the detector image must be processed. The line integration should be taken from the Yoneda region of silicon and polymer. After curve fitting, structural information can be obtained. *Figure 7* shows the analysis of P3HT (i) 9 mg/mL in CB polymer film. This polymer film shows two symmetric peaks near the Yoneda of the polymer, which comes from the repetitive structures. After curve fitting, the period of the structure can be found by the following formula:

$$\lambda = \frac{2 \pi}{x}$$

x means the distance between the structure peak and the 0 position. According to the results for P3HT (i) 9 mg/mL in CB, x = 0.015 nm⁻¹ and period of the microstructures equals to 418 nm.



Figure 7 Data analysis of GIUSAXS imaging by DPDAK software. a) line cut, b) line integration c) curve fitting.

3.3. Solvent Vapor Annealing of P3HT-based DBCs

DBCs have two different chains attached. That is why these kinds of polymers can have microphase separation due to different favourable interactions among chains. Microphase separation might be utilized during the organic device fabrication process as a scaffold [4]–[6]. Since two ends of the polymer have different side groups, some solvents can dissolve one end and provide mobility to this side of the polymer while the other end remains constant. After some time, the mobile chain gets it's a most thermodynamically stable configuration. Depending on the properties of both ends of the chain, this process might end up with some repetitive structures like lamella for P3HT-b-PS and P3HT-b-PMMA. Keeping polymer thin film in a closed container with saturated vapor results in microphase separation without damaging film integrity. This post-processing technique is called solvent vapour annealing. To test the effect of solvent annealing new polymer thin films are produced based on *Table 5* and toluene solutions- 3600 rpm parameters are used to increase the convention.

Sample	MSE	Thickness (Å)
center_p3ht_ii_5mgT	8.751	186.6
shortside_p3ht_ii_5mgT	7.96	180.88
longside_p3ht_ii_5mgT	7.142	176.18
center_p3ht_i_5mgT	2.03	52.06
shortside_p3ht_i_5mgT	2.103	53.75
longside_p3ht_i_5mgT	2.004	58.14
center_p3ht-b-ps_i_5mgT	12.146	453.31
shortside_p3ht-b-ps_i_5mgT	12.777	514.24
longside_p3ht-b-ps_i_5mgT	12.879	517.41
center_p3ht-b-ps_ii_5mgT	5.478	279.59
shortside_p3ht-b-ps_ii_5mgT	6.36	292.43
longside_p3ht-b-ps_ii_5mgT	5.75	277.71
center_p3ht-b-pmma_i_8mgT	2.26	348.59
shortside_p3ht-b-pmma_i_8mgT	2.227	406.53
longside_p3ht-b-pmma_i_8mgT	2.903	389.13
center_p3ht-b-pmma_ii_8mgT	2.677	558.29
shortside_p3ht-b-pmma_ii_8mgT	6.49	543.42
longside_p3ht-b-pmma_ii_8mgT	2.598	557.59

Table 6 Ellipsometry results of P3HT and P3HT-based DBC films which are produced basedon Table 5.

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Ellipsometry results show that all films are thinner than 40 nm except P3HT-b-PMMA samples. Especially, P3HT (i) samples show extremely low thickness around 5 nm. Further measurements are required to determine the thickness of the films precisely. After precise measurements, higher concentrations can be tested under GIUSAXS to check oscillations.



Figure 8 Comparison of before and after optical micrograph of P3HT-b-PMMA (i) 8 mg/mL in toluene solvent vapour annealing.

For solvent annealing, DBC thin films are kept in a closed container filled with acetone for 24 hours. Then, samples are compared to each other. *Figure 8* shows the effect of solvent annealing clearly. *Figure 8* a shows the sample, not solvent annealed which has some repetitive micrometre range structures (diagonal white lines). However, there is not a seen repetitive structure under an optical microscope for solvent-annealed samples. This means that solvent vapour annealing changes the structure of the polymer thin film by destructing bigger repetitive structures which are not part of the thermodynamically stable configuration.

AFM is one of the techniques to characterise the surface of the material. Surface structures and roughness can be determined by AFM images. The effect of solvent vapour annealing also can be detected by comparing the samples. Nanoscale microphase separation can be detected by analysing AFM images. Figure 9 shows the AFM images of both solvents annealed and just spin-coated polymers. All images are undergone fourth-order polynomial background subtraction by Gwyddion software. If the large artifacts are ignored, the overall surface roughness of films is low and acceptable. One of the reasons for these large artifacts might be dust particles that are attached to the surface after the fabrication of polymer thin film since the time between the production of film and AFM measurements is not negligible. According to the results, solvent vapour annealing does not affect the film structure as expected. Figure 9 d, f, h, j samples are expected to show some lamellar structures after 24 hours of solvent annealing. However, there is no visible sign of lamellar structures in the images. When images of just sputtered samples and solvent annealed samples are compared, the solvent vapour annealing changes the surface of P3HT-b-PMMA samples positively. Solvent vapour P3HT-b-PMMA samples have a smoother surface. For P3HT-b-PS, there is no distinguished effect of solvent vapour annealing.



Figure 9 AFM images a) P3HT (i) 5 mg/mL in T b) P3HT (ii) 5 mg/mL in T c) P3HT-b-PS (i) 5 mg/mL in T d)P3HT-b-PS (i) 5 mg/mL in T solvent annealed e)P3HT-b-PS (ii) 5 mg/mL in T f) P3HT-b-PS (ii) 5 mg/mL in T solvent annealed g) P3HT-b-PMMA (i) 8 mg/mL in T h) P3HT-b-PMMA (i) 8 mg/mL in T solvent annealed i) P3HT-b-PMMA (ii) 8 mg/mL in T j) P3HT-b-PMMA (ii) 8 mg/mL in T solvent annealed.

4. Conclusions

Polymer thin films are gathering attention due to their excellent material properties. Organic electronic devices need to be improved to utilize the polymer-metal composites more effectively. The key information lying under this goal can be revealed by in-situ analysis of the metal-polymer interface. GISAXS is one of the influential tools for in-situ measurements. In this study, polymer thin films for GISAXS measurements are prepared. The quality of these films is tested by AFM, ellipsometry, and GIUSAXS. There are some optimized recipes for some polymers, but the optimization study is conducted for P3HT homopolymers and P3HT-based DBCs (P3HT-b-PMMA, P3HT-b-PS). Results reveal that P3HT has different properties such as colour due to the different electronic properties compared to optimized polymer samples. In the end, P3HT-based polymer films with decent quality are obtained. However, the thickness of the films needs to be optimized precisely. For future studies, different solvents can be tested and the behaviours of films under GISAXS/GIUSAXS measurements can be observed to check thickness oscillations. Finally, different electronic properties of P3HT might also affect the growth mechanisms of metals. Therefore, in-situ analysis of the P3HT-metal interface should consider this difference while comparing in-situ data of insulator polymers and P3HT-based polymers.

5. Acknowledgments

I would like to thank Stephan V. Roth for giving a chance me to join this incredible program and the whole research group for welcoming me and organizing social events. Additionally, I am so grateful to work with Yusuf Bulut. He was always around when I need something and supported me the whole time. He guided me during this study and answered my all questions passionately. I would like to thank him for showing me the different aspects of academia and for his valuable advice. Lastly, special thanks to DESY Summer Student Programme 2022 organisation team for making this program real.

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7. Attachments

Attachment-1: All P3HT and P3HT based DBCs polymer thin film production parameters.

					Spin-	spin	Spin coat
		Concentration			coat	coat	time
Date	Polymer	(mg/mL)	Solvent	Filter	rpm	step	(s)
03.08.22	P3HT (i)	9	CB	none	3600	9	30
03.08.22	P3HT (i)	9	CB	PTFE	3600	9	30
03.08.22	P3HT (i)	9	CB	PTFE	6000	9	30
03.08.22	P3HT (i)	9	СВ	PTFE	2000	9	30
03.08.22	P3HT (i)	9	CB	PTFE	3600	9	10
03.08.22	P3HT (ii)	9	СВ	none	3600	9	30
03.08.22	P3HT (ii)	9	СВ	PTFE	6000	9	60
03.08.22	P3HT (ii)	9	CB	PTFE	6000	9	120
03.08.22	P3HT-PS (i)	9	CB	none	3600	9	30
03.08.22	P3HT-PS (i)	9	CB	PTFE	3600	9	30
03.08.22	P3HT-PS (i)	11	CB	none	3600	9	30
03.08.22	P3HT-PS (i)	11	CB	PTFE	6000	9	30
03.08.22	P3HT-PMMA (i)	9	CB	none	6000	9	30
03.08.22	P3HT-PMMA (i)	9	CB	PTFE	6000	9	30
04.08.22	P3HT (i)	4	СВ	none	3600	9	30
04.08.22	P3HT (ii)	4	CB	none	3600	9	30
04.08.22	P3HT-PS (i)	4	CB	none	3600	9	30
04.08.22	P3HT-PS (ii)	4	CB	none	3600	9	30
04.08.22	P3HT-PMMA (i)	4	СВ	none	3600	9	30
04.08.22	P3HT-PMMA (ii)	4	CB	none	3600	9	30
04.08.22	P3HT (i)	4	CB	none	2000	9	30
04.08.22	P3HT (i)	4	CB	none	1000	9	30
04.08.22	P3HT (i)	4	CB	none	1000	9	4
			~~		400:36		
05.08.22	P3HT (ii)	4	CB	none	00	9	20:10
05.08.22	P3HT (ii)	4	СВ	PTFE	600	9	30
05.08.22	P3HT (ii)	4	CB	PTFE	800	9	30
05 08 22	P3HT (ii)	Л	CB	DTEE	800:60	0	20.10
05.00.22		4		LITE	800.36	7	20.10
05.08.22	P3HT (ii)	4	CB	PTFE	00	9	15:15

					800:12		
05.08.22	P3HT (ii)	4	CB	PTFE	00	9	15:15
					800:12		
05.08.22	P3HT (ii)	4	CB	PTFE	00	9	25:5
05.00.00			CD	DTEE	800:12	0	25.5
05.08.22	P3HT (1)	4	CB	PIFE	01	9	25:5
05.08.22	P3HT (1)	6	CB	none	3600	9	30
05.08.22	P3HT (1)	6	CB	none	800	9	30
05.08.22	P3HT (i)	6	СВ	none	6000	9	30
05.08.22	P3HT (ii)	6	СВ	none	3600	9	30
05.08.22	P3HT (ii)	6	CB	none	800	9	30
05.08.22	P3HT (ii)	6	CB	none	6000	9	30
05.08.22	P3HT (i)	5	Т	none	3600	9	30
05.08.22	P3HT (i)	10	Т	none	3600	9	30
05.08.22	P3HT (i)	20	Т	none	3600	9	30
05.08.22	P3HT (ii)	5	Т	none	3600	9	30
05.08.22	P3HT (ii)	10	Т	none	3600	9	30
05.08.22	P3HT (ii)	10	Т	none	6000	9	30
05.08.22	P3HT (ii)	20	Т	none	3600	9	30
05.08.22	P3HT (i)	5	Т	none	3600	9	30
05.08.22	P3HT (i)	10	Т	none	3600	9	30
05.08.22	P3HT (i)	20	Т	none	3600	9	30
05.08.22	P3HT (i)	5	Т	PTFE	3600	9	30
05.08.22	P3HT (i)	10	Т	PTFE	3600	9	30
05.08.22	P3HT (i)	20	Т	PTFE	3600	9	30
05.08.22	P3HT (ii)	5	Т	none	3600	9	30
05.08.22	P3HT (ii)	10	Т	none	3600	9	30
05.08.22	P3HT (ii)	20	Т	none	3600	9	30
09.08.22	P3HT (ii)	5	Т	PTFE	3600	9	30
09.08.22	P3HT (ii)	5	Т	PTFE	500	9	30
09.08.22	P3HT (ii)	5	Т	PTFE	1000	9	30
09.08.22	P3HT (ii)	5	Т	PTFE	1500	9	30
09.08.22	P3HT (ii)	10	Т	PTFE	3600	9	30
09.08.22	P3HT (ii)	10	Т	PTFE	2000	9	30
09.08.22	P3HT (ii)	10	Т	PTFE	1000	9	30
09.08.22	P3HT (ii)	10	Т	PTFE	500	9	30
09.08.22	P3HT (ii)	20	Т	PTFE	3600	9	30
09.08.22	P3HT (ii)	20	Т	PTFE	6000	9	30
09.08.22	P3HT (ii)	20	Т	PTFE	1500	9	30
09.08.22	P3HT (ii)	20	Т	PTFE	1000	9	30
09.08.22	P3HT (ii)	20	Т	PTFE	500	9	30

09.08.22	P3HT (i)	10	CF	none	3600	9	30
09.08.22	P3HT (i)	10	CF	none	6000	9	30
09.08.22	P3HT (i)	10	CF	PTFE	3600	9	30
09.08.22	P3HT (i)	10	CF	PTFE	6000	9	30
09.08.22	P3HT (i)	20	CF	none	3600	9	30
09.08.22	P3HT (i)	20	CF	none	6000	9	30
09.08.22	P3HT (i)	20	CF	PTFE	3600	9	30
09.08.22	P3HT (i)	20	CF	PTFE	6000	9	30
09.08.22	P3HT (ii)	10	CF	none	3600	9	30
09.08.22	P3HT (ii)	10	CF	none	6000	9	30
09.08.22	P3HT (ii)	10	CF	PTFE	3600	9	30
09.08.22	P3HT (ii)	10	CF	PTFE	6000	9	30
09.08.22	P3HT (ii)	20	CF	none	3600	9	30
09.08.22	P3HT (ii)	20	CF	none	6000	9	30
09.08.22	P3HT (ii)	20	CF	PTFE	3600	9	30
09.08.22	P3HT (ii)	20	CF	PTFE	6000	9	30
10.08.22	P3HT-PS (ii)	11	Т	PTFE	3600	9	30
10.08.22	P3HT-PS (ii)	11	Т	PTFE	6000	9	30
10.08.22	P3HT-PS (ii)	11	Т	PTFE	6000	9	30
10.08.22	P3HT-PS (ii)	11	Т	PTFE	6000	9	60
10.08.22	P3HT-PS (ii)	11	Т	PTFE	6000	9	120
10.08.22	P3HT-PMMA (i)	11	Т	PTFE	3600	9	30
10.08.22	P3HT-PMMA (i)	11	Т	PTFE	6000	9	30
10.08.22	P3HT-PMMA (i)	11	Т	PTFE	6000	9	60
10.08.22	P3HT-PMMA (i)	11	Т	PTFE	6000	9	120
10.08.22	P3HT-PMMA (i)	11	Т	PTFE	6000	9	30
10.08.22	P3HT-PMMA (ii)	11	Т	PTFE	3600	9	30
10.08.22	P3HT-PMMA (ii)	11	Т	PTFE	6000	9	30
10.08.22	P3HT-PMMA (ii)	11	Т	PTFE	6000	9	60
10.08.22	P3HT-PMMA (ii)	11	Т	PTFE	6000	9	120
11.08.22	P3HT-PS (i)	5	Т	PTFE	3600	9	30
11.08.22	P3HT-PS (i)	5	Т	PTFE	1000	9	30
11.08.22	P3HT-PS (i)	5	Т	PTFE	1500	9	30
11.08.22	P3HT-PS (i)	5	Т	PTFE	750	9	30
11.08.22	P3HT-PS (i)	5	Т	PTFE	500	9	30
11.08.22	P3HT-PS (ii)	5	Т	PTFE	3600	9	30
11.08.22	P3HT-PS (ii)	5	Т	PTFE	1500	9	30
11.08.22	P3HT-PS (ii)	5	Т	PTFE	750	9	30
11.08.22	P3HT-PS (ii)	5	Т	PTFE	750	9	60
11.08.22	P3HT-PMMA (i)	8	Т	PTFE	3600	9	30

11.08.22	P3HT-PMMA (i)	8	Т	PTFE	1500	9	30
11.08.22	P3HT-PMMA (i)	8	Т	PTFE	1000	9	30
11.08.22	P3HT-PMMA (i)	8	Т	PTFE	750	9	30
11.08.22	P3HT-PMMA (i)	8	Т	PTFE	750	9	60
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	3600	9	30
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	1500	9	30
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	1000	9	30
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	750	9	30
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	1000	9	60
11.08.22	P3HT-PMMA (ii)	8	Т	PTFE	1000	9	120
22.08.22	P3HT (i)	5	Т	PTFE	3600	9	30
22.08.22	P3HT (ii)	5	Т	PTFE	3600	9	30
22.08.22	P3HT-PS (i)	5	Т	PTFE	3600	9	30
22.08.22	P3HT-PS (ii)	5	Т	PTFE	3600	9	30
22.08.22	P3HT-PMMA (i)	8	Т	PTFE	3600	9	30
22.08.22	P3HT-PMMA (ii)	8	Т	PTFE	3600	9	30