

Dielectric constant measurement of P3HT, polystyrene, and polyethylene

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1. Introduction

Dielectric constant is also known as relative permittivity. The term permittivity is a material property that affects the Coulomb force between two point charges in the material. Permittivity describes the amount of charge needed to generate one unit of electric flux in a particular medium. A charge will yield more electric flux in a medium with low permittivity. Therefore, permittivity is the measure of a material's ability to resist an electric field. Similarly, relative permittivity is the factor by which the electric field between the charges is decreased relative to vacuum. Dielectric constant is also a piece of essential information in a variety of fields. In chemistry, it is a relative measure of chemical polarity. In the field of electronics, it can help to interpret the capacitance of capacitors. [1]

In the field of organic solar cells, increasing the dielectric constant can result in a longer lifetime of an exciton. However, the short lifetime of an exciton is an important factor affecting the efficiency of organic solar cells. As a result, increasing the dielectric constant of an active layer has become a new concept of efficient organic solar cell fabrication. [2] Koster et al. also predicted a dramatic increase of power conversion efficiency of an optimized device from 13% to over 20% with the increase of the dielectric constant. [3]

At this point, a proper method to obtain the dielectric constant of polymers thin film is necessary. Here we tried to obtain the dielectric constants of three polymers: P3HT (Poly(3-hexylthiophene)), polystyrene and polyethylene by fabricating semi-conduct devices containing these polymers.

2. Methodology

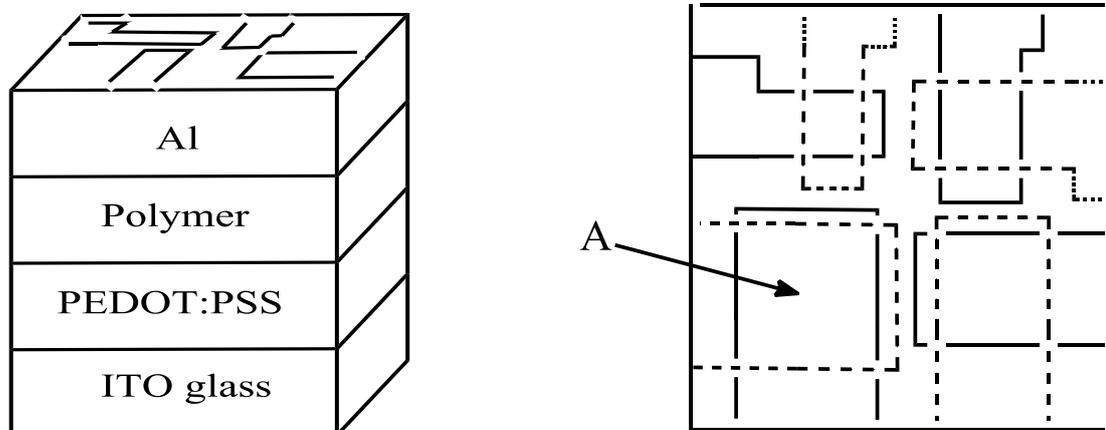


Figure 1 structure of device, solid lines represent aluminum electrode, dash lines represents

ITO electrode.

The structure of the device can be considered as a capacitor constructed of two parallel plates with both of (area A) separated by (distance d). With a sufficiently small d value, the following equation is of high accuracy:

$$C = \epsilon_r \epsilon_0 \frac{A}{d}$$

C is the capacitance, F;

A is the area of overlap of the two plates, m^2 ;

ϵ_r is the dielectric constant of the material between the plates;

ϵ_0 is the electric constant ($\epsilon_0 \approx 8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$);

d is the separation between the plates, m;

According to this equation, if C and d values are obtained, dielectric constant could be calculated. To acquire capacitance, the circuit in figure 2 should be established and connected to a frequency variable alternating current supply. The organic polymer would be considered as the capacitor in the circuit. By measuring the response of impedance to different frequencies, the impedance spectrum can be acquired. As shown in figure 2, ω is the frequency of alternating current, R_s is referred to the resistance of R_{series} and R_p is referred to the resistance of R_{parallel} . The value of ω , R_s , and R_p can be calculated via simulation. According to these data, the value of capacitance can be calculated via Ohm's law of reactive circuits with time varying signals. To acquire convincing data, the value of R_s should be small enough (usually less than $100 \ \Omega$). The value of R_p should be big enough so that almost no current can pass through.

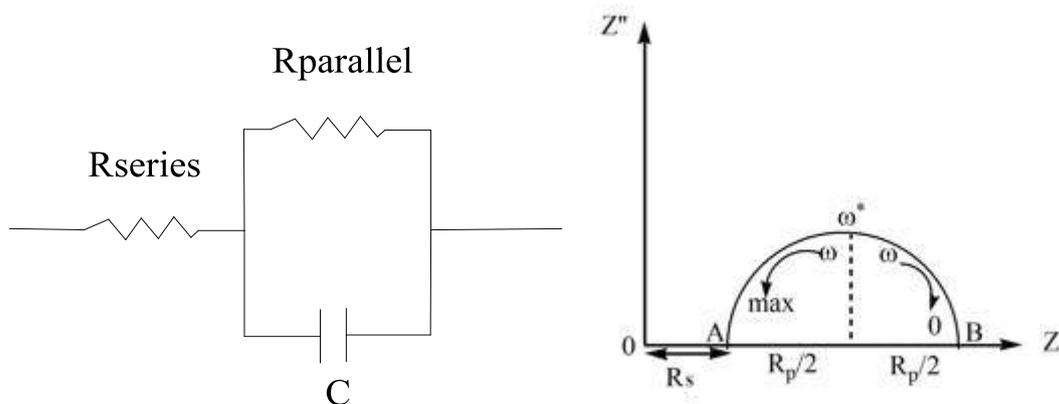


Figure 2 Circuit of impedance measurement and impedance spectrums.

The thickness can be considered as the thickness of polymer layer. After impedance measurement, scratches are made on the organic layer. The depth of scratches can be measured by step profiler. This value minus thickness of PEDOT:PSS layer is the thickness of polymer layer. (PEDOT:PSS layers are prepared with a certain spin-coating process, the thickness of PEDOT:PSS layer can be measured on a sample with only PEDOT:PSS layer.)

Reliable dielectric constant could only be obtained with smooth thin-film. We supposed the fabricated device to be a capacitor constructed of two parallel plates. However, a rough film has a larger area of the dielectric medium than the area we expected. On the other hand, the thickness of a rough film is difficult to measure. The measured thickness of films is also likely to be thicker than the real thickness. Thus, we would record a smaller value for the area and a greater value for the thickness of a rough film. Therefore, the rough film would result in a higher dielectric constant. Spikes of rough films could also result in short-cut of devices. At this point, atomic-force microscopy (AFM) has been applied to characterize the surface morphology of polymer thin film. Root mean square height value (Sq), which is equivalent to the standard deviations of height, could help to judge the roughness of the film. [4] We prefer the Sq value to be less than 1 nm.

3. P3HT (Poly(3-hexylthiophene))

Conjugated polymer P3HT is a common material for organic electronic devices. Dielectric Constant of P3HT is reported to be 3. [5] We tried to fabricate P3HT devices with 16mg/mL solution in chlorobenzene. Results of thickness, dielectric constant and Sq values are listed in table 1. Some dielectric constant data are not available because the results of impedance measurements at those areas could not be used for simulation.

Table 1 Thickness, Sq values and dielectric constant of devices with the P3HT thin films.

	250 rpm Sq= 8.70		500 rpm Sq= 8.60		800 rpm Sq= 6.37	
area	Thickness (nm)	ϵ_0	Thickness (nm)	ϵ_0	Thickness (nm)	ϵ_0
1	128.1	3.61	111.1	3.37	81.1	N/A
2	131.7	3.63	111.1	3.37	81.1	3.02
3	130.7	3.57	117.7	N/A	78.1	4.88
4	132.1	3.87	112.4	3.78	87.4	N/A

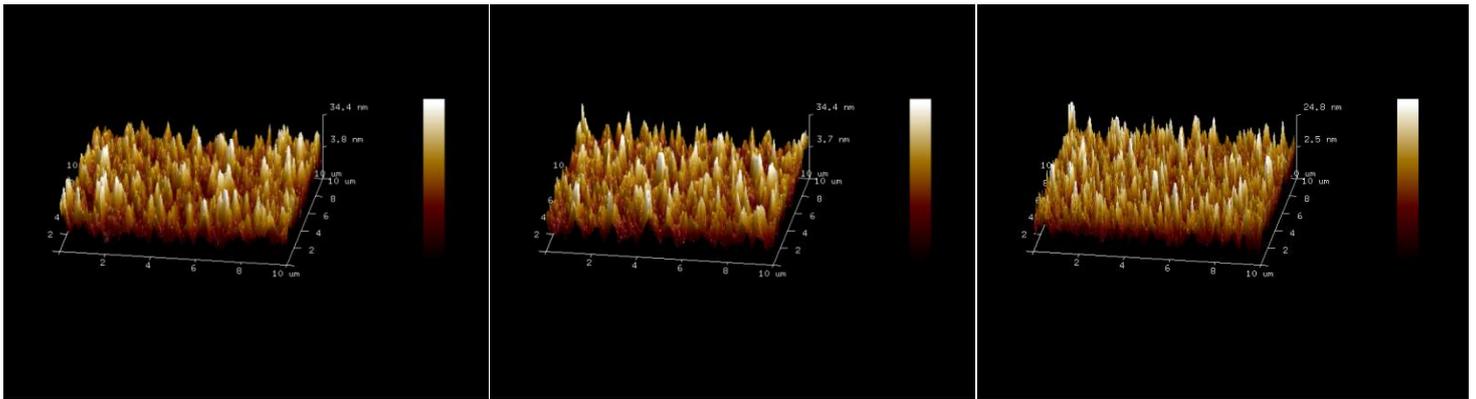


Figure 3 AFM image of the P3HT films fabricated with 250 rpm (left), 500 rpm (middle), and 800 rpm (right). All of the samples are rough. Different spin-speed makes no significant difference to the roughness of film.

According to these results, Sq values are not satisfying. We tried to anneal samples after spin-coating. However, annealing could not help to achieve a lower Sq value. As a result, we measured the dielectric constant of P3HT film to be 3.53. This value should be higher than the real dielectric constant value of a P3HT thin film.

4. Polystyrene

Polystyrene has a good solubility in organic solvents. A variety of solvents can be applied. Solvents combining chlorobenzene and chloroform (1:1 ratio) have been chosen for spin-coating. Films fabricated with chlorobenzene are not thick enough. On the other hand, film fabricated with chloroform is not homogeneous but has a better thickness. As a result, mixed solvents have been applied. Other solvents containing toluene have been tested. Still, mixed solvents of chlorobenzene and chloroform have the best performance. (see appendix)

The thickness and roughness of polystyrene could also be adjusted by the concentration of solvents and spin speed. Films fabricated with 30 mg/mL solutions are thick enough and with acceptable Sq value. On the other hand, the impedance spectrums of some devices fabricated with 20 mg/mL solutions showed no signal. Thus, 30 mg/mL solutions performed better than 20mg/mL solutions.

Results of device characterizations are listed in table 2. According to these results, 800 rpm spin speed seems to be the best choice for polystyrene spin-coating.

Table 2 Thickness, Sq values and dielectric constant of devices with polystyrene thin film.
(chlorobenzene : chloroform =1:1 as solvents, 30 mg/mL)

	250 rpm Sq=0.765 nm		500 rpm Sq=0.786 nm		800 rpm Sq=0.723 nm	
area	Thickness (nm)	ϵ_0	Thickness (nm)	ϵ_0	Thickness (nm)	ϵ_0
1	521.05	2.55	398.39	2.55	316.06	2.46
2	524.05	2.48	392.39	2.61	310.72	2.56
3	515.72	2.11	408.39	2.71	316.38	2.63
4	524.63	N/A	410.72	2.83	308.67	N/A

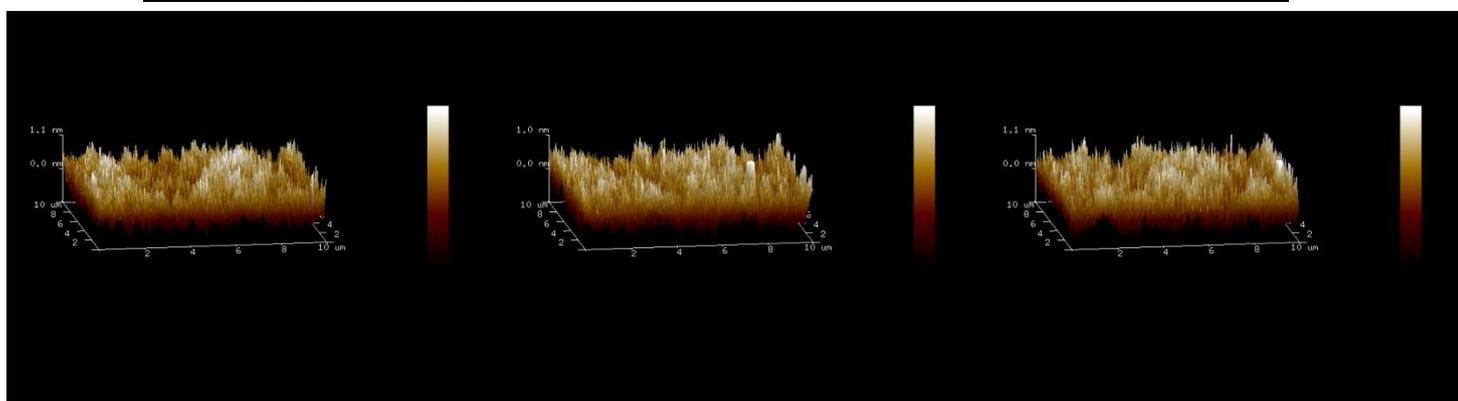


Figure 4 AFM image of polyethylene film fabricated with 250 rpm (left), 500 rpm (middle), and 800 rpm (right) (chlorobenzene: chloroform =1:1 as solvents, 30 mg/mL). These thin films are generally smooth with some spikes.

According to the results above, the dielectric constant of polystyrene thin film is 2.55.

5. Polyethylene

Polyethylene is difficult to dissolve into organic solvents. Therefore, a thin film of polyethylene is not easy to obtain via spin-coating.

Polyethylene can be dissolved into chlorobenzene or toluene at 60 °C. After stirring overnight on hot-plate with the concentration of 10mg/mL, colorless transparent solutions can be obtained. Unfortunately, after spin-coating, a jelly-like gel was formed instead of homogeneous thin film. Annealing could not help to obtain a thin film. In fact, severe aggregation happens while the cooling-down of solutions.

To avoid the aggregation of polymers, we tried to warm up substrate (ITO glass and PEDOT:PSS) on 80°C hot-plate for 6 minutes before spin-coating. A thin film is possible to be

formed before the solution cools down. Homogeneous and transparent thin film can be obtained by this method. After metal deposition process, Impedance spectrums were recorded. Devices fabricated with a spin speed of 500 rpm showed stable signal in impedance measurement. Other devices fabricated with the spin speed of 250 rpm and 800 rpm were dead. Results of 500 rpm experiment groups are listed in table 3. Sq values of chlorobenzene and toluene groups are 3.29 nm and 4.38 nm, respectively. Thicknesses and calculated dielectric constants are listed in table 3. Chlorobenzene seems to be a better choice of solvent than toluene according to these results. Dielectric constant is 2.55.

Table 3 Thickness, Sq value, and dielectric constant of devices fabricated via chlorobenzene and toluene solutions. (500 rpm)

Chlorobenzene Sq=3.29 nm			Toluene Sq=4.38 nm		
Area	Thickness (nm)	ϵ_0	Area	Thickness (nm)	ϵ_0
1	106	2.50	1	112	1.58
2	107	2.29	2	128	2.17
3	103	2.57	3	101	2.26
4	99	2.82	4	110	2.74

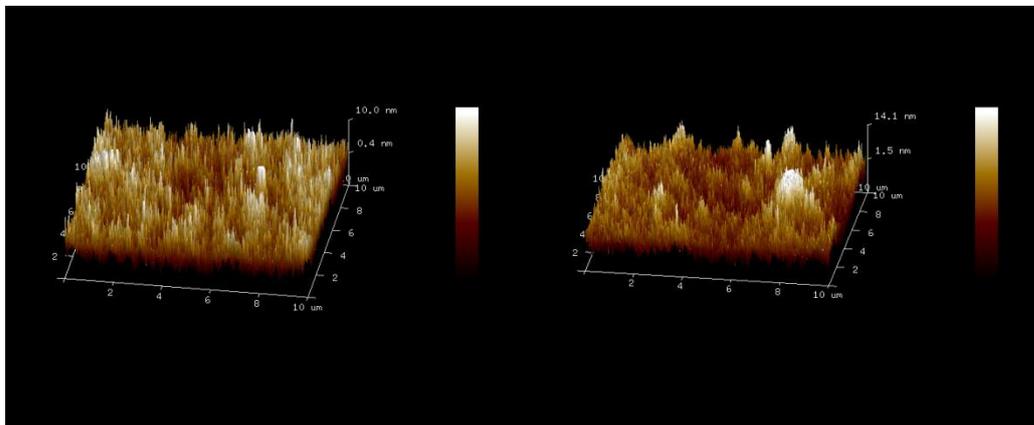


Figure 5 AFM image of polyethylene thin film fabricated with chlorobenzene (left) and toluene (right)

These films are still not smooth and thick enough. The obtained dielectric constant is also not convincing. We found that a method to produce high-quality polyethylene with the thickness of 300 nm to 2000 nm has been reported by Hjertberg et al. in 2001. [6] Polyethylene was dissolved into decalin at 180 °C. Equipment (substrate, pipets, chucks, and disks) was preheated to 100°C-180°C

in an oven nearby the spin-coater. However, these conditions could not be easily achieved in flow-box. As a result, to obtain a polyethylene thin film with good quality, more preheating strategies in glove-boxes should be investigated.

6. Experimental part

ITO substrate cleaning

ITO substrates were first scrubbed in warm soapy demi-water for 5 minutes. After scrubbing, these samples were cleaned in demi-water flow bath. Next, 10 minutes ultrasonic clean in acetone has been done. These samples were then cleaned by ultrasonic in isopropanol for 140 °C 10 minutes. After dry spinning, ITO substrates were dried in oven for 10 minutes followed by ultra-violet cleaning for 20 minutes.

Spin-coating

A layer of PEDOT:PSS was first prepared on the cleaned substrate via spin-coating. Water solution of PEDOT:PSS was warmed up for 20 minutes and then filtered through 0.45 µm filter before spin-coating. After spin-coating, Samples are dried in 140 °C for 15 minutes.

The dried samples were then transported into flow-box for polymer spin-coating. Solutions used for spin-coating were prepared before and stirring on 60 °C hot plate overnight. Spin-coating process contained two stages. Conditions for the first stage vary from different materials. The second stage is used for drying. Conditions for the second stage are 250 rpm of spin-speed, 1000 rpm/s acceleration, and 180s spin-time.

Metal deposition

After spin-coating, samples were then transported to glove-box for metal evaporation. Aluminum sticks were carried by tungsten boat. 100 nm thick aluminum anodes were deposited through masks. Devices for characterization are prepared.

Characterization

Samples were then connected to a frequency variable alternating current supply. Impedance spectrums were recorded. After impedance measurements, scratches were made on samples. By measuring the depth of scratches, the thickness of PEDOT:PSS and polymer layer can be obtained. AFM was also applied for surface characterization.

7. Conclusion

We have tried to measure the dielectric constant of P3HT, polystyrene, and polyethylene by fabricating devices containing ITO, PEDOT:PSS, polymer and aluminum anode. PEDOT:PSS and polymer layers are fabricated via spin-coating. Aluminum anodes are fabricated via metal evaporation.

The dielectric constant of P3HT thin film is tested to be 3.53. This value should be higher than the real dielectric constant value of a P3HT thin film.

The dielectric constant of polystyrene is tested to be 2.55. A recommended solution for polystyrene spin-coating should be a mix solution of chlorobenzene and chloroform (1:1 ratio) with the concentration of 30 mg/mL. Spin-speed is recommended to be 800 rpm.

The dielectric constant of polyethylene is tested to be 2.55. This result is not convincing because the roughness of polyethylene film is not satisfying. To obtain a smooth film of polyethylene, effective heating strategies in flow-box should be investigated.

Appendix

Table 4 Thickness, Sq value, and dielectric constant of polystyrene devices fabricated with chlorobenzene. (800 rpm)

20 mg/mL Sq=0.97 nm			30 mg/mL Sq=1.05 nm		
area	Thickness (nm)	ϵ_0	area	Thickness (nm)	ϵ_0
1	96.27	2.23	1	158.47	2.06
2	96.94	2.34	2	176.12	2.45
3	92.30	2.28	3	184.56	2.62
4	92.03	N/A	4	167.09	2.43

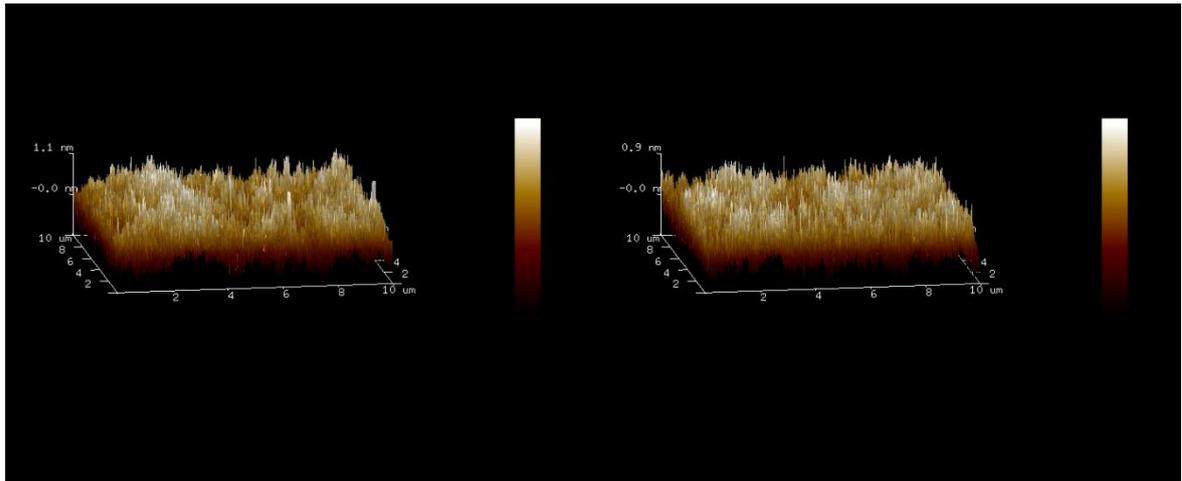


Figure 6 AFM image of polystyrene thin film fabricated with chlorobenzene 20 mg/mL (left) and 30 mg/mL toluene (right)

Table 5 Thickness, Sq value, and dielectric constant of polystyrene devices fabricated with toluene: chlorobenzene (1:1 ratio). (800 rpm)

area	Thickness (nm)	ϵ_0
1	208.60	2.70
2	205.33	2.82
3	211.62	2.95
4	210.36	3.13

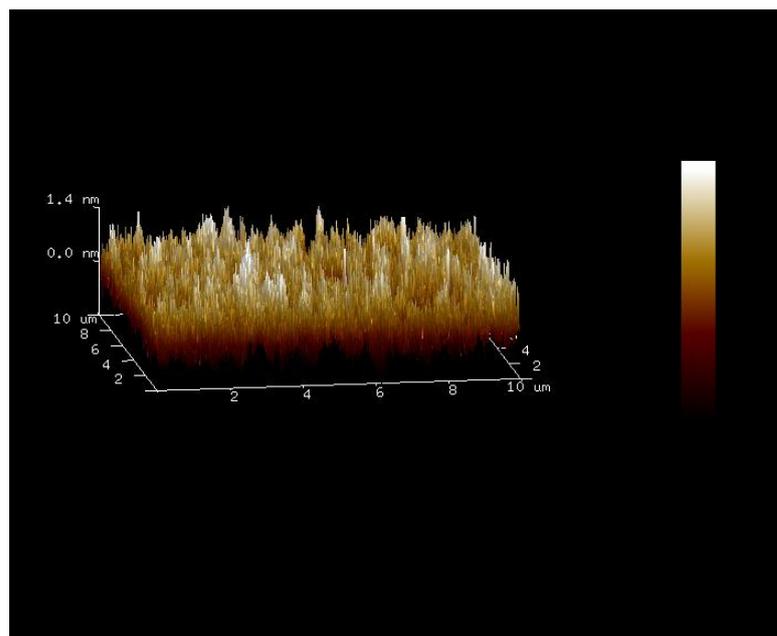


Figure 8 AFM image of polystyrene thin film fabricated with mixed solution of toluene and

chlorobenzene

Devices fabricated with mixed solvents of toluene and chloroform (1:1 ratio) do not have a good simulation curve in impedance spectrum.

Reference

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