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Fabrication of Poly (methyl methacrylate) and Poly(vinyl alcohol) Thin Film Capacitors on Flexible Substrates

Fabrication of Poly (methyl methacrylate) and Poly(vinyl alcohol) Thin Film Capacitors on Flexible Substrates

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Abstract— Flexible electronics is becoming more popular with introduction of more and more organic conducting materials and processes for making thin films. The use of polymers as gate dielectric has over ruled the usage of conventional inorganic oxides in Organic Thin Film Transistors (OTFTs) on account of its solution process ability and ease of making highly insulating thin film. In this work Capacitance is fabricated with polymeric dielectrics namely poly (methyl methacrylate) - PMMA and poly (vinyl alcohol) – PVA. The electrodes used for these capacitors are Indium Tin Oxide (ITO) and Aluminium. Capacitance value of 9.5nF/cm^2 and 33.12nF/cm^2 is achieved for thickness of 510 nm of PMMA and 80 nm of PVA respectively. This study on capacitance can be used for assessing the suitability of these polymers as gate insulators in OTFTs.

1. Introduction

The choice of dielectric in the development of a thin film transistor is very crucial. The use of polymer as dielectric has the advantage that they can be made into a solution and spin coated or drop casted. Spin coating of polymers has been considered to be a simple and reliable method of forming thin films by several researchers. Although several polymers are used as gate dielectric in OTFTs, poly(methyl methacrylate) and poly(vinyl alcohol) have drawn great attention by the researchers. S. Mandel *et al* [1] have made a comparative study on the capacitance and dielectric constant of PVA, PMMA and poly(vinyl phenol)-PVP thin films and found that PMMA exhibited a higher capacitance of 13.3nF/cm^2 with dielectric constant of 4.5 at 100 KHz. PMMA has been extensively used as gate insulator in pentacene Thin Film Transistors(TFTs) as growth of pentacene over PMMA was highly favoured than on SiO_2 and that the grains of pentacene grew bigger, thereby increasing the field effect mobility [2]. Capacitances of PMMA layer of different thicknesses have been measured using an LCR meter on ITO/PMMA/Au parallel plate capacitor structure in the development of pentacene photo detectors [3]. Impedance Spectrometer studies have been carried out on varying concentrations of PMMA thin films sandwiched between ITO and aluminium [4] for a frequency range of 0 to 10 KHz. Dielectric composite made of PMMA with 40% $CaCu_3Ti_4O_{12}$ has been proved to have very low dielectric loss at 100 KHz, making it a promising choice for capacitor application [5]

In this paper, we present the morphological study of PMMA and PVA coated on glass and the fabrication of thin film capacitors with PMMA and PVA as dielectric over a flexible substrate. Capacitance values were measured using an LCRQ bridge. This study is useful for choosing dielectric material for development of flexible OTFT.

2. Material and Methods

The capacitor fabrication used spin coating for dielectric and physical vapour deposition for electrode deposition. In the process of fabricating PMMA and PVA capacitors on ITO coated PET, thickness measurements were done apriori on spin coated polymeric films on chemically cleaned glass substrates by RCA treatment. PMMA and PVA are dissolved in toluene and deionized water with 300mg PMMA in 10ml toluene and 0.5g PVA in 10ml deionized water respectively by magnetic stirring at room temperature. These solutions were spin coated on RCA cleaned, flat glass slide using the SPECTROSPIN spin coater-SC8000 at different spin rates for 60 sec. PMMA and PVA spin coated films were then vacuum dried at 100°C and 80°C respectively. The dried polymeric thin films on glass substrates were investigated using the Atomic Force Microscopy (AFM) for observing the morphology and Spectroscopic Ellipsometer for measuring the thickness, which have been detailed in section 4. ITO coated PET is chosen as the flexible substrate where ITO acts as the bottom electrode and aluminium is deposited on the dielectric to form the top electrode. The schematic of the capacitor structure is shown in Fig 1.

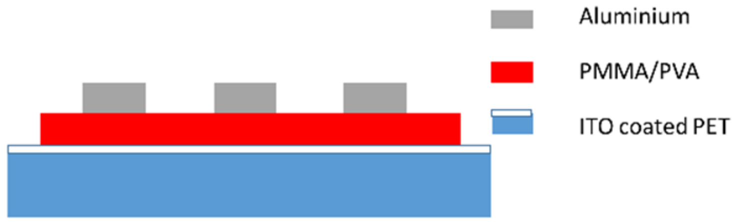

Figure 1. Structure of capacitor

The various masks used for fabrication of the capacitor is shown in Fig 2. ITO coated PET sheets (Sigma Aldrich) were cut to 4.5cm^2 area. They were cleaned by ultra-sonication with acetone, ethanol, and deionized water and then dried. The flexible substrates with ITO on one side were masked on all the four sides with a width of 5mm to form the bottom electrode contact for the capacitor. Then, the polymeric dielectric – PMMA or PVA was spin coated in the middle unmasked area as shown in Fig 2b, subsequently vacuum annealed at 100°C or 80°C for 1 hour.

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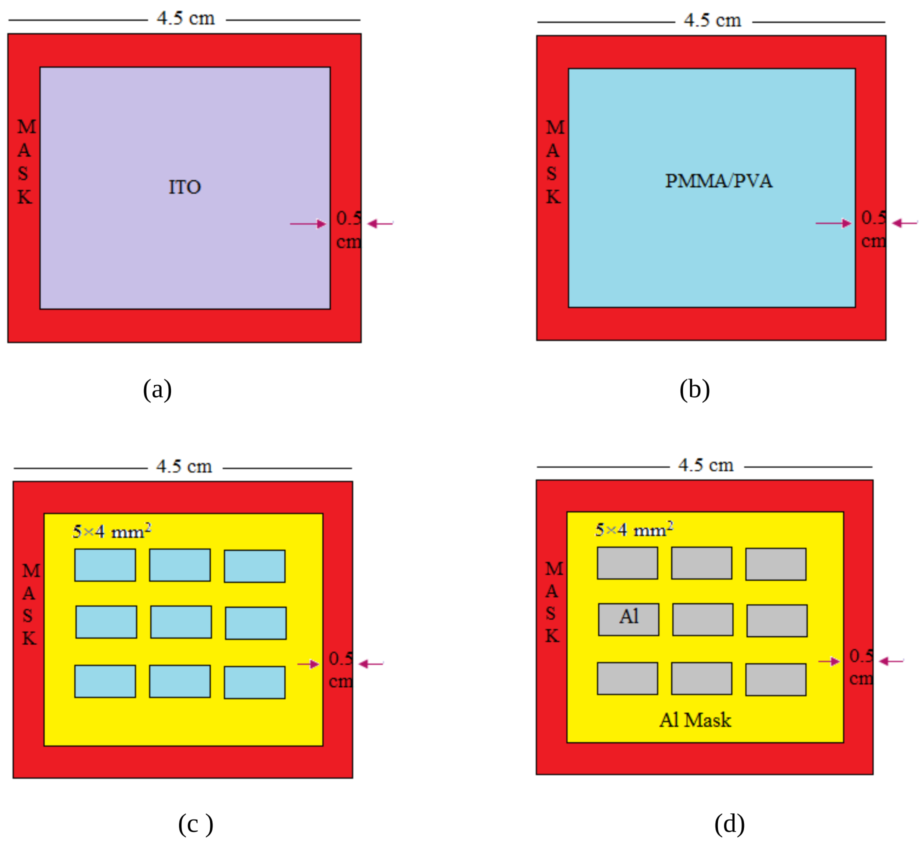

Figure. 2. Steps in Fabrication of PMMA/PVA Flexible Capacitor – Top View (a) Masking ITO of flexible ITO coated PET substrate; (b) Spin Coating PMMA/PVA; (c) Shadow mask with open windows of 20mm^2 each; (d) Aluminium deposition

The deposition of aluminium was carried out with a mask of window dimensions 5×4 mm^2. The metal film is annealed at 100°C for half an hour to enable the proper adhesion of the metal atoms to the polymeric film.

3. Theory/calculation

As spin coating is the method adopted to make the polymeric thin film, a general equation that relates the thickness of spin coated films, concentration of solution and spin speed has been proposed by C.B.Walsh [6] is given as follows.

$$h = Ac^n \omega^{-\alpha} \qquad (1)$$

where h is the thickness of the spin coated film, c is the solution concentration, ω is the spin speed, A and α are constants due to other parameters that influence thickness and n is concentration dependent system parameter. Further, an exponential relation governing the thickness of spin coated thin films with the solution concentration has been given by T.Tippo *et al* [7] and is given by Eq. 2

$$h = Ae^{nc} \omega^{-\alpha} \qquad (2)$$

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With decreasing film thickness, an increasing trend in capacitance was observed which is in correlation with capacitance equation given in equation 3.

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{3}$$

where, ε_0 is the permittivity of free space, εr dielectric constant, A is area of the capacitor, d thickness of the dielectric.

4. Results and Discussion

(a) AFM analysis:

Surface morphology observations of the two chosen dielectrics – PMMA and PVA spin coated on glass substrates using AFM over a 7µm^2 scan area are described here. Fig. 3 and Fig. 4 shows the 2D and 3D topographical profiles of spin coated PMMA at two different spin speeds: 3500 and 4000 rpm respectively.

(a) (b)

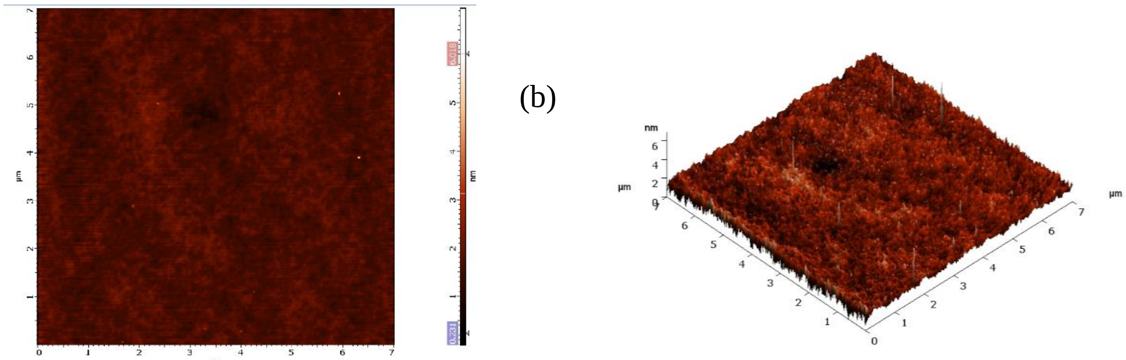
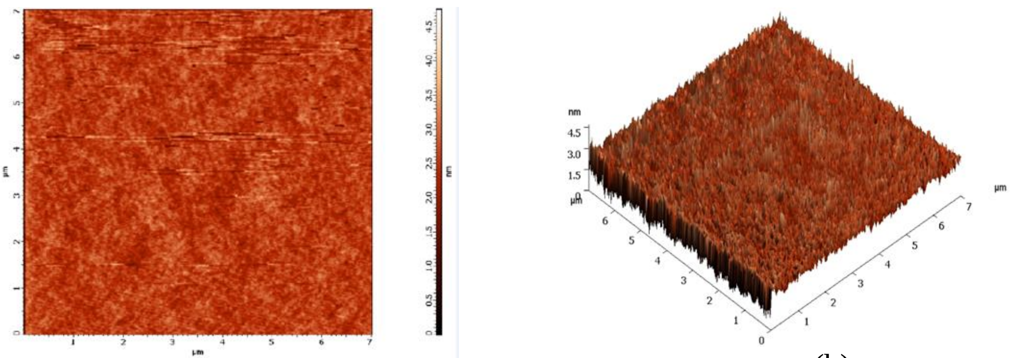


Fig. 3. a) 2D AFM Image of Spin Coated PMMA at 3500rpm; b) 3D AFM Image of Spin Coated PMMA at 3500rpm.

Fig. 3a shows the 2D micrograph of PMMA spin coated at 3000rpm with very few bright spots that denote the peaks in the 3D image of Fig. 3b. It is highly desirable that in case of an OTFT, the organic semiconductor coating to be done above the polymeric dielectric should be pore free. The presence of pores in the dielectric surface would make poor insulation between the gate electrode and the organic semiconductor. In addition appropriate surface roughness must be extended by the dielectric for the proper adhesion of the above lying semiconducting film.



(a) (b)

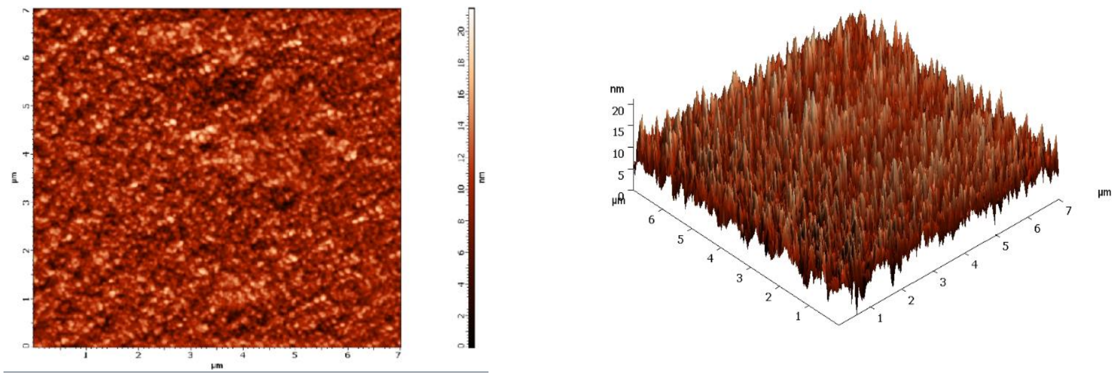
Fig. 4. a) 2D AFM Image of Spin Coated PMMA at 4000rpm; b) 3D AFM Image of Spin Coated PMMA at 4000rpm.

The 2D AFM image of Fig. 4a with PMMA spin coated at 4000rpm appears to have smooth morphology and there occurs less number of peaks in Fig. 4b when compared to Fig. 3b.
The surface topography in terms of flatness, asymmetry, presence of grooves and pits can be well explained by roughness, skewness and kurtosis tabulated in Table 1.

Table 1.Morphological Parameters of PMMA Thin Films at Selected Spin Rates.

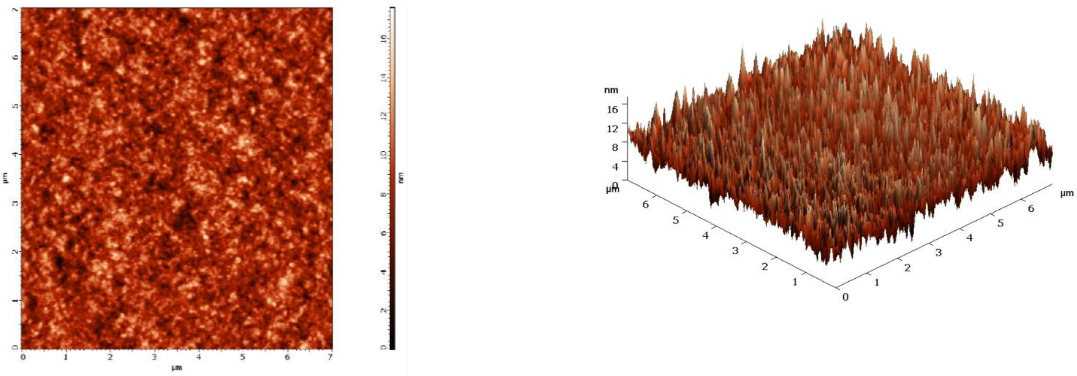
Spin Speed (*rpm*)	Surface Roughness (*nm*)	Skewness	Kurtosis
3500	0.19	0.375848	7.77016
4000	0.24	-0.517825	2.58208

The average roughness value which is an estimate of the average deviation in height above and below an imaginary central plane is found to be more for the spin coated PMMA at a higher spin rate. The degree of symmetry of a surface about a mean line, denoted by skewness is positive for 3500rpm spin coated film, representing a surface that has more peaks than valleys or pits in the film and can be confirmed from the countable number of protruding peaks in 3D image of Fig 3b. Skewness being negative for the film spin coated at 4000rpm denotes a surface having more valleys than peaks as seen in Fig 4b. As defined in [8], kurtosis indicates the sharpness of a surface and supports the skewness results. Kurtosis above a value of 3 means the sample has more peaks than pits and when goes below 3, as in the case of 4000rpm spin coated thin film, the number of pits are more than the number of peaks.



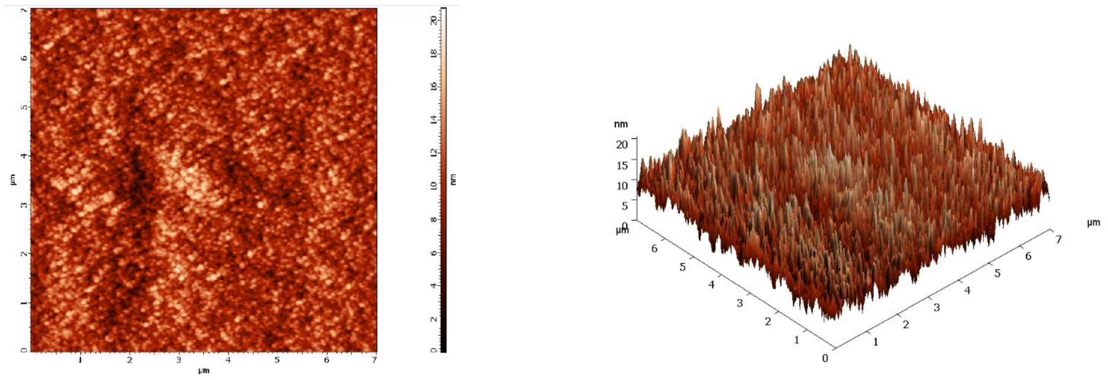
(a) (b)

Fig. 5. a) 2D AFM Image of Spin Coated PVA at 1000rpm; b) 3D AFM Image of Spin Coated PVA at 1000rpm.



(a) (b)

Fig. 6. a) 2D AFM Image of Spin Coated PVA at 1500rpm; 6.b) 3D AFM Image of Spin Coated PVA at 1500rpm.



(a) (b)

Fig. 7. a) 2D AFM Image of Spin Coated PVA at 2000rpm; 7 b) 3D AF.M Image of Spin Coated PVA at 2000rpm.

The spin coated PVA films more or less show similar morphological nature at the three different spin rates: 1000, 1500 and 2000rpm. These films are found to have spherical structures with very small variations in average surface roughness, skewness and kurtosis tabulated in Table 2.

Although no significant inference can be drawn from the grainy patterns of the 2D images of PVA thin films, there are sharper peaks in all the three cases of spin coated PVA films confirmed by the 3D images of Fig. 5b, Fig.6b and Fig.7b. At the three selected spin rates: 1000,1500 and 2000rpm, skewness and kurtosis values listed in Table 2, are close to zero which indicate the number of peaks and valleys in the film are almost equal. This indicates a planar thin film of PVA formed over glass.

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Table 2. Morphological Parameters of PVA Thin Films at Selected Spin Rates.

Spin Speed (*rpm*)	Surface Roughness (*nm*)	Skewness	Kurtosis
1000	2.11242	0.241732	0.0688455
1500	1.67592	0.13162	0.0458512
2000	2.0561	0.0915515	0.0275083

(b)Thickness and Capacitance measurement:

The thickness measurements of PMMA and PVA thin films were done using Spectroscopic Ellipsometer and listed in Table 3 and Table 4 respectively. Table 3 and 4 also shows the measured capacitance for various film thickness. A decreasing trend in thickness of the film with increasing spin speed was observed. As discussed in section 3, the thickness values of the spin coated thin films hold an inverse relation with spin speed as defined by Eq. 1 and 2.

Table 3.Thickness of PMMA Thin Films at Various Spin Rates

Spin Speed (*rpm*)	Thickness (*nm*)	Capacitance (nF/cm^2)
3500	1556.02	5.35
4000	1274.45	6.35
6000	713.25	6.94
6500	610.25	8.74
7000	560.76	9.015
7500	510.32	9.5

Table 4. Thickness of PVA Thin Films at Various Spin Rates

Spin Speed (*rpm*)	Thickness (*nm*)	Capacitance (nF/cm^2)
1000	150.00	18.33
1500	105.00	30.745
2000	80.00	33.12

When thickness of PMMA films are exponentially fitted as shown in Fig.8, the error bars are reduced at higher spin speeds. So, the same Eq.2 represents the thickness of spin coated PMMA thin films and the same holds good for the PVA thin films.

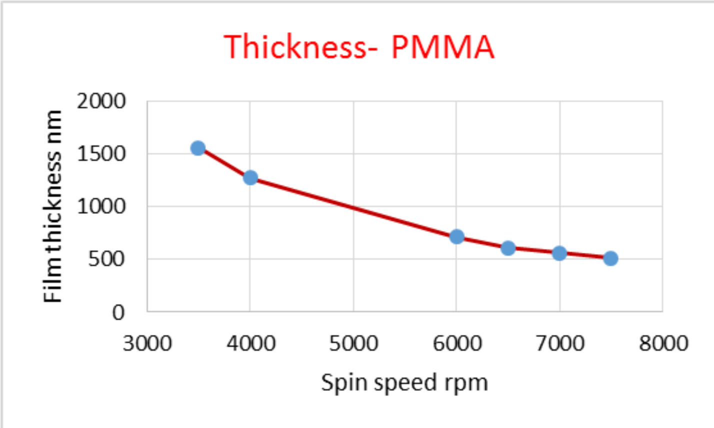

Fig. 8. Thickness vs. Spin Speed of PMMA Thin Films.

The three layer capacitor structures fabricated as described in section 1, with nine capacitors of same dimensions formed on a single substrate at a particular spin rate is shown in Fig. 9.The average capacitance of all the capacitors were measured using an LCR-Q Bridge 6018 at a fixed input frequency of 1 KHz in parallel mode.

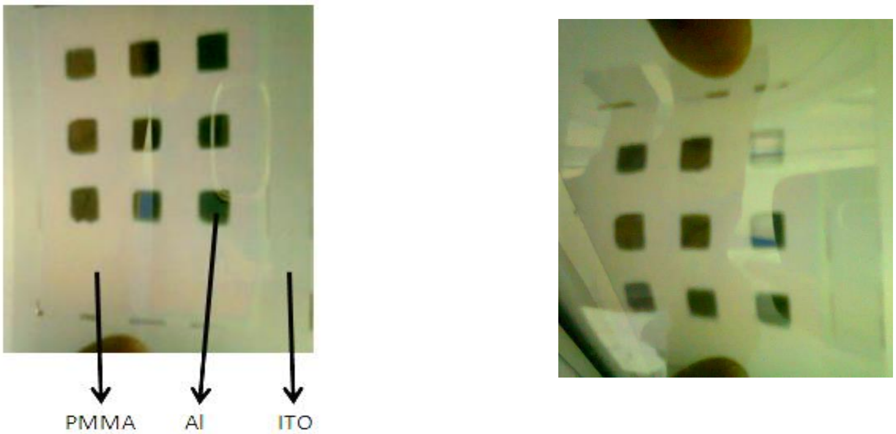

Fig. 9. Flexible PMMA Thin Film Capacitor.

The capacitance values measured for nine capacitors averaged is plotted in Fig. 10 for PVA as dielectric and in Fig. 11 for PMMA as dielectric. The capacitance values obtained obeys equation 3.

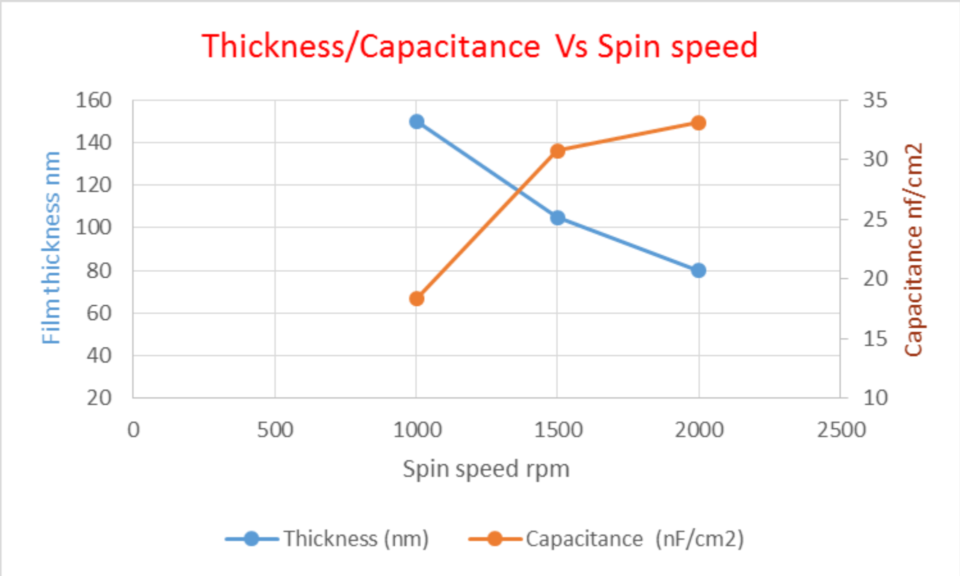

Fig. 10. Plot of Thickness/ Capacitance vs. Thickness of PVA Thin Films.

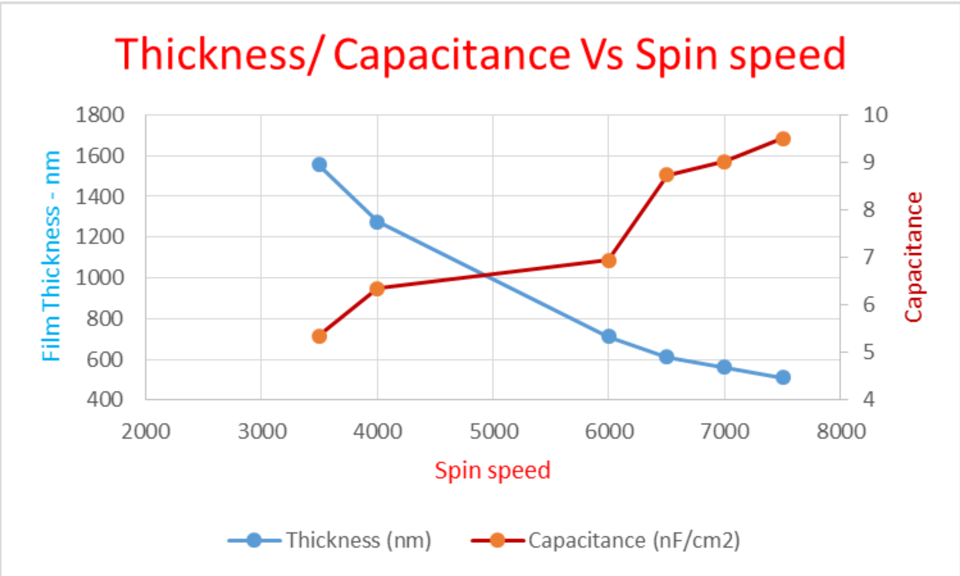

Fig. 11. Plot of Capacitance vs. Thickness of PMMA Thin Films.

As capacitance decreases with increase in frequency, it is necessary to study the capacitive behaviour of PMMA for large frequency range and varying applied gate bias by C-V measurements. This will give an insight into the accumulation, depletion and inversion regimes of the final OTFT device. Further, the decreasing capacitance with increasing frequency at a fixed bias voltage may be attributed to trapping and detrapping of charge carriers, increasing inability of the dipoles to orient themselves in a rapidly varying electric field and slow release of charge carriers from relatively deep traps in the amorphous PMMA film [9].

However at higher frequencies, there is some amount of energy being absorbed by the dielectric from the applied voltage which is referred to as the dielectric loss. Hence in addition to the capacitance measurements at varying voltages, leakage current studies on the dielectric for varying electric field will help in understanding the breakdown field strength of the material. This will decide if the polymer will make a good dielectric in the transistor. The capacitance offered by the dielectric greatly influences the operation of Organic Thin Film Transistors (OTFTs).

5. CONCLUSIONS

We have presented step by step procedure for fabricating flexible capacitors using organic dielectrics namely PMMA and PVA. Both are coated by the spin coating process. A very simple method to measure the capacitance using an LCRQ bridge was adopted which yielded 9.5nF/cm^2 and 33.12nF/cm^2 for lowest thickness of PMMA and PVA respectively. Also the surface analysis of these thin films on glass substrates is investigated under AFM confirms their dielectricity at a very low thickness.

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