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Preparation and characterization of nano scale PMMA thin films

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Thin films of nano scale poly (methyl methacrylate) (PMMA) were prepared by fast dip coating technique (FDCT). XRD spectra indicated the amorphous nature of the films. The closer SEM inspection revealed that self-assembled mesoscopic cells for both as grown and annealed PMMA films. Low leakage current was observed in the *J-V* characteristics for the voltage ranges studied. The absence of hysteresis in the *J-V* characteristics for the forward and reverse sweep direction eliminates the presence of deep traps in the PMMA thin films studied. The observed surface morphology, thermal stability and *J-V* behaviour indicated that these films could be used as AFM data storage devices as an efficient dielectric layer in field effect organic thin film transistors.

Keywords: PMMA, Fast dip coating technique, Morphology, Mesoscopic, FTIR, XRD, SEM**,** Thin film, Characterization

1 Introduction

Polymer films attract much attention because of their unique properties, resistivity, electrical properties and their ease of processing and fabrication. The main advantage of polymer thin films is that they can be prepared easily at low cost. Poly (methyl methacrylate) (PMMA) is one of the promising representatives of polymeric materials and there are numerous proposals for its applications as dielectric in organic thin film transistors (OTFTs), advanced electronic, opto-electronic devices, as optical lenses in cameras and optical fibers[1-3]. As a dielectric layer in OTFT structure along with high dielectric constant value, it need to satisfy various constraints concerning band offsets, limits on charge traps, amorphous nature, stability against degradation, small leakage current, high breakdown potential, processability and reproducibility. Extensive work has been carried out on synthesis, preparation and various properties such as morphology, optical, dielectric and aging behaviour of PMMA films[4-10]. In the present study, detailed investigations such as FTIR, XRD, SEM, *J-V* characteristics and annealing behaviour of PMMA thin films prepared by fast dip coating technique (FDCT) were carried out with a view to use nano scale thin PMMA film as an AFM data storage devices and an efficient dielectric layer in field effect organic thin film transistors.

2 Experimental Details

PMMA obtained from Sigma-Aldrich was used without further purification to form the dielectric layer. The cleaned micro slides were held vertically above the PMMA solution (with a concentration of 2% with benzene as a solvent) by means of mechanical arrangement capable of slow and steady vertical movement. After bringing the solution to the room temperature, the substrates were immersed in the solution for different time period (ranging from 1 min to 1 hour). After withdrawal from the solution, the substrates with the deposited film were dried in a cleaned atmosphere for 20 min and then kept inside an oven at 333K for one hour. The films were annealed for 1 hour inside an oven kept at 373K in order to find the effect of temperature on the prepared nano scale thin PMMA films. The thickness of the coated films was measured by using an electronic thickness measuring instrument (Tesatronic-TTD-20), gravimetric method and cross checked by optical spectrophotometer. The PMMA films coated were identified by using FTIR spectrometer. The structure of the as grown and annealed nano scale thin PMMA films were studied by using XRD. The surface morphologies of the as grown and annealed PMMA films were investigated by means of scanning electron microscope (SEM). The current density-voltage (*J-V*) characteristics were studied by using HP 5270A for various delay times from 0 s to 20 s.

3 Results and Discussion

FTIR spectroscopy has proved to be valuable tool to provide information on the functional groups present in the polymer film[11]. Figure 1(a-b) shows the FTIR spectrum of as grown and annealed PMMA films. The bands at about 677 cm^{-1} and 750 cm^{-1} are assigned to out of plane OH bending. The band at around 980 cm^{-1} is the characteristic absorption vibration [12] of PMMA. The bands at about 1060 cm^{-1}, 1245 cm^{-1}, 1730 cm^{-1} and 2926 cm^{-1} are assigned to ʋ(C-O) stretching vibration, wagging vibration of C-H, C=O stretching and C-H stretching, respectively. The relatively broad and intense absorption observed at around 3400 cm^{-1} indicates the presence of bonded O-H stretching vibration. It was also found that both as grown and annealed films showed similar FTIR spectrum which eliminated the probability of the presence of any impurity in the PMMA thin films.

The X-ray diffractograms of the as grown and annealed PMMA film is shown in the Fig. 2 (a,b). The X-ray diffraction pattern indicates the amorphous nature with large diffraction maximum that decreases at large diffraction angles. The shape of the first main maximum indicates the ordered packing of the polymer chains. The intensity and shape of the second maxima are related to the effect inside the main chains.[13] The observed broad humps in the XRD spectrum indicate the presence of crystallites of very low dimensions. The absence of any prominent peaks in the PMMA thin films indicates the amorphous nature of the films.

Surface morphology of dielectric layer is very important because it affects the property of the semiconductor layer coated over it. Figure 3 (a,b) shows the SEM image of as grown and annealed PMMA films of various thickness magnified for various orders of magnitude.

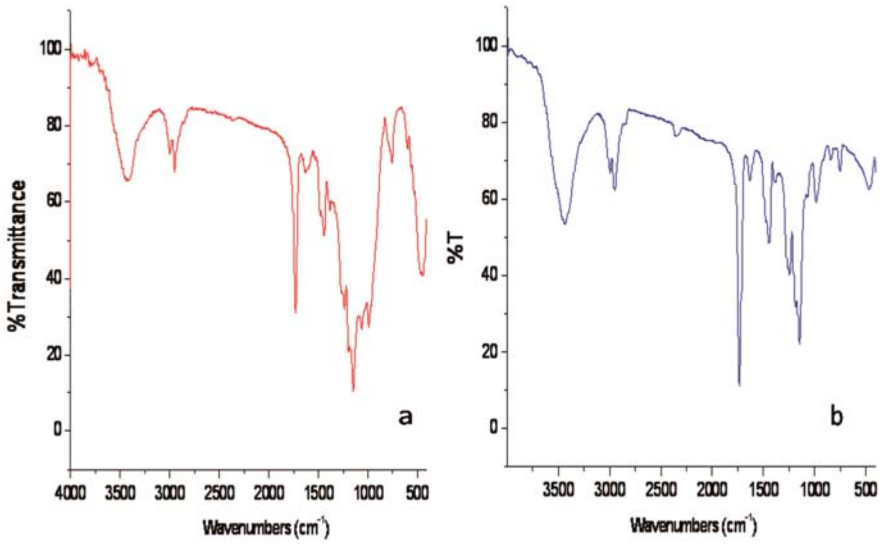

Fig. 1 — FTIR spectrum of PMMA film (a) as grown(d=160 nm) (b) annealed at 100°C (d= 94 nm)

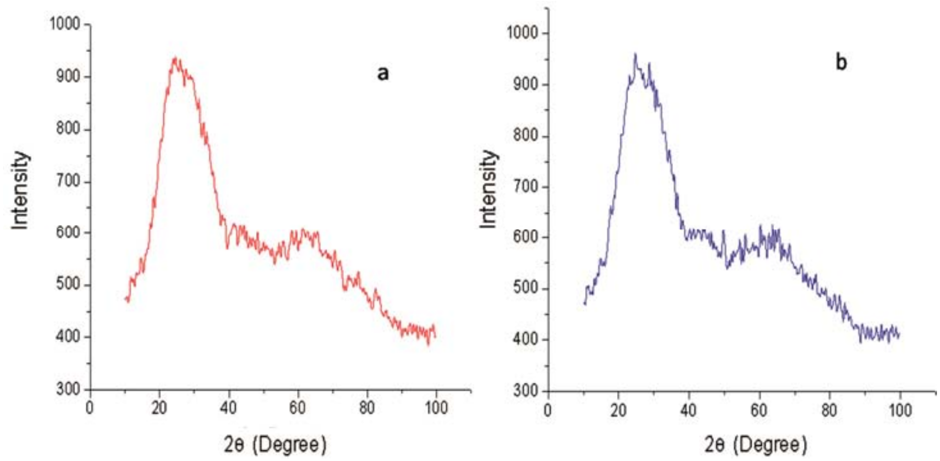

Fig. 2 — XRD pattern of PMMA film (a) as grown(d=160 nm) (b) annealed at 100°C (d= 94 nm)

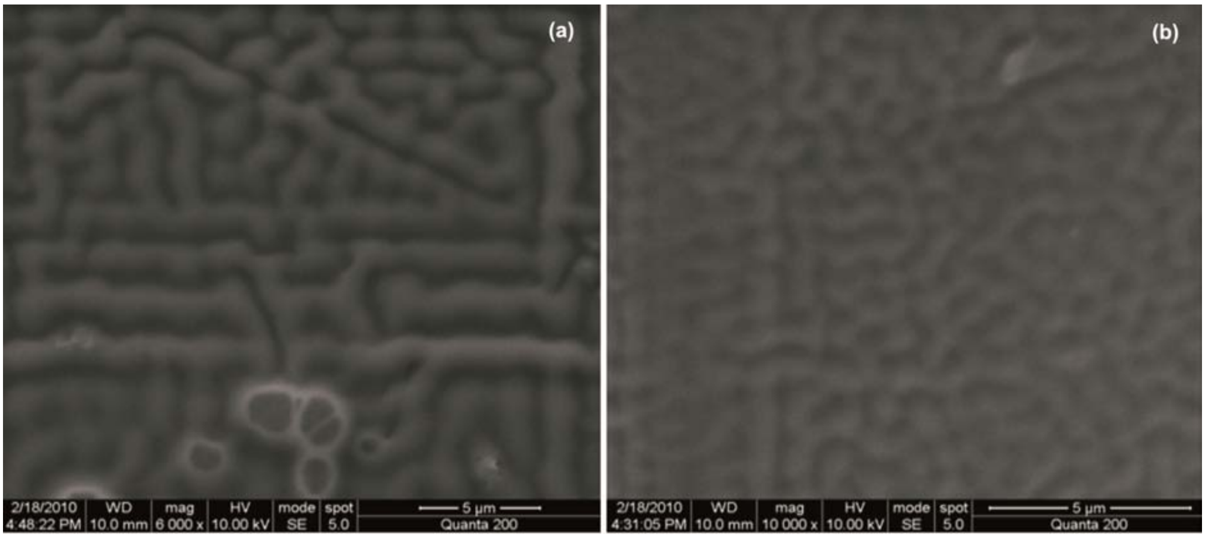

Fig. 3 — SEM images of PMMA film (a) as grown (*d*=160 nm) (b) annealed at 100°C (*d*=94 nm)

The SEM study of deposited films led to the conclusion that PMMA produced self-assembled mesoscopic structured films as presented in Fig. 3, when deposited under dip coating process[14,15]. Closer SEM inspection reveals various structures of mesoscopic cells for both as grown and annealed PMMA films. The formation of the mesoscopic structures may be described as follows. Due to fast external drying, all solvents which leave the solution are immediately removed from the system. Then at an early stage of the evaporation process, a polymer rich layer is formed. The thickness of such layers may be of the order of mesoscopic scale range. The mesoscopic structures obtained for the very thin film of PMMA could be used as an AFM-based data storage which is promising alternative to conventional magnetic data storage because it offers great potential for considerable storage density improvements. The fast dip coating process presented in this work is simple, highly reproducible and permits fabrication of large areas of mesoscopic structured films, which have a potential as membranes, long period gratings and photonic molecules. The stripped pattern from cylinders or perpendicular lamellae obtained for annealed PMMA film could be used as an optically tunable high and low pass transflective spatial filters. No pits and pinholes were found on as grown and annealed films. The surface morphology is quite homogenous and amorphous in nature. It is observed from the SEM analysis that both as grown and annealed films showed smooth surface, which is one of the most important requirement of a dielectric layer in organic thin film transistors.

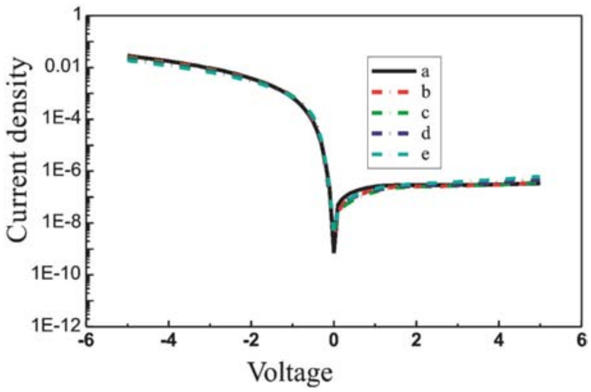

Fig. 4 — Variation of current density with voltage (*J*-*V*) for Al/PMMA/P-Si/Al structure (a) 50°C (b) 75°C (c) 100°C (d) 125°C and (e) 150°C

The variation of current density with voltage for Al/PMMA/P-Si/Al is shown in Fig. 4. In a MISM structure, a negative voltage applied to top metal contact (Al) with respect to *p*-Si substrate will act as a forward bias where as a negative voltage applied to the *p*-Si substrate with respect to the top metal contact acts as a reverse bias. When the top Al contact is connected to negative charge, it injects electrons into the PMMA layer resulted in the reduction of barrier height.

So in the forward bias the loss current increases with the increase of applied negative voltage to the top Al contact. The current in the MISM structure in the forward bias characteristics is completely controlled by the electrons flowing from the top Al contact. On the other hand if *p*-Si substrate is negatively biased, it injects electrons in to the conduction band of PMMA. So the current flowing through the MISM structure in the reverse bias is essentially due to injected electrons from *p*-Si substrate and not due to holes from the positively biased top Al contact because they face a large barrier height in the reverse bias.

In the case of reverse bias, some of the injected electrons on gaining sufficient energy create electron-hole pairs in the PMMA layer either by impact ionization or by excitation from traps to band. Under the reverse bias conditions, a substantial fraction of holes generated in PMMA are driven towards the negatively biased *p*-Si substrate where these become trapped in a localized region near the *p*-Si substrate. The magnitude of loss current in the reverse bias direction is very low when compared to forward bias direction. In particular, the forward biased characteristics were influenced by the organic thin film insulator layer where as under reverse bias, the junction leakage was primarily dominated by the generation and recombination of charges within the bulk of the *p*-Si substrate. The observed low leakage current in the reverse bias direction is mostly assigned to the hole trapping sites near *p*-Si substrate and the existence of a barrier in the reverse bias direction[16].

No hysteresis is observed in the *J-V* characteristics for the forward and reverse sweep direction. The absence of hysteresis in the *J-V* characteristics eliminates the possibility of deep traps in the PMMA films[17,18]. This intrinsic change may lead to the rougher and corrugated interfaces at the Al contact and *p*-Si substrate sides. This results in occurrence of weak spots at the contact which serve as high-field regions and induce increased leakage current[19].

4 Conclusions

The FTIR analysis indicated the absence of any impurity in the as grown and annealed nano scale thin PMMA films. The X-ray diffractogram revealed the amorphous nature of the films studied. The SEM studies indicated the phenomenon of self-assembly on the mesoscopic scale. The fast dip coating process presented in this work is simple, highly reproducible and permits fabrication of large areas of mesoscopically structured films. The mesoscopic structured films have the potential as membranes, long period gratings, photonic molecules and AFM based data storage system. *J-V* characteristics of the MISM structures with Al/PMMA/*p*-Si/Al have been studied. The *J-V* characteristics showed low leakage current for the voltage range studied. The absence of hysteresis in the *I-V* characteristics for the forward and reverse sweep direction eliminates the presence of deep traps in the nano scale thin PMMA films studied. The observed amorphous nature without having any pin holes, pits, low leakage current and good thermal stability indicated that these films could be used as an efficient dielectric layer in field effect organic thin film transistors.

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References

1 Puigdollers J, Orpella C V A, Quidant R, Martín I, Vetter M & Alcubilla R, *Org Elect*, 5 (2004) 67.
2 Uemura S, Yoshida M, Hoshino S, Kodzasa T & Kamata T, *Thin Solid Films*, 438-439 (2003) 378.
3 Yang D X, Yu J, Tao X & Tam H, *Mater Sci & Eng A*, 364 (2004) 256.
4 Magda A & Shahawy E I, *Polym Test*, 18 (1999) 389.
5 Sakai H, Konno K & Murata H, *Thin Solid Films*, 518 (2009) 510.
6 Kim T G, Jeong E H, Lim S C, Kim S H, Kim G H, Kim S H, Jeon H Y & Youk J H, *Syn Metals*,159 (2009) 749.
7 Hu Y, Gu G, Zhou S & Wu L, *Polym*, 52 (2011) 122.
8 Mthethwa T P, Moloto M J, De Vries A & Matabola K P, *Mater Res Bull*, 46 (2011) 569.
9 Yilmaz E & Suzer S, *Appl Surf Sci*, 256 (2010) 6630.
10 Singh P, Kumar R, Virk H S & Rajendra P, *Indian J Pure & Appl Phys*, 48 (2010) 321.
11 Wee S W & Park S M, *Bull Korean Chem Soc*, 22 (2001) 914.
12 Duan G, Zhang C, Li A, Yang X, Lu L & Wang X, *Nano Res Lett*, 3 (2008)118.
13 Chandar Shekar B, Na M, Lee J & Rhee S W, *Mol Liq Cryst*, 424 (2004) 43.
14 Booker A, Muller A H E & Krausch G, *Macromolecules*, 4 (2001) 477.
15 Balsamo V,Collins S & Hamley I W, *Polym*, 43 (2002) 207.
16 Pham G, Kampen T U, Thurzo I, Friedrich M & Zahn D R T, *Appl Surf Sci*, 212-213 (2003) 542.
17 Nguyen P H, Scheinert S, Berleb S, Brutting W & Paasch G, *Org Elect*, 2 (2001) 105.
18 Sadeghi M, Jauhiainen A, Liss B, Sveinbjornsson E O & Engstrom O, *Solid-State Elect*, 42 (1998) 2233.
19 Rastogi A C & Sharma R N, *J. Appl Phys*, 71 (1992) 5041.