Processing and performance of organic insulators as a gate layer in organic thin film transistors fabricated on polyethylene terephthalate substrate

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Abstract. Fabrication of organic thin film transistor (OTFT) on flexible substrates is a challenge, because of its low softening temperature, high roughness and flexible nature. Although several organic dielectrics have been used as gate insulator, it is difficult to choose one in absence of a comparative study covering processing of dielectric layer on polyethylene terephthalate (PET), characterization of dielectric property, pentacene film morphology and OTFT characterization. Here, we present the processing and performance of three organic dielectrics, poly(4-vinylphenol) (PVPh), polyvinyl alcohol (PVA) and poly(methyl methacrylate) (PMMA), as a gate layer in pentacene-based organic thin film transistor on PET substrate. We have used thermogravimetric analysis of organic dielectric solution to determine annealing temperature for spin-coated films of these dielectrics. Comparison of the leakage currents for the three dielectrics shows PVA exhibiting lowest leakage (in the voltage range of -30 to $+30$ V). This is partly because solvent is completely eliminated in the case of PVA as observed by differential thermogravimetric analysis (DTGA). We propose that DTGA can be a useful tool to optimize processing of dielectric layers. From organic thin film transistor point of view, crystal structure, morphology and surface roughness of pentacene film on all the dielectric layers were studied using X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). We observe pyramidal pentacene on PVPh whereas commonly observed dendritic pentacene on PMMA and PVA surface. Pentacene morphology development is discussed in terms of surface roughness, surface energy and molecular nature of the dielectric layer.

Keywords. Organic dielectric; organic thin film transistors; polyethylene terephthalate substrate; surface energy; roughness.

1. Introduction

From mobility point of view, organic semiconductors may never be competitors to their inorganic counterparts, but in a few applications organic semiconductors are the preferred option, e.g. flexible and transparent electronics. This is because processing on flexible substrates, viz. paper or plastic, requires temperature to be <200 °C.

Flexible devices, such as displays (Sheraw *et al* 2002), inverters (Byun *et al* 2005; Singh *et al* 2006; Kim *et al* 2010), ring oscillators (Klauk *et al* 2003), logic circuits (Jeon *et al* 2010) have been demonstrated. Organic thin film transistor (OTFT) is one of the key components in these devices. Fabrication of OTFT on flexible substrates is a challenge, because of its low softening temperature, high roughness and flexible nature. Here, we focus on organic gate insulators used in OTFTs. Several polymeric gate insulators, such as poly(vinyl phenol) (PVPh) (Klauk *et al* 2002, 2003; Byun *et al* 2005), poly(methyl methacrylate) (PMMA) (Tunnell *et al* 2008), polyvinyl alcohol (PVA) (Singh *et al* 2005, 2006), polyimide (PI) (Ahn *et al* 2008, 2009), parylene

(Jakabovic *et al* 2009), poly(vinyl acetate) (Sung *et al* 2006), poly(styrene) (Liu *et al* 2011) and benzocyclobutene (BCB) (Sheraw *et al* 2000) have been used in OTFTs (table 1).

Still the selection for a given application is not easy. One requirement is that it should have high dielectric constant for low voltage operation of the OTFTs (Dimitrakopoulos and Mascaro 2001). In addition to that leakage behaviour, roughness and surface energy of the dielectric layer have strong influence on the performance of the transistor (Steudel *et al* 2004; Chua *et al* 2005). In our study, three different dielectrics were selected, crosslinked poly(vinyl phenol) (PVPh), poly(methyl methacrylate) (PMMA) and polyvinyl alcohol (PVA), because these three offer high field effect mobility of pentacene according to the literature (refer to table 1). The motivation of this study is to do a comparative evaluation of these dielectrics as a gate layer in pentacene-based OTFTs with respect to their processing temperature, dielectric constant, leakage current, surface roughness, interface quality with pentacene and pentacene morphology. We have carried out thermogravimetric analysis to determine the annealing temperature for the spin-coated films of these insulators. This is important for processing on polyethylene terephthalate (PET) substrate as maximum temperature that

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Table 1. Best reported performance of pentacene-based OTFTs using different organic layers.

Dielectric material	Mobility (cm^2/Vs)	Threshold voltage (V)	I_{on}/I_{off}	Subthreshold swing (V/dec)	Reference
Crosslinked PVPh	3	−5	10^5	1·2	Klauk *et al* 2002, 2003; Byun *et al* 2005; Jang and Han 2006; Xia *et al* 2008
PVPh	0·5	0			Singh *et al* 2005
PMMA	0·32		2–4 × 10^5		Deman *et al* 2008; Tunnell *et al* 2008; Lucas *et al* 2009
PI	0·36		2 × 10^5	2·1	Ahn *et al* 2008, 2009
Crosslinked PVA	0·036	−2·9	10^5	1·72	Becker *et al* 2003; Seo *et al* 2007
PVA	0·5	−27·6			Singh *et al* 2005, 2006
Parylene	<10^{-4}				Jakabovic *et al* 2009
PS	0·1	−30			Liu *et al* 2011
Poly(vinyl acetate)	0·06	−10·2	10^2	10	Sung *et al* 2006
Photoacryl	0·07	−6	10^5		Kim *et al* 2002

we can use is 180 °C without introducing curvature in the substrate.

We fabricated metal–insulator–metal (MIM) capacitor on PET substrate using PVPh, PMMA and PVA. In each case, leakage current was measured. PVA dielectric exhibits lowest leakage current which can be correlated with the differential thermogravimetric analysis. It is observed that almost zero content of the residual solvent in the PVA film is partly responsible for low leakage current.

Pentacene film, used as active material for OTFTs, was studied on each dielectric surface, as OTFT performance depends on the nature of pentacene film and its interface with the dielectric layer. It has been reported that dielectric layer's roughness (Dimitrakopoulos and Mascaro 2001) and surface energy (Yang *et al* 2005) are important in determining the interface quality with pentacene film. Yoon *et al* (2006) also correlated the interface quality of various organic semiconductors with chemical structure of the dielectric layer. Another recent report correlates OTFT performance and pentacene morphology with the surface energy or chemical structure of the dielectric (Koo *et al* 2009). Our results also show that pentacene morphology is affected by the dielectric layer—pyramidal morphology was observed on PVPh surface and dendritic grain along with rope-like features was noticed on PMMA and PVA surface. The rope-like features are formed due to de-wetting assisted growth in the inter-grain area as observed in the SEM image of pentacene film on PVA dielectric. Finally, OTFTs were characterized on PVPh and PMMA.

2. Experimental

Poly(4-vinylphenol) (PVPh), poly(methyl methacrylate) (PMMA) and polyvinyl alcohol (PVA) were chosen for this study. PVPh (10 wt%) along with crosslinker agent (CLA) was dissolved into propylene glycol methyl ether acetate (PGMEA) solvent. PMMA (5 wt%) and PVA (5 wt%)
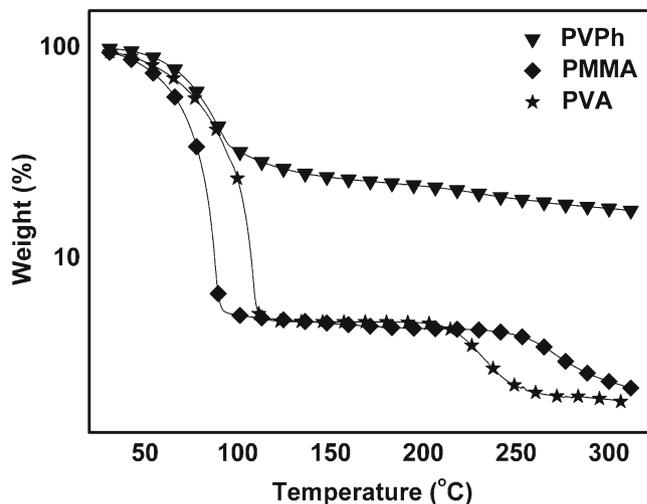

Figure 1. Thermogravimetric analysis (TGA) graph of PVPh, PMMA and PVA solution.

were dissolved in *n*-butyl acetate and DI water, respectively. Thermogravimetric analysis (TGA) of three solutions was performed at slow rate (1 °C/min) in N_2 atmosphere, to observe minor thermal changes with temperature as shown in figure 1. Organic dielectric was spin coated on top of the ITO-coated PET after three-stage organic cleaning of the substrate using toluene, isopropanol and methanol. In case of PVPh system, weight percent remains 23% even at 150 °C, because some amount of PGMEA are covalently attached with CLA and will not be evaporated. In case of PMMA and PVA, weight percent approaches 5% at 130 °C and 124 °C, respectively. This is in agreement with the initial weight percentage used.

PVPh, PMMA and PVA were spin coated at 1000 rpm (30 s), 2000 rpm (40 s) and 1500 rpm (60 s), respectively. Finally aluminum was evaporated on top of the baked dielectric film at vacuum level <6 × 10^{-6} mbar using shadow
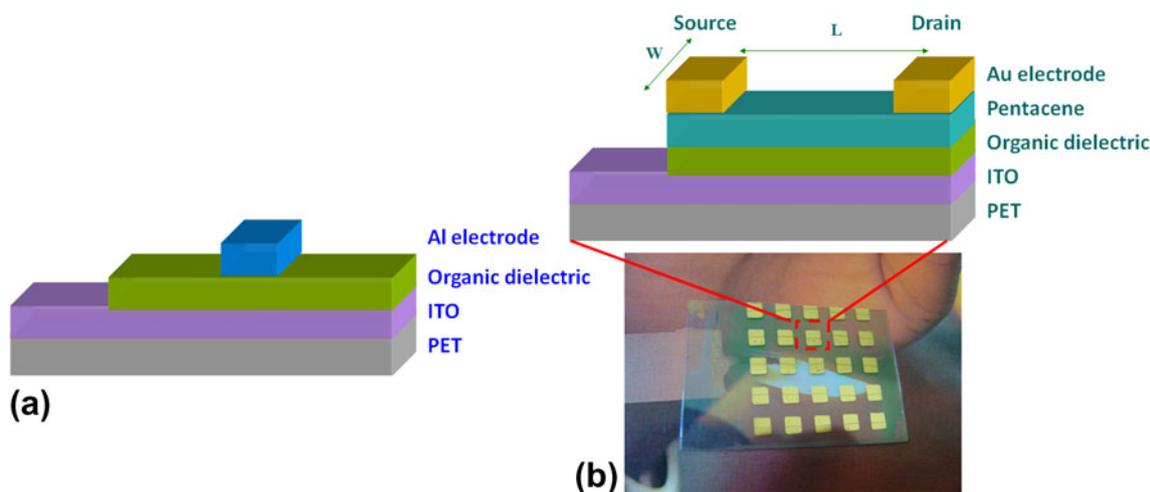
Figure 2. Schematic diagram of (**a**) MIM capacitor and (**b**) OTFT device and sample of organic transistor on PET substrate.

mask. Metal–insulator–metal capacitor was made with each organic dielectric (figure 2(a)). C–V was measured by Agilent impedance analyser. Thicknesses of the dielectric films were measured using thickness profilometer. The leakage current was measured using Keithley 2602.

Top contact OTFTs were made on ITO-coated PET substrate; schematic is given in figure 2(b). Organic dielectric was spin coated on top of the cleaned ITO-coated PET substrate. Pentacene was evaporated at vacuum level $<3 \times 10^{-6}$ mbar on each dielectric layer. Substrate temperature and deposition rate were kept at 70 °C and 1·5 nm/min, respectively. Gold was thermally evaporated on top of the pentacene layer to make source and drain at vacuum level $<6 \times 10^{-6}$ mbar. The channel length and width were 50 μm and 2000 μm, respectively. Output and transfer characteristics were studied using Keithley 2602. Output and transfer characteristics were corrected for contribution from gate current (Shih *et al* 2001; Zeitzoff *et al* 2003). Half of the gate current was added to the drain current which is the effective current through the channel. Crystallinity and surface features of pentacene films were investigated using XRD and AFM.

3. Results and discussion

To decide the baking temperature of the spin coated organic insulators, we have used TGA curves (figure 1). Figure 3 shows derivative of thermogravimetric analysis (DTGA) with temperature. In case of PVPh, large peak was observed at 91·5 °C due to the elimination of the solvent, PGMEA. The boiling point of PGMEA is 145 °C, but it starts evaporating much earlier during heating. The inset diagram of figure 3 also shows that DTGA never approaches zero, indicating all the solvent is not removed during heating up to 195 °C. But, slope is almost constant between 159 °C and 195 °C (figure 3 inset), and this is the temperature range for baking of PVPh,
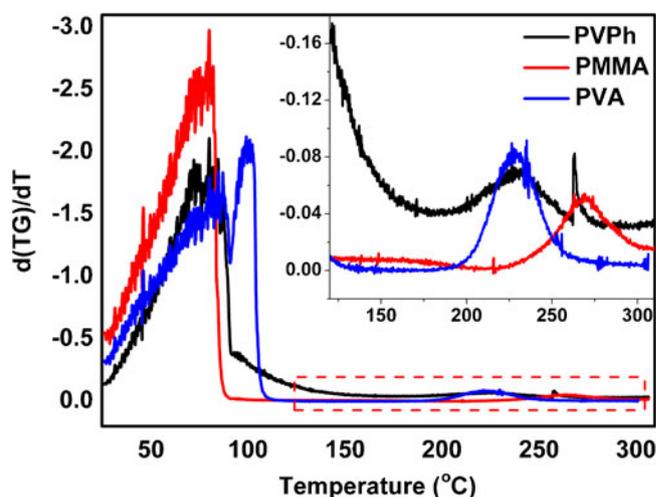

Figure 3. Derivative of thermogravimetric analysis (DTGA) graph of PVPh, PMMA and PVA solution. Inset shows detailed analysis between temperature range of 130 °C and 320 °C.
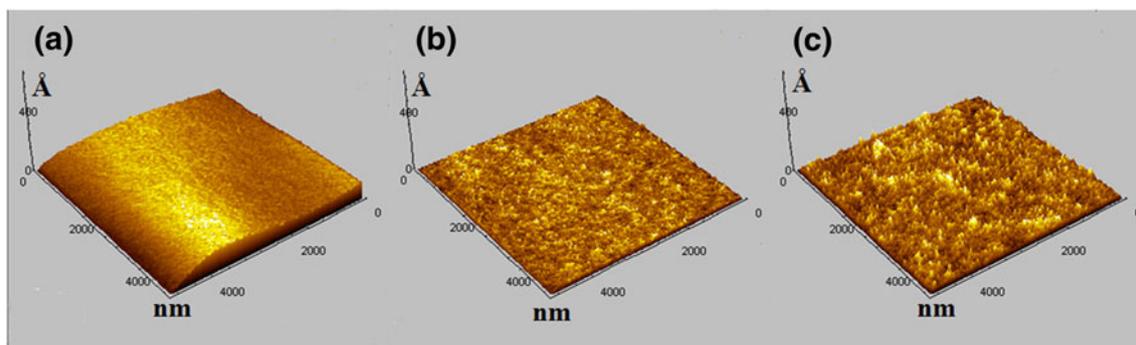
after that degradation starts which appears as a hump. Based on these results PVPh film was annealed at 160 °C for 1 h.

In case of PMMA system, large peak was observed at 83·2 °C. This peak is due to elimination of solvent *n*-butyl acetate. The boiling point of *n*-butyl acetate is 126 °C. DTGA curve of PMMA is constant and from 128 °C to 218 °C, it is almost zero (figure 3). This range will be the baking temperature zone for PMMA; after that further degradation of polymer occurs as shown by the hump in figure 3. Spin-coated PMMA films were baked at 170 °C for 1 h.

Solvent evaporation is complicated in case of PVA system, where two peaks appear at 91·5 °C and 107 °C (figure 3). One possible explanation could be that first one is due to physically adsorbed and second one is due to chemically absorbed water in PVA. Here, slope becomes constant

Table 2. Film thickness, roughness, capacitance and dielectric constant of organic dielectric film.

Dielectric	Layer thickness (nm)	Roughness (nm)	Capacitance/area (nF/cm^2) at 100 kHz	Dielectric constant
PVPh	950	8·5	4·6 ± 0·3	5·0
PMMA	310	2·0	13·3 ± 0·5	4·5
PVA	510	2·3	13·1 ± 0·5	7·4

Figure 4. AFM micrograph of (**a**) PVPh, (**b**) PMMA and (**c**) PVA film.

and almost zero between 135 °C and 194 °C, after that degradation starts. So, complete elimination of solvent is possible in case of PVA system. We have used two-stage baking, 110 °C for 30 min followed by 140 °C for 30 min, in case of PVA film.

Table 2 summarizes obtained thickness, roughness, capacitance and dielectric constant values of PVPh, PMMA and PVA films. The roughness was calculated using AFM analysis as shown in figure 4, where 10×10 μm area was scanned. In terms of roughness, PMMA and PVA films are similar. In case of PVPh film, roughness was 8·5 nm due to wavy nature of the PVPh surface resulting in thickness variation in the film. If we evaluate the roughness of smaller area (2×2 μm), PVPh also exhibits very smooth film having a roughness of 1·5 nm (figure 5). All three dielectrics show similar roughness at smaller scale, hence effect of roughness is not the primary variable in deciding the dielectric–pentacene interface and pentacene film morphology.

Figure 6 shows leakage current for three capacitors. PVPh and PMMA exhibit high leakage current and can be used only at low voltages. But, PVA film has minimum leakage current compared to the other two dielectric films. This can be explained with the help of differential thermogravimetric analysis (figure 3), where we observe that complete removal of solvent was obtained only in the case of PVA solution. DTGA graph also shows similar behaviour for PMMA, but leakage is more. This could be due to lower thickness of PMMA here.

Finally transistor was fabricated on top of the three dielectric surfaces. Output and transfer characteristics of OTFTs using PVPh and PMMA as dielectric layer are given in
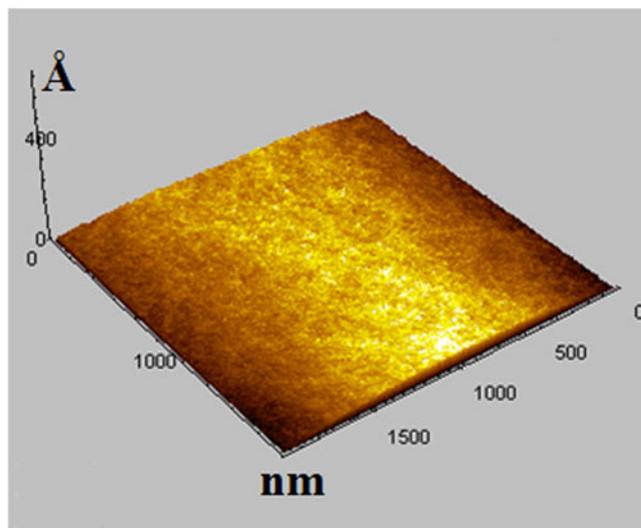

Figure 5. Small area (2×2 μm) AFM micrograph of PVPh film.

figure 7. And, details of the transistor characteristics are mentioned in table 3. The field-effect mobility of pentacene was four times lesser for PVPh. This can be correlated to the morphological analysis of pentacene (figure 8). The pentacene grain size is almost double on PMMA as compared to the film on PVPh dielectric. This is the reason for higher mobility of PMMA system. Details of morphological analysis are given in table 4. PVPh surface promotes compact pyramidal pentacene morphology
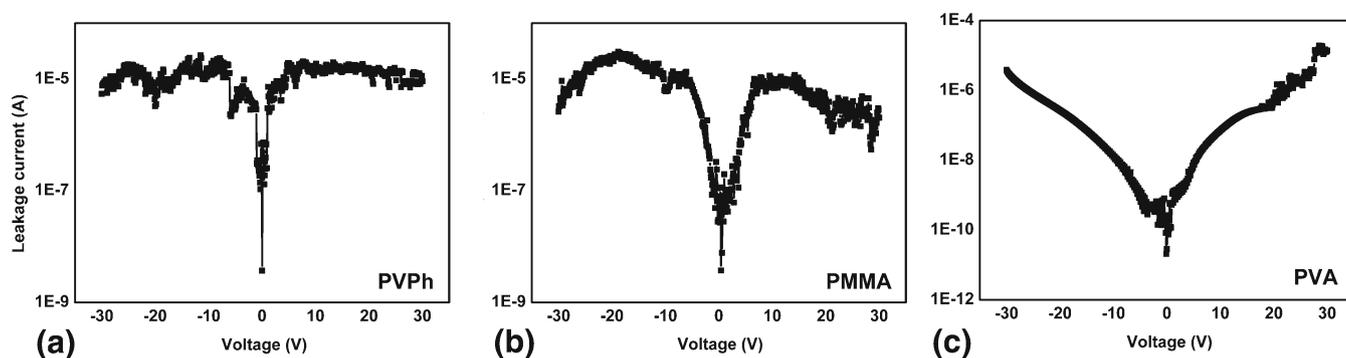
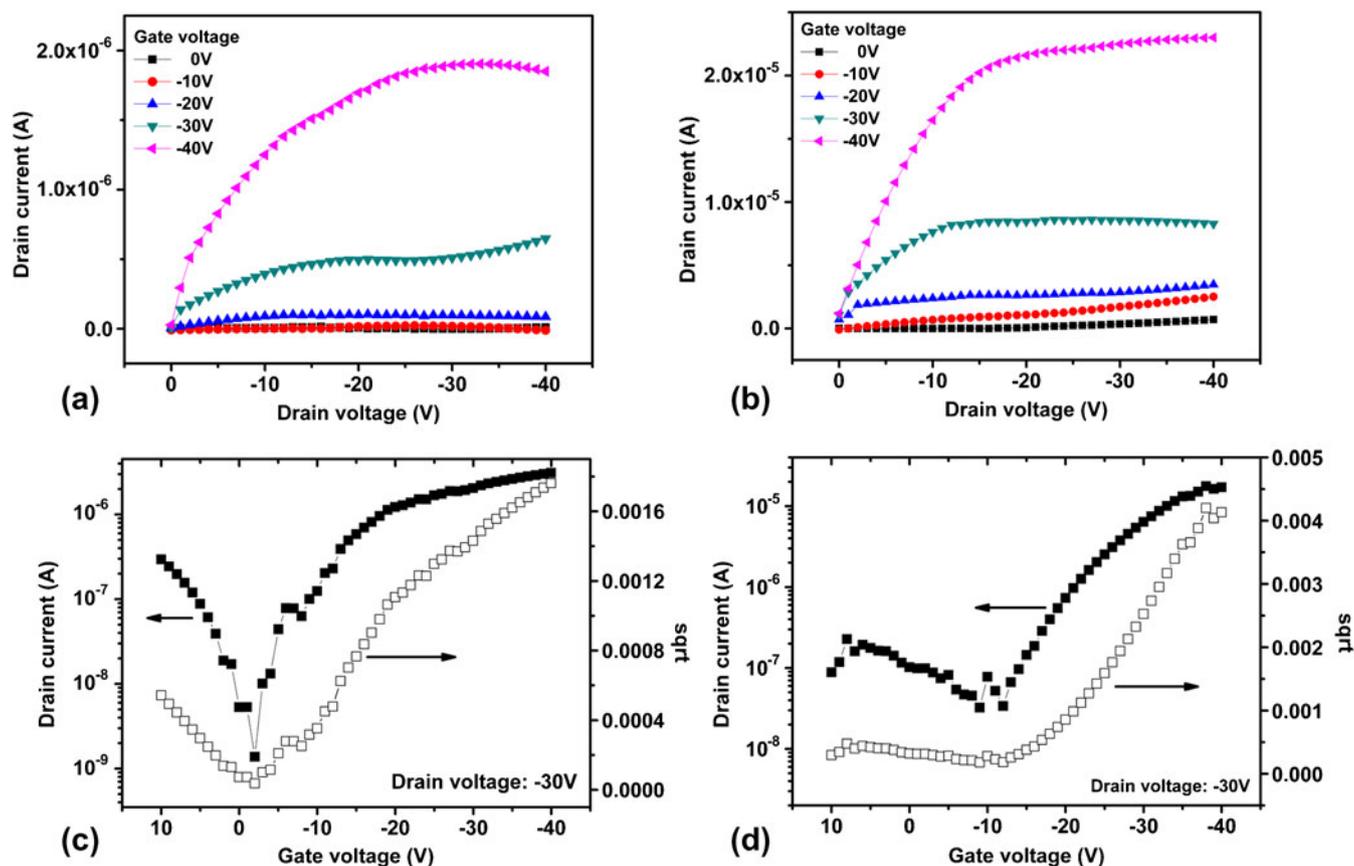**Figure 6.** Leakage current studies of (**a**) PVPh, (**b**) PMMA and (**c**) PVA film.

Figure 7. Output (**a**) and transfer (**c**) characteristics of PVPh-based OTFT and output (**b**) and transfer (**d**) characteristics of PMMA-based transistor.

(figures 8(a) and (d)), and dendritic pentacene morphology was observed on PMMA (figures 8(b) and (e)). Another interesting feature observed is de-wetting of pentacene on PMMA as well as PVA dielectric giving rise to large rope-like morphological features on the surface. Prominent (001) crystalline peak of pentacene film was observed on PVPh and PMMA (figures 8(g) and (h)), whereas (001) peak intensity considerably deteriorates on PVA surface (figure 8(i)) due to significant de-wetting of pentacene film.

To further investigate the morphology of pentacene film on PVA surface, SEM image of pentacene film is taken (figure 9). Three different regions were observed: (i) dendritic grain region, (ii) de-wetted rope-like feature that predominantly forms in the intergranular region and (iii) PVA surface without pentacene film. Since all the dielectric films had similar roughness, the morphological changes in pentacene film can be seen as effect of the surface property of the dielectric. PMMA is most hydrophobic, followed by PVPh

and PVA, water contact angle of PMMA, PVPh and PVA are 70–77° (Deman *et al* 2008), 50° (Klauk *et al* 2002) and 45° (Yoon *et al* 2006), respectively. Higher contact angle indicates lower surface energy of the dielectric surface. When depositing pentacene on SiO₂ dielectric, it has been observed that dendritic morphology is formed on hydrophilic SiO_2 (high surface energy) and after surface treatment, small granular morphology is obtained on hydrophobic surface (low surface energy). In contrast to that, here we observe dendritic morphology on most and least hydrophobic dielectrics—PMMA and PVA. Further, PVPh having intermediate surface energy shows pyramidal morphology.

Table 3. Mobility, threshold voltage, I_{on}/I_{off} ratio and subthreshold swing (after gate leakage correction) of OTFTs.

Dielectric	Mobility (cm^2/Vs)	Threshold voltage (V)	I_{on}/I_{off} ratio	Subthreshold swing (V/dec)
PVPh	0.03 ± 0.01	-7.2 ± 4.2	10^3	10.1 ± 8
PMMA	0.12 ± 0.04	-17.5 ± 2.6	10^3	13.6 ± 12.1
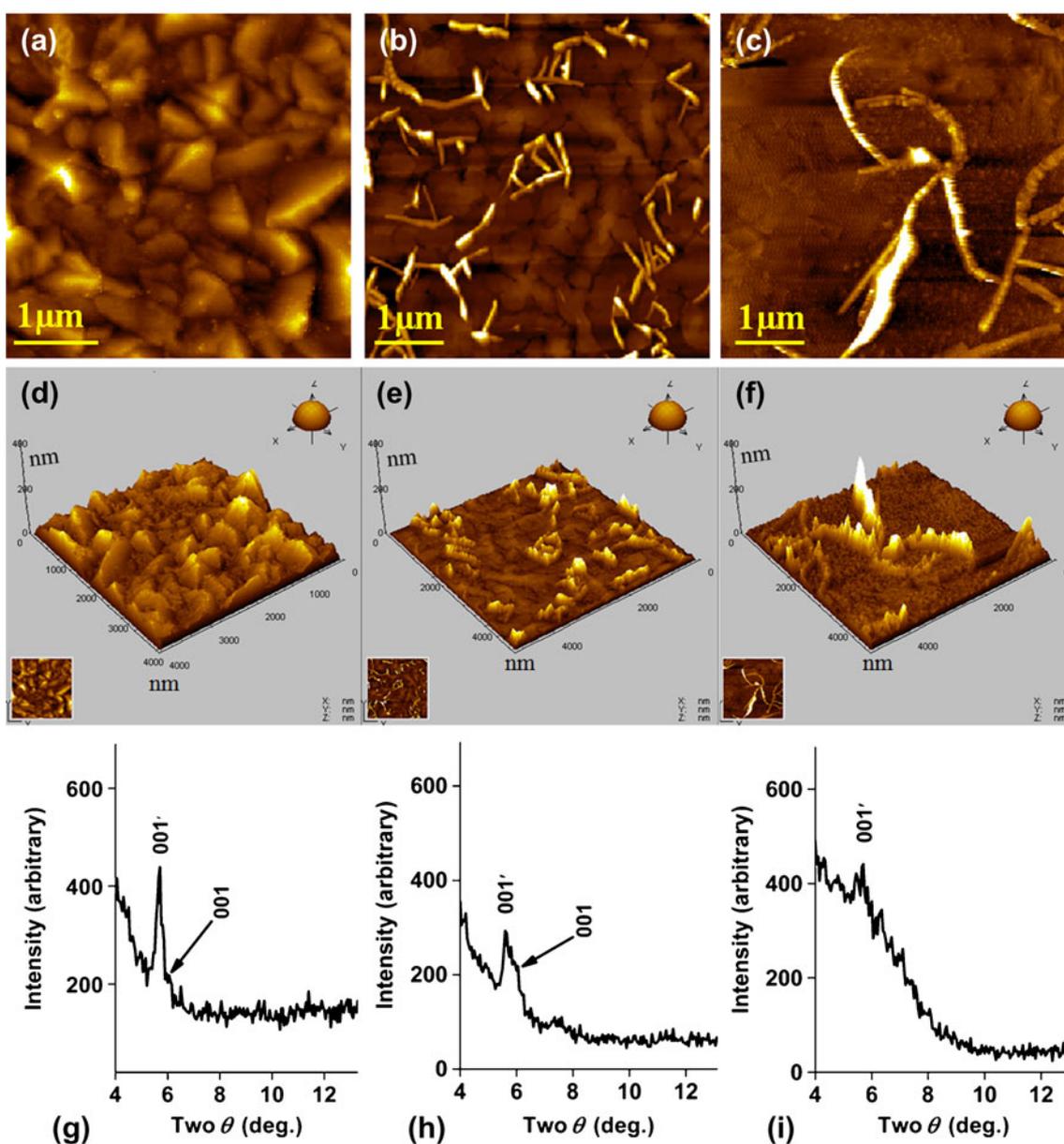
Figure 8. AFM of 50 nm thick pentacene film on PVPh (**a**) and (**d**), PMMA (**b**) and (**e**) and PVA surface (**c**) and (**f**). XRD of 50 nm pentacene film on top of (**g**) PVPh, (**h**) PMMA and (**i**) PVA surface.

Table 4. Phases, morphology and grain size of pentacene films deposited on PVPh and PMMA.

Dielectric surface	Pentacene phase	Morphology	Grain size (μm)
PVPh	Thin film and bulk	Pyramidal	0·5 ± 0·1
PMMA	Thin film and bulk	Dendritic with rope-like feature	0·9 ± 0·2
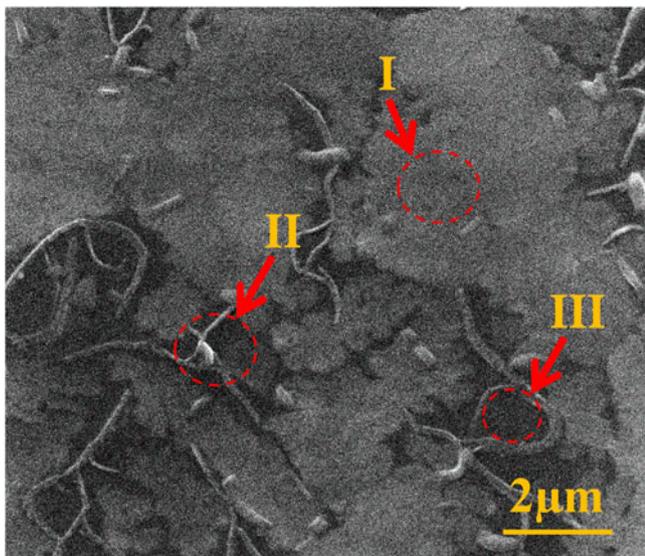
Figure 9. SEM micrograph of pentacene film on top of PVA surface, having three zones: (i) smooth film, (ii) de-wetted pentacene rope and (iii) no film zone.

In our experiments, surface energy is decreasing in the order PVA>PVPh>PMMA and in this sequence the morphology changes first from dendritic to pyramidal and then again to dendritic. This indicates that, in addition to surface energy, the molecular structure of the dielectric is also important in deciding the pentacene morphology. Comparing our results with the literature, we find different pentacene morphologies have been reported on the PVA dielectric, e.g. dendritic (Singh *et al* 2005; Seo *et al* 2007) and smooth granular morphology (Yoon *et al* 2006). This is because in addition to the dielectric's surface energy pentacene deposition parameters are also responsible in determining the morphology.

4. Conclusions

We have presented comparative studies of three organic dielectrics (spin coated) with respect to their dielectric properties and performance in an evaporated pentacene based OTFT on PET substrate. The dielectric constant obtained is 7·4, 5 and 4·5 for PVA, PVPh and PMMA, respectively. Among these, PVA exhibits minimum leakage current which could be correlated to DTGA data that shows complete removal of the solvent during baking in the case of PVA. From OTFT point of view, interface with the pentacene

is important. Since roughness is similar for all dielectrics of about 2 nm, the surface energy of the dielectric layer dictates the interface quality and morphology of the pentacene film. We find that field effect mobility of pentacene is higher in OTFT using PMMA compared to OTFTs using PVPh, because pentacene grains are almost double in size on PMMA surface. There was significant de-wetting of pentacene on PVA surface and we were not able to get functional OTFTs. Surface treatment on PVA needs to be explored to fabricate pentacene OTFT on PVA, since leakage current for PVA is very low and there is good chance to make devices with better characteristics. We also concluded that surface energy of the dielectric is not the only parameter determining the pentacene morphology, therefore, effect of molecular nature of the dielectric layer can further be investigated.

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