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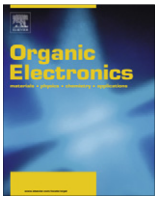

An effective method to minimize the leakage current in organic thin-film transistors by using blends of various molecular weights

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ABSTRACT

We report on an effective method to minimize the leakage current in an organic thin-film transistor (OTFT) by using a polymeric gate insulator, poly(vinyl phenol) (PVP). When the molecular weight (M_w) of the PVP varies, only the leakage current is affected under constant remaining electrical parameters. More importantly, through a binary mixing between two different M_w, it is found that the leakage current can be minimized. This is attributed to a reduction of the free volume in the blended PVP layer, leading to a more vigorous cross-linking reaction, as compared to a single molecular weight PVP.

1. Introduction

Owing to the many advantages of organic materials, including low-temperature processing at low-cost, mechanical flexibility, and large-area applicability, organic based electronic devices have been widely studied [1–5]. Among several classes of electronic devices, organic thin-film transistors (OTFTs) have drawn much attention because the transistor is the main basic components of microelectronic circuits. In the beginning, most researches on OTFTs focused on semiconducting organic materials such as conjugated polymers and small conjugated molecules [6–9] used together with inorganic dielectrics such as SiO_2. More recently, for more practical and flexible applications, most OTFTs also comprise organic materials as a gate insulator.

Organic based gate insulators include poly(vinyl phenol) (PVP), polyimide, and poly(vinyl cinnamate) [10–13]. To date, PVP shows the best electrical properties and has thus become the most widely used polymeric insulators. Most PVP formulations have excellent film forming properties, giving a homogeneous film with a smooth surface. However, the chemical structure of PVP is known to be sensitive to oxygen and moisture, thus leading to high gate leakages and dramatic hysteresis. Thanks to numerous experimental work on this matter, the problem can be worked around by using thermally cross-linked PVP with methylated poly(melamine-co-formaldehyde) (MMF) as a cross-linking agent [10,14–16]. In the same line, it has been reported that electrical parameters such as mobility, threshold voltage, and gate leakage current can be improved by optimizing the mixing ratio between PVP and the cross-linking agent [16,17]. In particular, it has been reported that the gate leakage current and hysteresis behavior can be reduced by increasing the amount of the MMF in the PVP formulation. However, with the exception of the addition of the cross-linking agent, no full study of the role of the organic gate dielectric itself has been carried out so far.

In this work, we report on an effective method to minimize the leakage current in an OTFT by controlling

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the molecular weight (M_w) of the PVP layer by setting the amount of MMF. When changing the M_w of the PVP, only the leakage current is affected with no change of other electrical parameters such as mobility, threshold voltage, and current on/off ratio. Based on the effects of the M_w on the leakage current, we suggest a viable method to minimize the leakage current based on a binary mixing between two different M_w. The improvement is attributed to the reduction of the free volume in the binary mixture, thus leading to an improved cross-linking reaction.

2. Experimental

The top-contact, bottom-gate structure of the OTFTs is shown in Fig. 1. Indium-tin-oxide (ITO) on a glass substrate was used as a gate electrode. The ITO patterned substrate was cleaned in sequence with acetone, isopropyl alcohol, methyl alcohol, and deionized water in an ultrasonicator for 10 min. For the gate insulator, poly-4-vinylphenol (PVP) with M_w of 8000 g/mol and 20,000 g/mol was dissolved in propylene glycol methyl ether acetate (PGMEA) at 10 wt.%. The polymer was used at a single M_w or as a mixture of the two M_w's at various ratios. In a previous work, in order to minimize the hysteresis behavior, methylated poly(melamine-co-formaldehyde) (MMF) was added in the PVP solution as a cross-linker [16]. It was reported that the optimum value of the MMF is 125 wt.% for generating fully cross-linked reaction in the PVP film. Since we want to examine the M_w dependent degree of the cross-linking reaction, we added the MMF at less percentage (50 wt.%) than the optimum value (125 wt.%). If we added more MMF (above 50 wt.%), the effect of M_w on the cross-linking reaction in relation with the leakage current would be not clearly observed. On the other hand, if we added less MMF (below 50 wt.%), the magnitude of device performance take a turn for the worse. Thus, we decide the 50 wt.% of the MMF to manage the trade-off relation. The PVP solution was spin-coated on the ITO patterned glass substrate at 3000 rpm for 30 s, cured at 100 °C for 1 min and subsequently cured for 5 min at 200 °C to generate a thermal cross-linking process in the PVP film [18]. Note that the thickness of the PVP films was found to be almost similar as 350 ± 30 nm, regardless the M_w.

As an organic semiconductor, pentacene, purchased from TCI Ltd., was vacuum deposited onto the PVP layer under a pressure of about 10^{-6} Torr with no further purification process. The deposition rate of pentacene was maintained uniformly at 0.5 Å/s at room temperature. Au was evaporated on top of the pentacene film to generate source and drain electrodes under the same pressure at a rate of 1.0 Å/s. The thickness of the pentacene and Au film were 60 nm and 80 nm, respectively. The channel length and width were 50 μm and 1 mm, respectively. The electrical properties of the transistors were measured in air using a semiconductor parameter analyzer (HP4155A) at room temperature and ambient pressure.

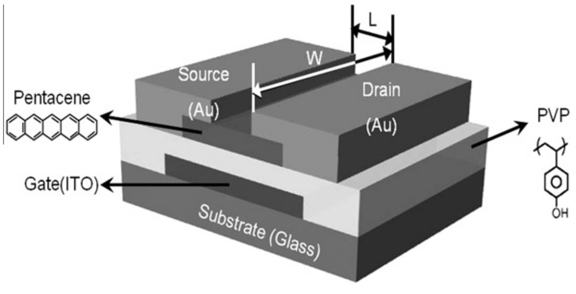

Fig. 1. Schematic diagram of a bottom-gate, top-contact OTFT and chemical structure of pentacene and PVP. *L* and *W* represent the channel length and width, respectively.

3. Results and discussion

It is generally recognized that the surface roughness, given by its root-mean-square (RMS) value, and the surface energy, measured by the contact angle, strongly affect the electrical properties of OTFTs [19,20]. Here, we first discuss how the surface morphology and energy of cross-linked PVP are affected by its M_w. Fig. 2(a)–(c) correspond to a M_w of 8000 g/mol, 20,000 g/mol, and a binary mixture (8000 g/mol and 20,000 g/mol), respectively. As clearly shown in Fig. 2, there is essentially no difference in surface roughness and the surface energy, regardless the M_w. In a previous work, it was reported that the surface roughness and the surface energy of the PVP layer were not severely changed after cross-linking process [21]. Note that we measured the surface roughness and contact angle after the cross-linking process in our experiment. The RMS value for the surface roughness and the contact angle were 0.3 ± 0.03 nm and 60 ± 1°, respectively. Based on these results, it can be inferred that the difference in M_w do not affect the surface property of the gate insulator.

On the other hand, it has been reported that the grain size of organic semiconductors is critically related to the electrical properties of the OTFTs [22,23]. Now, we examine how the M_w affects the grain size of pentacene deposited on the PVP insulator. As clearly shown in Fig. 2(d)–(f), the grain size of pentacene essentially shows no difference, whichever the M_w of the PVP insulator, with an average value of about 1 μm.

At this point, because the different M_w's of PVP lead to similar properties of the PVP surface and identical grain size of pentacene, we can expect similar magnitude for the mobility and drain current. Fig. 3(a)–(c) shows the output curves and corresponding transfer curves for the three types of OTFTs with PVP of M_w of 8000 g/mol, 20,000 g/mol, and binary mixture (8000 g/mol and 20,000 g/mol), respectively. Note that the output curves are obtained by varying the gate voltage from 0 V to −40 V in steps of −10 V. In three output curves, the magnitude of the drain current at a drain voltage of −40 V and gate voltage of −40 V is found to be nearly same, at about −20 μA, irrespective of the M_w. In addition, as clearly seen from the three transfer curves, the threshold voltage and the slope, which represent the field-effect mobility, are almost independent of the M_w of the gate insulator. The mobility and threshold voltage are about 0.14 $cm^2/V\,s$ and −6 V, respectively, in all of cases. Note that these numbers correspond to mean values extracted from 20 different devices. Furthermore, the current on/off ratio was over 10^3 in all the OTFTs. Note that our measured mobility is relatively

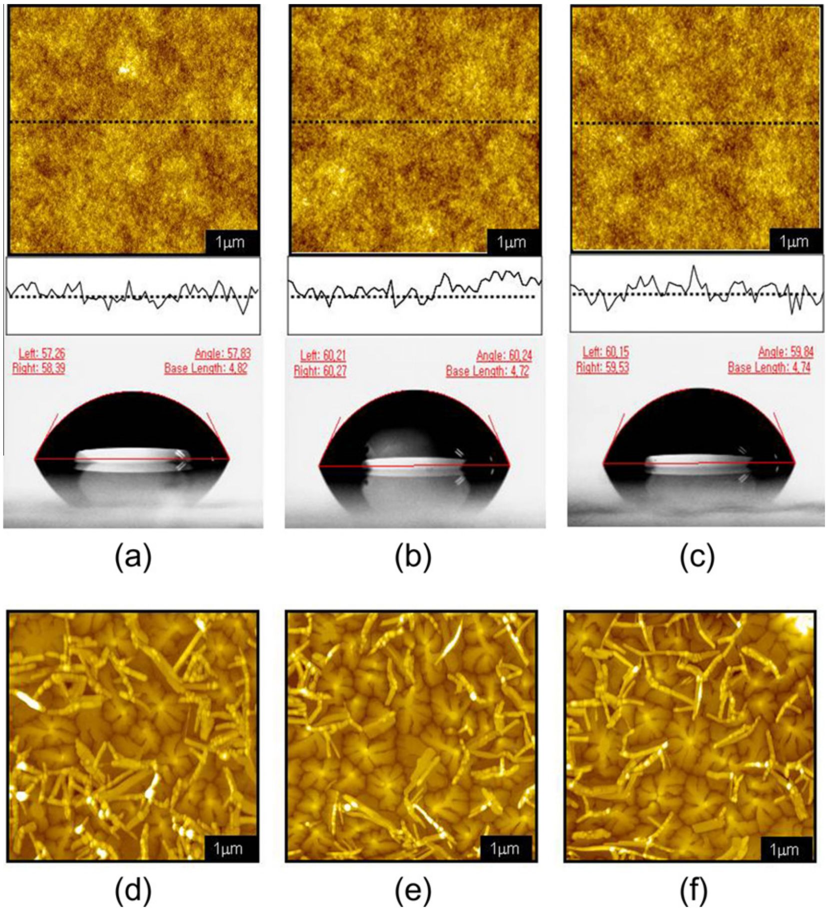

Fig. 2. AFM images with the morphological profiles and corresponding contact angle of PVP films with (a) molecular weight of 8000 g/mol, (b) molecular weight of 20,000 g/mol, and (c) mixture with a 1–1 ratio between 8000 g/mol and 20,000 g/mol. Morphological profiles were obtained along the black dotted lines in the AFM images. The corresponding AFM images of pentacene films deposited on each PVP layer. 60 nm-thick pentacene films were grown on PVP with (d) molecular weight of 8000 g/mol, (e) molecular weight of 20,000 g/mol, and (f) mixture with a one to one ratio between the 8000 g/mol and 20,000 g/mol.

lower than some values reported in other works [8]. However, the values of the same order of magnitude are often reported [24,25]. In addition, it can be expected that the electrical performance of our devices will definitely improve after some optimizing processes such as purification of pentacene, and adjustment of the growth rate, and substrate temperature during the deposition. Based on the transfer curve, the turn-on voltage is found to be slightly shifted for the positive voltage direction when the binary mixture case, compared with the non-mixture cases. The shift of the turn-on voltage is governed by the built-in electric field of the gate dielectrics [26]. Thus, the carrier density in the channel would be varied according to the status of the PVP films. For the binary mixture case, the cross-linking reaction is more intense due to the reduction of the free volume in the PVP layer. About the cross-linking according to the molecular weight, we will discuss at the end of this section. Among many electrical parameters shown in Fig. 3, it should be noted that only the leakage current is affected by varying the M_w of the PVP. The leakage current with the 8000 g/mol PVP, 20,000 g/mol PVP, and binary mixture is −85 nA, −156 nA, and −3 nA, respectively. The leakage current is strongly minimized when the insulator consists of a binary mixture between low M_w and high M_w polymers. Note that the hysteresis is known to be caused by the influence property and/or bulk of the dielectric and the inherent properties of the dielectric. The degree of cross-linking in the PVP film also was reflected in the device hysteresis. As shown in Fig. 3, the organic transistor using the single molecular weight PVP shows a little hysteresis behavior. However, for the binary mixture case, the hysteresis is much reduced together with minimizing the off current. It means that the binary mixture has better cross-linking reaction, and therefore reduces the free volume in the dielectric.

Fig. 4 shows the change of the electrical parameters of our OTFTs by varying the mixing ratio of M_w in the binary mixtures. Fig. 4(a) and (b) indicates that, the mobility and threshold voltage remain do not depend on the composition of the mixture. However, it is worth noting that the leakage current significantly varies when changing the composition ratio, as shown in Fig. 4(c). Note that tens of organic devices were fabricated to examine the mobility, threshold voltage, and leakage current as a function of

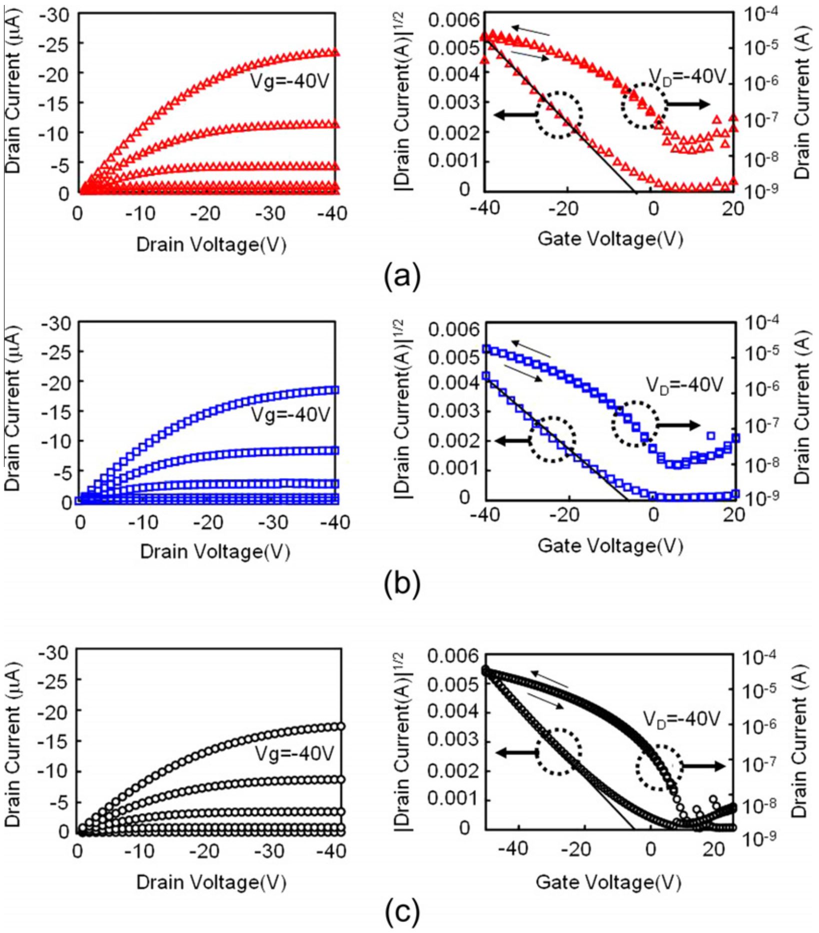

Fig. 3. Current–voltage characteristics of the OTFTs with different molecular weight PVP layers. (a) Molecular weight of 8000 g/mol, (b) molecular weight of 20,000 g/mol, and (c) the mixture with a 1–1 ratio between the 8000 g/mol and 20,000 g/mol. Left and right panel represent the output and transfer curves, respectively. In the transfer curves, the data at a drain voltage of −40 V was used to estimate the mobility.

molecular weight in the polymeric insulator, PVP. The error bars simply represent the maximum and minimum value for each parameter deduced from tens of different devices. However, for each electrical parameter, it should be noted that only a few samples show the extremes such as maximum or minimum value. Most of parameters are observed at almost average value between the extremes denoted by the closed circles on the error bars in the Fig. 4.

Now, we discuss the reason why the M_w of the gate insulator only affects the leakage current. First, in order to have a better physical approach of the leakage process, we fabricated a simple device consisting of a metal–insulator–metal (MIM) capacitor as shown in Fig. 5. All experimental conditions such as the thickness and deposition rate of gold are exactly the same as those for the OTFT fabrication. The leakage current density in the MIM capacitor is found to be reduced when the binary mixture between the low M_w and high M_w is introduced, compared to other single M_w PVP case. This trend is in good agreement with the change of the magnitude of the leakage current as shown in Fig. 3.

The physical origin why the M_w of the PVP strongly only affects the leakage current cannot be explained by the surface properties investigated using AFM and contact angle. Thus, the bulk study of the PVP should be investigated to completely understand the relationship between M_w and leakage current. FT-IR spectroscopy measurements were carried out as shown in Fig. 6. FT-IR spectroscopy is widely used to qualitatively and quantitatively analyze chemical bondings in organic molecules. Note that the FT-IR spectra was normalized at the wavenumber of 1510 cm^{-1} which is the C=C bond for comparing the each peak height in our study. As shown in Fig. 6, the peak of the hydroxyl group density (at 3370 cm^{-1} wavenumber) shows big differences between the single M_w (8000 g/mol) and the 1:1 binary mixture. In addition, as shown in inset of Fig. 6, the integrated intensity of the peak of the hydroxyl group is lower in the binary mixture than for the 20,000 g/mol M_w. This means that the number of hydroxyl group per unit volume differs accordingly. It can be inferred that the density of hydroxyl group is only affected by the M_w of the PVP because every experimental condition except the molecular weight is similar in all three samples. Accordingly, the free volume in the PVP layer is reduced in the binary mixture, so that the cross-linking reaction is more intense in the mixture than a single M_w PVP.

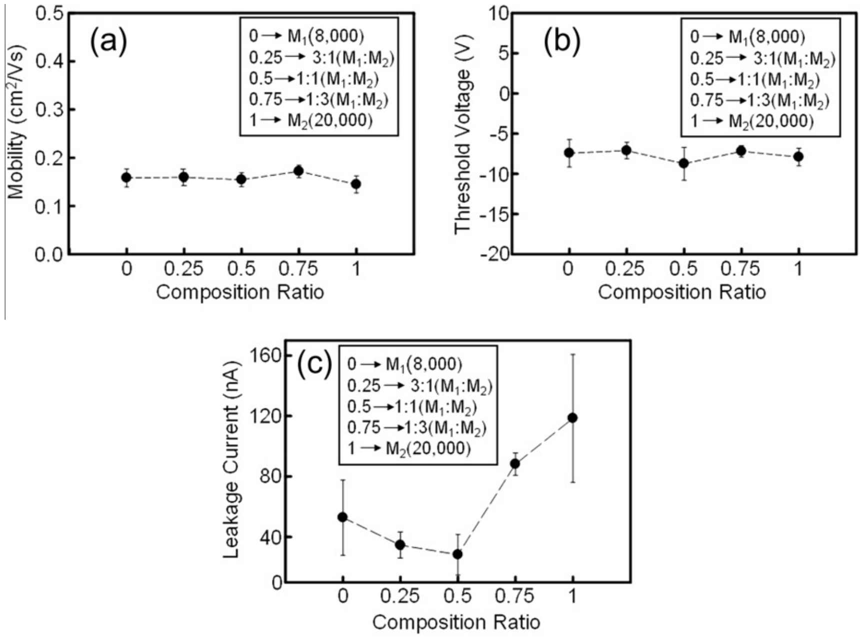

Fig. 4. As a function of the composition ratio between 8000 g/mol and 20,000 g/mol PVP polymers, variation of (a) mobility, (b) threshold voltage, and (c) leakage current. The error bars represent the maximum and minimum value for each parameter deduced from tens of different devices.

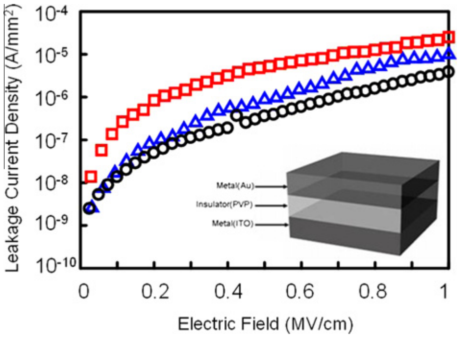

Fig. 5. Leakage current density as a function of electric field between two electrodes in the MIM structure. Open triangles, squares, and circles correspond to the molecular weight of (a) 8000 g/mol PVP, (b) 20,000 g/mol, and (c) the mixture with a 1–1 ratio between the 8000 g/mol and 20,000 g/mol.

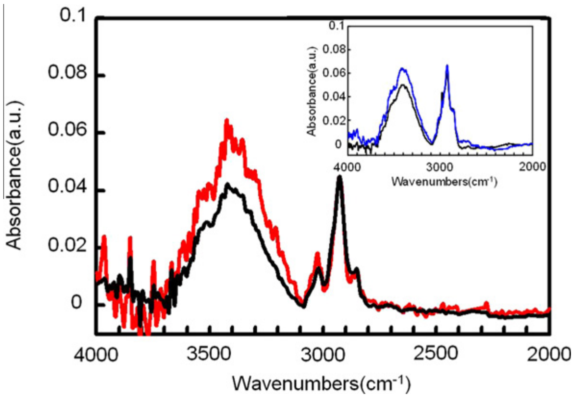

Fig. 6. Fourier-transform-infra-red (FT-IR) spectroscopy of the 8000 g/mol PVP and the binary mixed PVP. The inset shows the FT-IR spectra of the 20,000 g/mol PVP and the binary mixed PVP.

An hydroxyl group is removed from a PVP polymer when the formaldehyde of MMF, which is used as the cross-linking agent, makes a covalent bond with the PVP during the cross-linking reaction. The amount of hydroxyl groups removed from the PVP molecule is therefore a marker of the amount of cross-linked polymer chains. Accordingly, it can be concluded that the decrease of hydroxyl group density in the binary mixture is indicative of a more frequent occurrence of the cross-linking reaction. It was reported previously that changing the ratio of MMF to PVP produces a variation of the leakage current density because of the change of the hydroxyl group density [16,17]. To eliminate the effects of the ratio of the MMF to PVP ratio on the leakage current, the amount of MMF was kept equal in all the PVP layers used in this work.

4. Conclusions

We have demonstrated a viable method to minimize the leakage current in an OTFT by mixing different M_w's of the polymeric gate insulator, PVP. Based on the experimental results, it is found that only the leakage current is affected with no significant variation of the other key electrical parameters when changing the M_w of the PVP. More importantly, through a binary mixing between two different M_w's, it is found that the leakage current can be minimized due to the reduced free volume in the PVP layer, which guaranteed a more active cross-linking reaction in the PVP layer with a fixed amount of MMF. More studies on various polymeric insulators should be carried out for understanding more clearly about the exact role on of the molecular weight on the electrical properties in the organic transistor. This work is expected to provide a scientific basis for developing an organic based electronics having low leakage current.

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