

Field Effect Transistors Based on Composite Films of Poly(4-vinylphenol) with ZnO Nanoparticles

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In order to adjust the characteristic of pentacene thin film transistor, we modified the dielectric properties of the gate insulator, poly(4-vinylphenol), or PVP. PVP is an organic polymer with a low dielectric constant, limiting the performance of organic thin film transistors (OTFTs). To increase the dielectric constant of PVP, a controlled amount of ZnO nanoparticles was homogeneously dispersed in a dielectric layer. The effect of the concentration of ZnO on the relative permittivity of PVP was measured using impedance spectroscopy and it has been demonstrated that the permittivity increases from 3.6 to 5.5 with no percolation phenomenon even at a concentration of 50 vol.%. The performance of OTFTs in terms of charge carrier mobility, threshold voltage and linkage current was evaluated. The results indicate a dramatic increase in both the field effect mobility and the linkage current by a factor of 10. It has been demonstrated that the threshold voltage can be adjusted. It shifts from 8 to 0 when the volume concentration of ZnO varied from 0 vol.% to 50 vol.%.

Key words: Organic field effect transistor, pentacene, mobility carrier, poly(4, vinylphenol), zinc oxide nanoparticles, complex permittivity

INTRODUCTION

The development of organic electronics is associated with the development and study of organic light-emitting diodes, transistors and solar cells.¹ Recently, composites based on inorganic nanoparticles hosted into an organic polymers matrix have attracted particular attention as promising materials for organic field effect transistors (OFETs). Depending on the desired properties, the nanoparticles are admixed with the active layers² or the insulating layer.^{3,4} An important advantage of composite films lies in their higher functionality and electrical stability in comparison with polymeric analogues. In OFETs, the choice of the insulator is crucial as its dielectric properties

influence fundamentally the electrical characteristic and carrier transport in the transistor, as demonstrated by various studies devoted to the characterization of OFETs.^{5–8} Insulator materials must have a high resistivity to prevent the leakage current between the metal gate and the semiconducting channel, and high dielectric constant to have enough capacitance for channel current flow.⁹ This capacitance may be increased by reducing the insulator thickness, but usually it results in a large gate-leakage current.

Poly(4-vinylphenol), or PVP, has a relatively low static dielectric constant of about 3.6¹⁰ which limits the performance of organic thin film transistors (OTFTs). Zinc oxide (ZnO) is a composed semiconductor with a direct band gap of about 3.37 eV, with rather high sheet resistance at 27°C (more than 100 Ω) when undoped and a static dielectric constant of about 8, depending on electric field polarization.^{11–13} Moreover ZnO has a high chemical

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stability and good piezoelectric properties. Here will be reported the dielectric properties of ZnO:PVP blends for which real and imaginary permittivity were measured. Also, compatibility between the insulating polymer and nanoparticles has been studied as the distribution of the nanoparticles in the dielectric increases the roughness of the gate/insulator and insulator/semiconductor interfaces. Finally the blend ZnO:PVP is incorporated into an OTFT as gate insulator. The increase of the dielectric constant of the composite compared to that of pristine polymer generates a strong increase of the saturation current for a given gate voltage.

EXPERIMENTAL

Polymer Dielectric Layer Preparation

The permittivity variation is obtained for different concentrations of ZnO nanoparticles in PVP polymer matrix. ZnO:PVP nano-composites are obtained by mixing commercial ZnO nanoparticles purchased from Genes' Ink and PVP from Sigma Aldrich. The ZnO particle concentration in solution was 1 wt.%, and the nanoparticle diameters were below 10 nm. To improve the compatibility of the nanoparticles with the PVP polymer matrix, a ligand based on stearic acid was added (1 g of stearic acid in 10 mL of ZnO solution). The PVP [$\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{OH})$] solution was prepared by dissolving 1 g of PVP powder in 5 mL of isopropanol alcohol. Five solutions of PVP were prepared for different proportions of ZnO nanoparticles ranging from 0% to 80% in volume. The obtained solution was mixed, stirred and annealed at 50°C for 30 min. The films were deposited by sol-gel spin-coating technique and their thickness measured by means of a surface profilometer (Bruker DEKTAK XT).

The real ϵ' and imaginary part ϵ'' of the complex permittivity of the studied blend were obtained from impedance spectroscopy (IS) measurement. This technique is the equivalent of a simple circuit consisting of a resistance and a capacitance in parallel and were given for a frequency of 1 kHz.

Organic Field Effect Transistor Fabrication

Two series of field effect transistors based on our ZnO:PVP layer were realized. First, the insulator polymer solution was prepared by dissolving 1 g of PVP in 5 mL of isopropanol alcohol (0% ZnO + 100% PVP) in volume ratio. Second, the polymer solution was prepared by dissolving 1 g of PVP in 2.5 mL of isopropanol alcohol and 2.5 mL of ZnO nanoparticles (50% ZnO + 50% PVP) in volume ratio. Pentacene thin film transistors (TFTs) were fabricated on indium tin oxide (ITO) glass substrate with the classical inverted and staggered configuration called top-contact, where the drain and source electrodes are deposited on the pentacene layer as the last step of the process. The first electrode (gate)

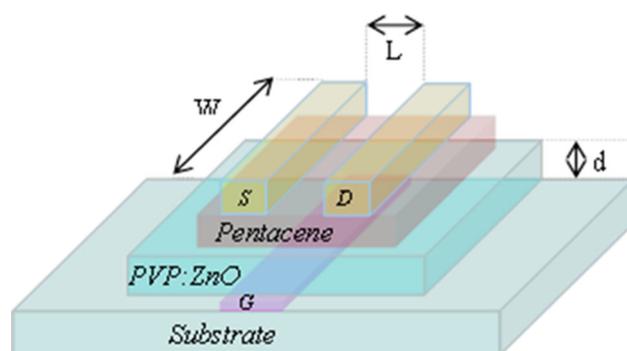


Fig. 1. Structure of the top contact transistor studied with PVP:ZnO gate insulator, where W is the channel width, L is the channel length and d of the layer thickness of insulator polymer.

was etched in the ITO layer. Pentacene thin films were deposited by thermal evaporation in a high-vacuum set-up with a low pressure of 2.10^{-6} mbar. The deposition rate at room temperature was of 0.1 nm/s to reach a final thickness of 30 nm. The pentacene was obtained from Aldrich Chemical (97% pure) and further purification processes were not performed. Silver electrodes (source and drain) were deposited with the same technique. Electrode thickness was around 30 nm, and the electrode width was around 4 mm. Figure 1 shows the bottom gate top contact (BGTC) structure of the field effect transistor with organic insulator.

Influence of ZnO Nanoparticles on Electrical Characteristics of OTFT

To observe the influence of the ZnO nanoparticles on the electrical properties of field effect transistors, we have realized two series of transistors. The first gate insulator was prepared by dissolving 1 g of PVP in 5 mL of isopropanol alcohol. The second gate insulator was prepared by dissolving 1 g of PVP in 5 mL of ZnO nanoparticles. The two solutions of insulator polymer were continuously stirred and annealed for 30 min at 50°C to yield homogeneous solutions.

Direct current–voltage characteristics of field effect transistor structures based on only PVP and ZnO:PVP were measured in dark, in an atmospheric vacuum at 300 K at different voltages in the range of -40 V to $+40$ V. Using an automated setup for measuring I – V characteristics, based on a Keithley-4200 SMU.

Figure 2 shows the improvement in current drain with the ZnO nanoparticles by a factor of 40. This result can be explained by the important role of ZnO nanoparticles on the functioning of the organic transistor; they have an influence on the characteristics of the transistor. The field effect is better for the second solution and the three modes perform well compared to the first solution.

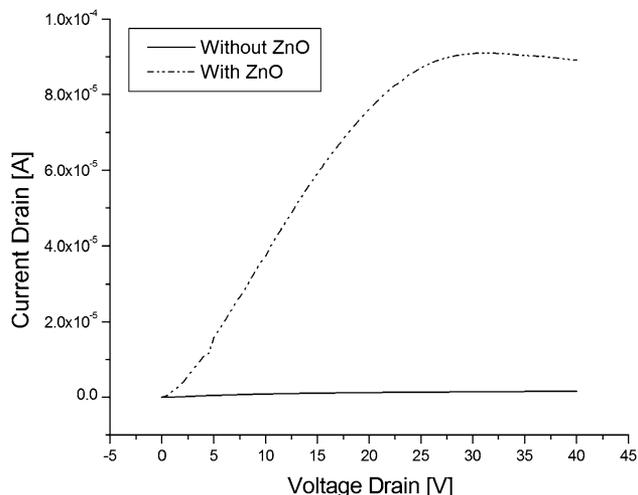


Fig. 2. Current–voltage characteristics of a field effect transistor with $V_{GS} = -10$ V and channel length = $100 \mu\text{m}$. Series 1: 1 g of PVP in 5 mL of isopropanol alcohol (without ZnO nanoparticles). Series 2: 1 g of PVP in 5 mL of ZnO nanoparticles (with ZnO nanoparticles).

EXPERIMENTAL RESULTS

Morphology Insulator Polymer Surface

Atomic Force Morphology Study

Key parameters of the gate insulator are the surface morphology, the leakage current density and the dielectric constant. The morphology evolution of the five solutions was obtained by using the atomic force microscope (AFM) ‘CSI-Nano-Observer’ in non-contact mode. The dielectric layers were obtained from five solutions where ZnO volume concentration was varied from 0% to 80%. Figure 3 reveals that the addition of stearic acid in the ZnO nanoparticles solution lead to effective dispersion even for a high concentration. This shows that the chemical interaction between the ligands and the polymer chains increases the miscibility of the ZnO nanoparticles in PVP. However, it is still possible that there exist aggregates in the insulating layer. The first layer with 100% PVP ($1 \mu\text{m}$ thick) is very smooth; it has a root mean square (RMS) roughness of 0.250 nm . Figure 4 presents the RMS of the layers with ZnO nanoparticles increased from 0.750 nm to 3 nm with the ZnO concentration, not in a sufficient way that can prevent proper operation of transistors.

Figure 5 shows the variation of the real part of the relative permittivity of the ZnO:PVP layer, and ZnO volume concentration in the PVP matrix. It is clear that up to 50 vol.%, the change in permittivity follows the Maxwell–Garnett (MG) approximation. This approximation is valid for isotropic and separated nanoparticles with diameters 3–30 nm. In that case, the effective dielectric permittivity in the MG theory¹⁴ is given by:

$$\varepsilon_e = \varepsilon_h \frac{\varepsilon_n + 2\varepsilon_h + 2f(\varepsilon_n + \varepsilon_h)}{\varepsilon_n + 2\varepsilon_h + 2f(\varepsilon_n + \varepsilon_h)} \quad (1)$$

where ε_h is the permittivity of the host material in which nanoparticles, with ε_n as permittivity, are dispersed. The volume fraction of nanoparticles is denoted by f . From the curve and the experimental results one can see that the percolation threshold is just above $f = 50\%$.

TRANSISTORS CHARACTERISTICS

Figure 6 shows the I – V output characteristics of the field effect transistor with PVP as insulator (Fig. 6a) and with composite insulator gate based on PVP:ZnO (Fig. 6b). An improvement of drain current is observed with the addition of ZnO nanoparticles in the matrix of insulating polymer PVP. The two operating modes (linear and saturated) of a field effect transistor exist for the two transistors, but the saturation is far less pronounced in the case of composite insulator where the saturation current increases by a factor of approximately 25. The change in the dielectric constant cannot explain this variation, but it has been demonstrated that there is huge dependence on the ZnO nanoparticle’s dielectric constant with low frequencies¹⁵. At 100 Hz, a dielectric constant higher than 100 has been measured; such values should explain the drain current. The linear regime observed in the case of composite insulator is attributed to a sharp drop in the resistivity of the insulating layer. We measured an increase of two orders of magnitude from $3.34 \times 10^{-8} \text{ S}$ to $5.38 \times 10^{-6} \text{ S}$ in the conductivity of the insulating layer.

In Fig. 7 the square root of the drain current in the saturated region at $V_{DS} = -40 \text{ V}$ is plotted as a function of gate voltage V_{GS} for both the devices with or without ZnO nanoparticles in the insulating layer. From the linear fit, the threshold voltage V_{th} is measured and the field effect mobility in the saturation region μ is determined from the well-known equation:

$$I_D = C\mu \frac{W}{2L} (V_G - V_{th})^2 \quad (2)$$

where C is the capacitance per unit length of the polymer insulator, W is the channel width and L is the channel length.

The threshold voltage in the case of pentacene OTFT with PVP as insulator is positive (around 8 V), as has already been observed in previous work.¹⁶ In the case of the composite, the threshold voltage shifts in the negative direction and is almost zero. This change is assumed to depend on the existence of interface or bulk trap states or on the morphology of the pentacene film sublimated on two different gate insulators. It has been demonstrated that traps with energy states in the band gap of the semiconductor influence the subthreshold slope.¹⁷

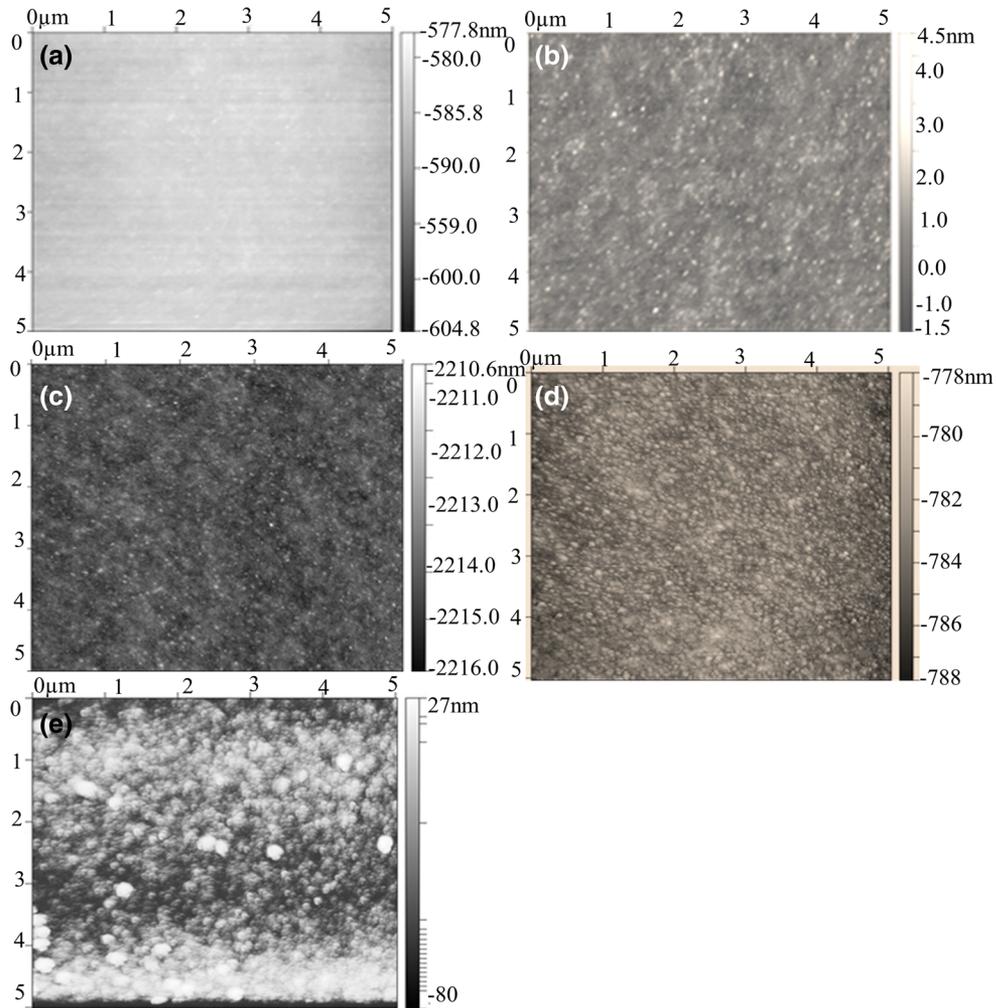


Fig. 3. Morphology insulator polymer layer of the five solutions: (a) with pure PVP (0% ZnO + 100% PVP), (b) insulator polymer layer with 20% ZnO + 80% PVP, (c) insulator polymer layer with 40% ZnO + 60% PVP, (d) insulator polymer layer with 60% ZnO + 40% PVP and (e) insulator polymer layer with 80% ZnO + 20% PVP.

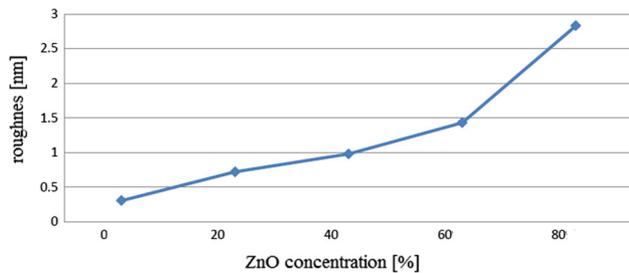


Fig. 4. Variation of insulator roughness versus ZnO nanoparticle concentration.

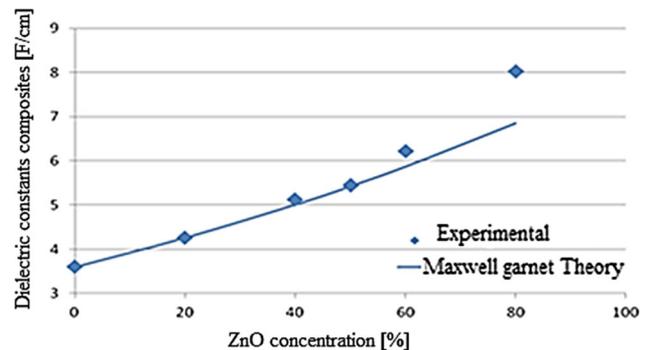


Fig. 5. Dielectric constants of composites with various ZnO contents in PVP measured at 1 kHz.

In the case of the polymer dielectric gate OTFT, a carrier mobility of $4.10^{-3} \text{ cm}^2/\text{V.s}$ was measured, compared with $3.10^{-2} \text{ cm}^2/\text{V.s}$ in the case of the composite dielectric gate. This result, linked to the threshold voltage evolution, seems to indicate less trap at the interface, although the carrier mobility is generally affected in the case of high dielectric

insulator constant, due to randomly oriented dipole near the interface.¹⁸ The latter increases the energetic disorder of the trap state in the semiconductor. As the rugosity is not significantly modified, we can

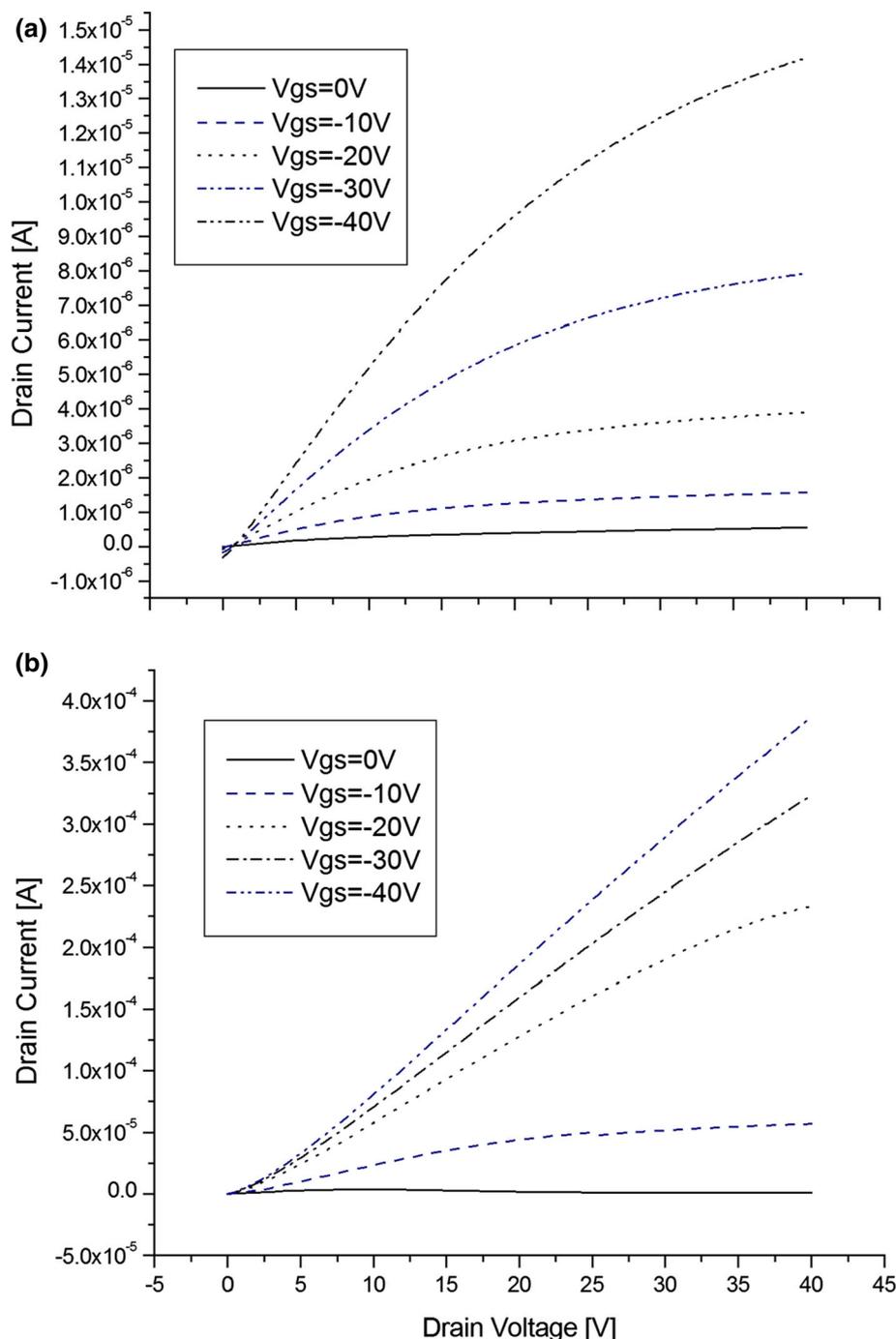


Fig. 6. Current–voltage characteristics of the field effect transistor with: (a) insulator layer based on solution with 100% PVP and 0% ZnO, (b) insulator layer based on solution with 50% PVP and 50% ZnO.

assume that this increase of mobility is connected to the presence of ZnO nanoparticles not so far from the percolation threshold. According to the work of Yanakisawa,¹⁹ the mobility is not affected by the morphology of the pentacene layer. Indeed, the morphology of pentacene is affected by the roughness and the surface energy of the substrate. The AFM results presented in Fig. 8a and b show the

morphology of the pentacene active layer deposited on the two gate insulator layers, without ZnO nanoparticles and with ZnO nanoparticles, respectively. The scanning surface is $2 \mu\text{m} \times 2 \mu\text{m}$: First, the layer of pentacene deposited on pure PVP shows a typical morphology of pyramidal grains. Second, the layer of pentacene deposited on the composite PVP has a morphology of dendritic grains with a

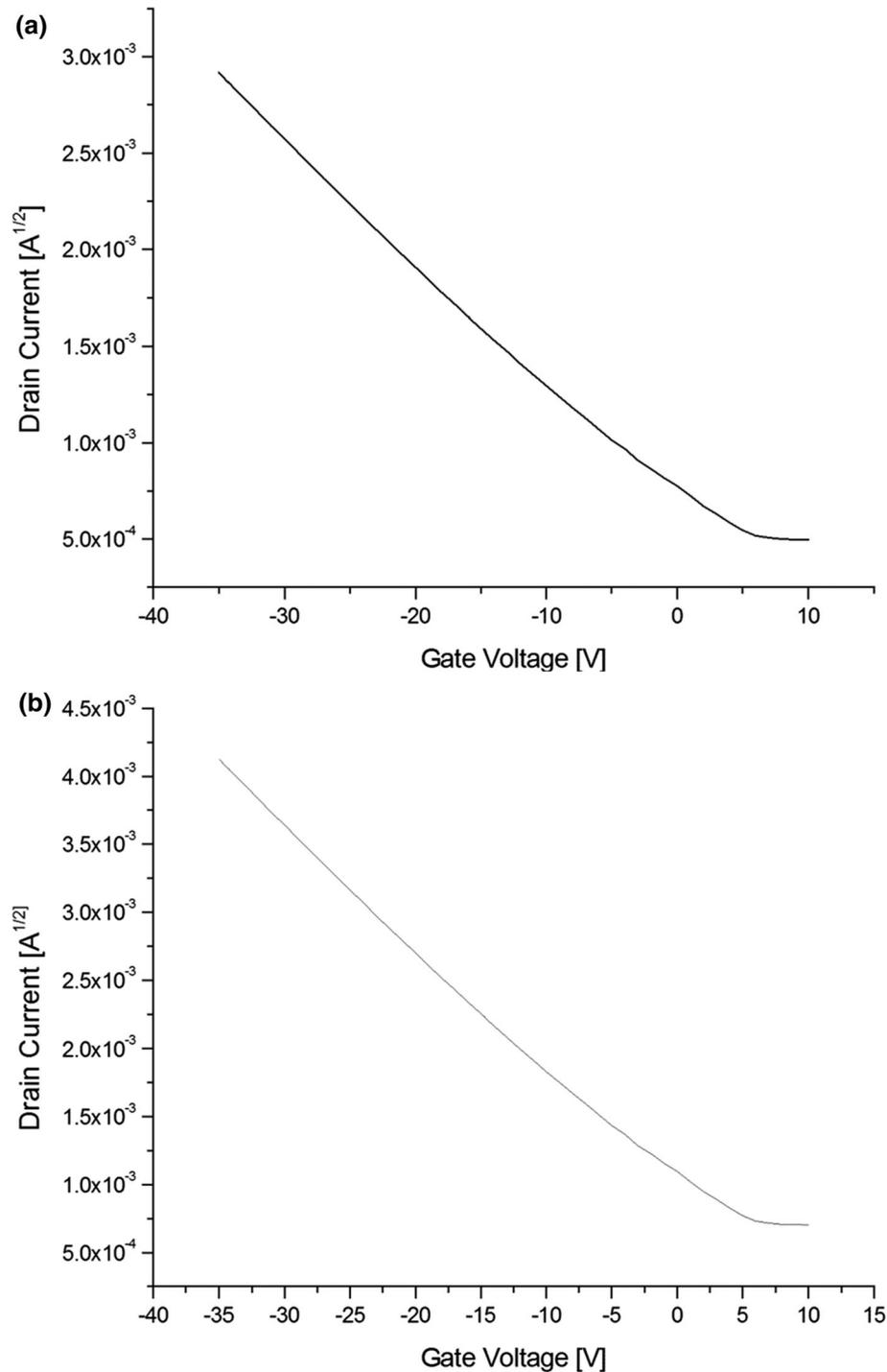


Fig. 7. $|I_{DS}|^{1/2}$ versus $|V_{GS}|$ for $V_{DS} = -40$ V for a pentacene OTFT prepared (a) with pure PVP and (b) with composite insulator PVP.

branching structure. The pyramidal and dendritic morphologies consist of c-axis orientation and usually have relatively high mobility.

CONCLUSION

The influence of ZnO nanoparticles hosted into a PVP matrix on the dielectric constant of PVP has

been demonstrated and a percolation threshold of 50% by volume has been identified. The PVP:ZnO nanoparticles composite was realized, with a good dispersion of the nanoparticles by using of 4-hydroxybenzoic acid ligand. On the one hand, the interaction between PVP and ZnO was increased and no aggregation or phase separations was

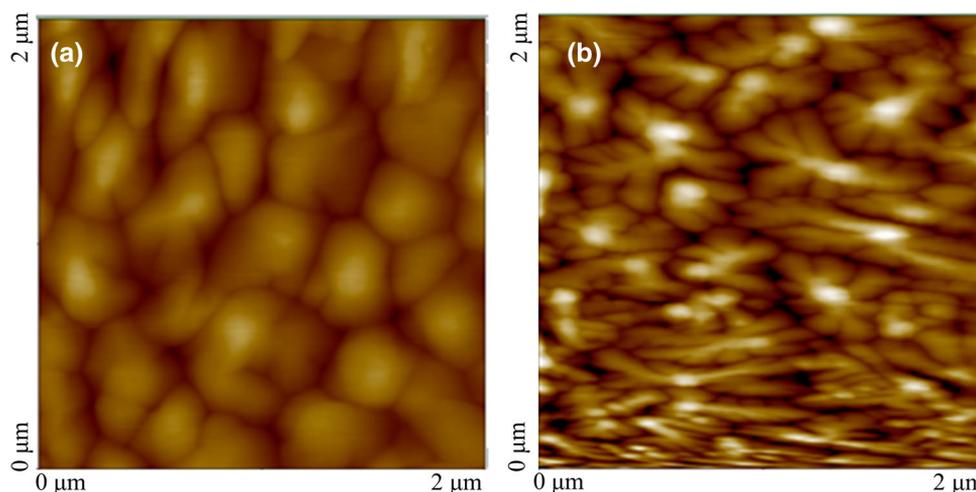


Fig. 8. Morphology of pentacene layer deposited on the two solutions: (a) insulator polymer layer with 100% PVP and 0% ZnO and (b) insulator polymer layer with 50% PVP and 50% ZnO.

observed. OTFTs were successfully fabricated and mobility was significantly improved when ZnO nanoparticles were included in PVP. On the other hand, this gives rise to important linkage current (small on-to-off ratio). The results of this study can be highlighted in logic applications where it is sometimes necessary to adjust the threshold voltages. It is also possible to use such transistors in voltage amplifier circuits, where the linear part of the output characteristic is used.

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