



ISSN (PRINT) : 2320 -1967
ISSN (ONLINE) : 2320 -1975



ORIGINAL ARTICLE

CHEMXPRESS 7(1), 23-29, (2014)

Effect of molecular weight of gate dielectric (Polyvinylalcohol) and solvents on operational stability of organic field effect transistors

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Abstract : The effects of molecular weight and the solvents used for gate dielectric deposition on output and transfer characteristics of OFET devices with bottom gate contact have been studied. Polyvinylalcohol (PVA) with molecular weights 30000 and 145000 g/mol (PVA1 and PVA2, respectively) was used as gate dielectric and deionized-water and dimethylsulfoxide (DMSO) as solvents. This study demonstrated that both the molecular weight and solvent affect the output and transfer characteristics of the OFET devices. Consider-

able improvement in threshold voltage has been achieved for each molecular weight in the case of DMSO used as solvent. The observed clockwise hysteresis from the $V_{gs}-I_{ds}$ curves and their solvent dependence implies that the presence of the polar groups inside the gate dielectric can control device characteristics.

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Keywords : Threshold voltage; OFET; Hysteresis; Solvent.

INTRODUCTION

Organic field-effect transistors (OFETs) are not only essential building blocks for the production of high-performance organic based circuits, but OFETs also provide an important insight into the relevant mechanism of conduction in π -conjugated systems. Interests in OFETs come from their great potential for use in low-cost, fast fabrication and flexible devices in low-end electronics,

such as displays^[1,2] radio frequency identification tags^[3], microelectronic logic, some other small-scale integrated circuits^[4] and gas sensor^[5,6]. For practical applications of the OFETs in analog circuits, it is important to study the limits of device performance and the origin of the limits. For decades, transfer characteristics has been a good indicator to evaluate the performance limits of OFETs, because they determine hysteresis behavior that leads to a shift in the threshold voltage depending on

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the sweeping direction of the gate–source voltage and can result in an unpredictable circuit operation.

Although the performance of organic semiconductor based FETs has improved in the last 20 years enormously^[7], high leakage current density and stability issues such as hysteresis still exist as serious obstacles to the commercial use of the OFETs with polymeric gate insulators^[8–11]. Reports of a dependence of the OFET performances on the dielectric constant of the gate dielectric^[12] illustrate clearly the importance of selecting the right gate dielectric material. Among the rather various organic gate dielectrics such as, poly(4-vinylphenol) (PVP)^[10], poly(methylmethacrylate) (PMMA)^[13] and polystyrene (PS)^[14], poly(vinyl alcohol) (PVA) has been considered as one of the most potential organic dielectric for various electronic applications such as OFET because of its good solution processability^[15], excellent chemical and thermal resistance^[16] and its favorable dielectric and electrical properties^[17,18]. Dielectric properties such as, charging and discharging, of PVA films have been studied in some detail by various workers^[19,20]. However, little previous work has been performed on the effect of molecular weight and solvent used for PVA deposition on OFET's transfer characteristics. Hydroxyl influence on device characteristics of ambipolar OFET is investigated by comparing insulating polymers with and without hydroxyl by H. Kawaguchi *et al.*^[21]. They used PVA for the insulating polymer with hydroxyl and poly(cyanoethylacrylate) (PCA) which is developed by replacing the hydroxyl of PVA with the cyanoethyl group without hydroxyl. More than 10-fold higher mobility and a large threshold voltage were observed in the OFET with PCA. Parashokov *et al.*^[22] reported a strong correlation between the dielectric constant of the insulator and the organic field-effect mobility. They used polyvinylphenol (PVP), PVA, and cyanoethylpullulan (CYEPL) as dielectric materials and, poly(3-butylthiophene) as the semiconductor. In the case of the CYEPL dielectric, carrier mobilities as large as $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained.

This work reports the effects of molecular weight of gate dielectric and solvents used for gate dielectric deposition on output and transfer characteristics, operational stability (hysteresis behavior) of OFETs by comparing two PVP based gate dielectrics with different molecular weight and solvent. The fabricated OFETs

were based on regioregular poly(3-hexylthiophene) (RR-P3HT), one of the most promising and widely investigated organic semiconductors.

EXPERIMENTAL

The substrates used to prepare the OFETs were Indium Tin Oxide (ITO) coated glass slides with sheet resistivity in the 8–12 $\Omega \text{ cm}$ range. The ITO substrates were carefully cleaned using several rounds of ultrasonic rinsing in ethyl alcohol, deionized water, and acetone. After drying in a flow of argon gas, dielectric layer was deposited on the ITO coated substrates. Polyvinyl alcohol (PVA) with two different molecular weight (30000 (PVA1), and 145000 (PVA2)) was used as gate dielectric. In order to investigate the effect of the solvent on the OFETs stability, PVAs were dissolved in two different solvents (Deionized-water (DI-water) and dimethylsulfoxide (DMSO)). Thin films of the PVAs were deposited onto a previously well-cleaned ITO coated glass substrate by spinning a small volume of the spreading solution at 2500 rpm. After drying the PVA film at 65 °C for 48 h in a fully automated glowbox (Jacomex), a solution of active layer (rr-P3HT, from Aldrich) in dichlorobenzene with a concentration of 35 mg/ml, was spun on top of the PVA film rotating at 1500 rpm. The deposited films were then dried in the glowbox at 110 °C for 15 min to allow complete evaporation of solvent and surface moisture. On top of the rr-P3HT layer, silver (Ag) was vacuum evaporated (below 5×10^{-6} mbar) through a patterned shadow mask to make source/drain contact. The channel length and width of the OFETs were 80 μm and 4 mm, respectively. The electrical characteristics of the OFETs were obtained at room temperature under ambient condition using Keithley 4200 SCS. The thicknesses of the PVA films were measured by a KLA-Tencor P-6 Surface Profiler. The capacitance values of the dielectric films were determined by an HP 4194A Impedance analyser, by employing a sandwich structure of the film with ITO and evaporated Ag electrodes.

RESULTS AND DISCUSSION

To investigate the effect of the solvent used for the gate dielectric deposition, the output ($I_{\text{ds}} - V_{\text{ds}}$) and trans-

fer characteristics of the produced OFETs were measured as function of gate voltage and drain-source voltage, respectively. Figure 1 compares the effect of the solvents on the output characteristics for OFET with PVA2 where DI-water (a) and DMSO (b) were used as solvents. Figure 1 shows that the solvent used for the deposition of the dielectric layer has a strong effect on the output characteristics of the OFET. The linear and saturation regions are clear with the increase of drain-source voltage in the case of the DMSO used as solvent but not for DI-water as solvent. The operating voltage of the OFETs determined from the measurements are found to be a strongly depend on the solvent used. The values of the operating voltage were found to be as 17 V and 2 V for DI-water and DMSO, respectively. This discrepancy between these two output characteristics of the OFET and the reduction in oper-

ating voltage might be attributed to the solubility of PVA in various solvents. It is well established that the output characteristic of an OFET device depends strongly on the molecular ordering, controlling the film morphology of the gate dielectric and active layer.

It is well known that the stacking arrangement, interplanar spacing of polymer units and morphology of an organic dielectric or semiconducting material depends on the processing conditions such as solvents and annealing steps^[23,24]. It is also well known that the degrees of hydrolysis and polymerization affect the solubility in water^[25]. It has been shown that PVA grades with high degrees of hydrolysis have low solubility in water^[26]. As a result, several factors associated with PVA may explain the effects of the solvent shown in Figure 1. The dissolution of PVA depends on the nature of the solvent, temperature and the extent of hy-

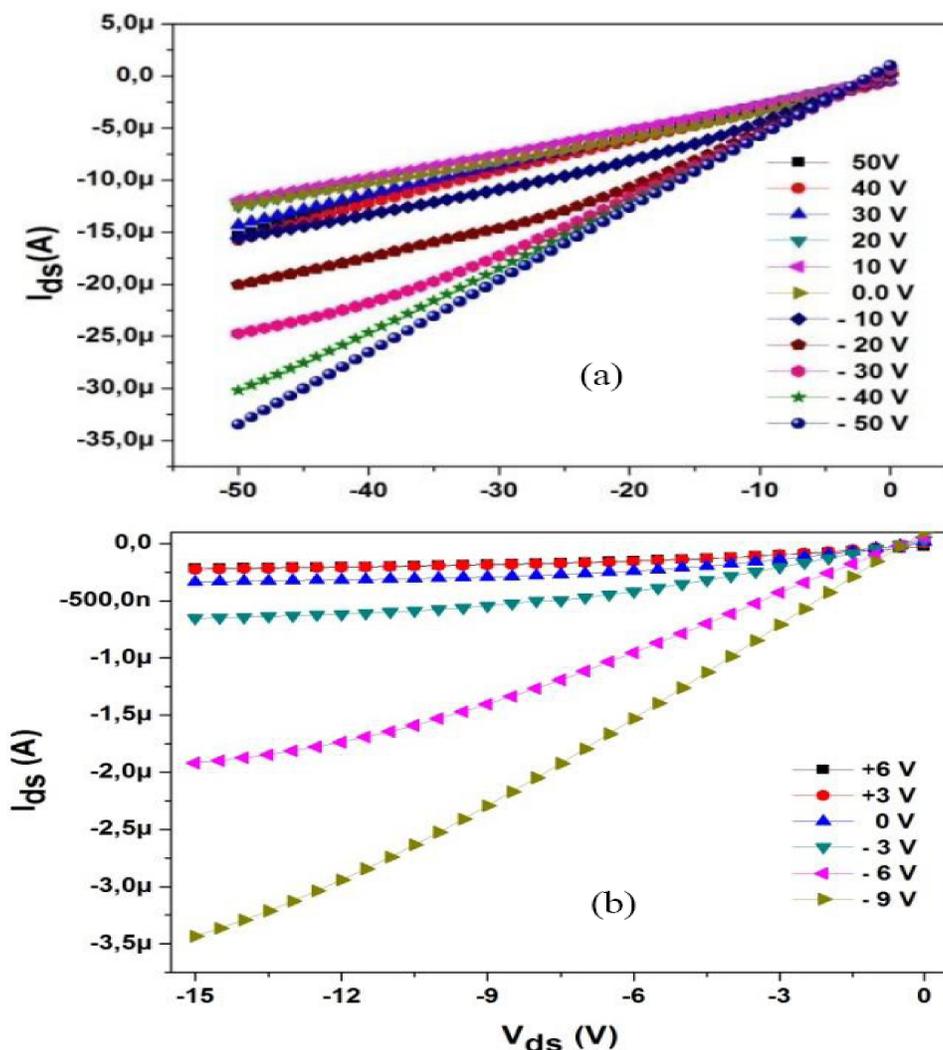


Figure 1 : Plots of I_{ds} versus V_{ds} at various gate voltage values for OFETs using PVA2 in water (a) and DMSO (b).

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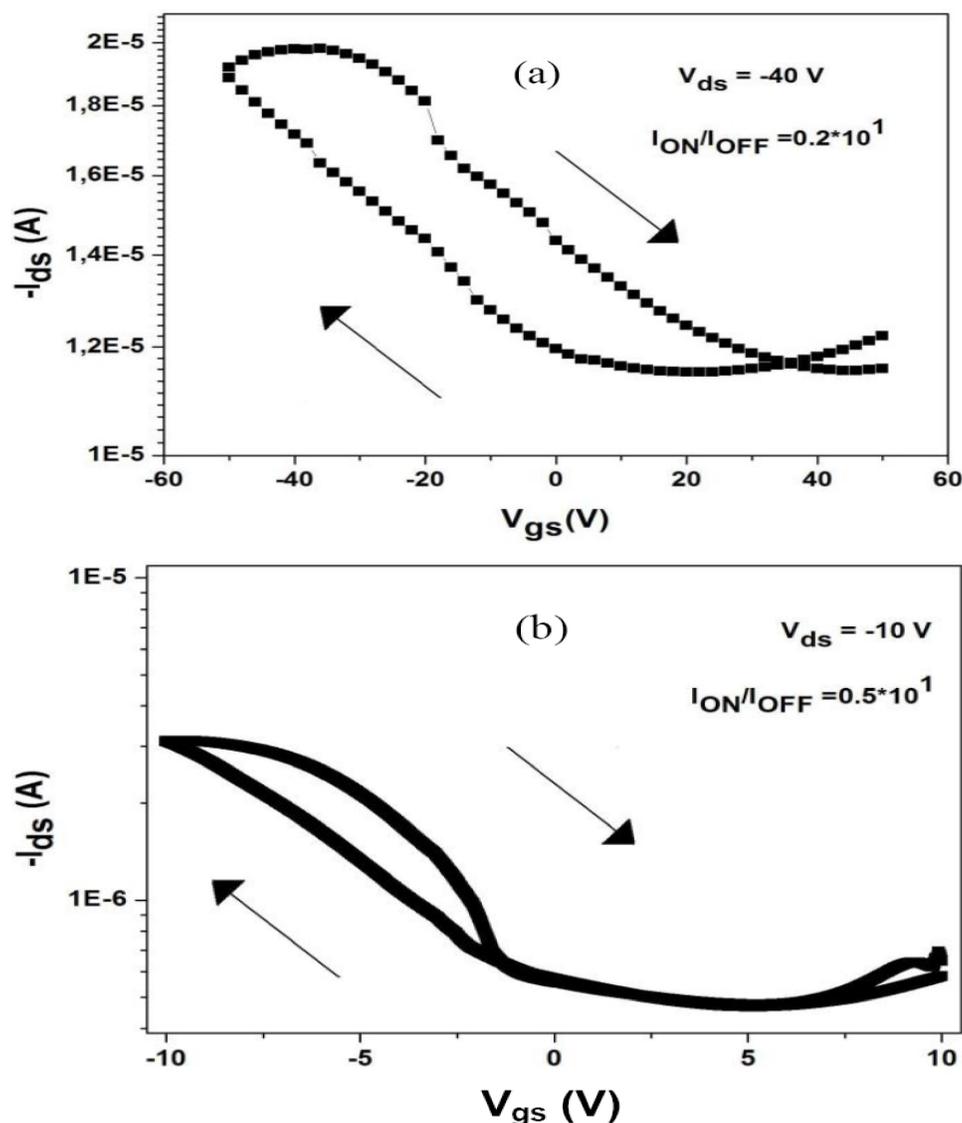


Figure 2 : The effect of the solvents on the transfer characteristics of the OFETs with DI-Water (a) and DMSO (b).

drolisis in the polymer. In aqueous solutions, there is inter- and intra chain bonding between the polar hydroxyl groups in the PVA molecules. In addition, hydrogen bonding between the PVA chains and the water molecules is also established after dissolution^[27]. Hence, after dissolution, the molecules of semi-crystalline PVA are not completely dispersed and microgel particles containing paracrystalline regions and amorphous domains may remain. Kawaguchi et al. showed that the presence of the hydroxyl in the polymer insulating film had a large influence not only on the interfacial electron trapping but also on the morphology of the organic semiconductor layer and the magnitude of the mobility could be controlled by the presence of the hydroxyl in the gate-insulating film^[21]. Therefore the observed behav-

ior can be attributed to the different solubility properties of PVA in DI-water and DMSO. The transfer characteristics of the OFETs at different fixed V_{ds} are shown in Figure 2. Although the hysteresis behavior of the OFET device with DMSO has been improved as compared with DI-water, both devices were exhibited hysteresis upon sweeping of the gate bias in the forward and reverse scans. Similar hysteresis effects were recently reported for various gate dielectric such as, poly (4-vinyl phenol)^[28], cross-linked high-k cyanoethylated pullulan polymer^[29] and PVA Polyvinyl alcohol (PVA, Mol. Weight: 100 000^[13]). The origin of the hysteresis behavior in the transfer characteristics were investigated by Hwang et al.^[30] in some detail. They conclude that the origin of the hysteresis behavior is generally based

on three mechanisms. According to Hwang et al., *i.*) traps in channel/dielectric interface or semiconductor, *ii.*) charges injected from the gate electrode and then trapped inside the dielectric and, *iii.*) residual dipole or mobile ions are the three sources of the observed hysteresis effect. Case *i.*) is often associated with the electrons trapped in the functional groups at channel/dielectric interface and give rise to an anticlockwise hysteresis in transfer characteristics. Anti-clockwise hysteresis can also be resulted from the charge trapping on grain boundaries, and impurities inside the semiconductor^[31]. The injection or ejection of charge carriers in the gate dielectric will lead to a clockwise hysteresis. It was also pointed out that hysteresis with polymer gate insulator was bulk related rather than interface related, which

was quite different from SiO₂ dielectric^[32]. When a large negative gate bias is applied, the injected carriers are trapped in the interface, leading to the built in electric field along the direction opposite to the applied field. This built in electric field screens the external field, resulting in more negative gate bias needed to turn the transistors on. Polar group is believed to be responsible for the observed clockwise hysteresis in our case. Polar groups inside the dielectric can reorient under the applied electric field and make the drain current lap the bias sweep, resulting in a clockwise hysteresis.

For further analysis of the effect of the molecular weight of PVA, output characteristics of the OFETs with PVA1, in which DI-water (a) and DMSO (b) were used as solvents, are shown in Figure 3. From the plots,

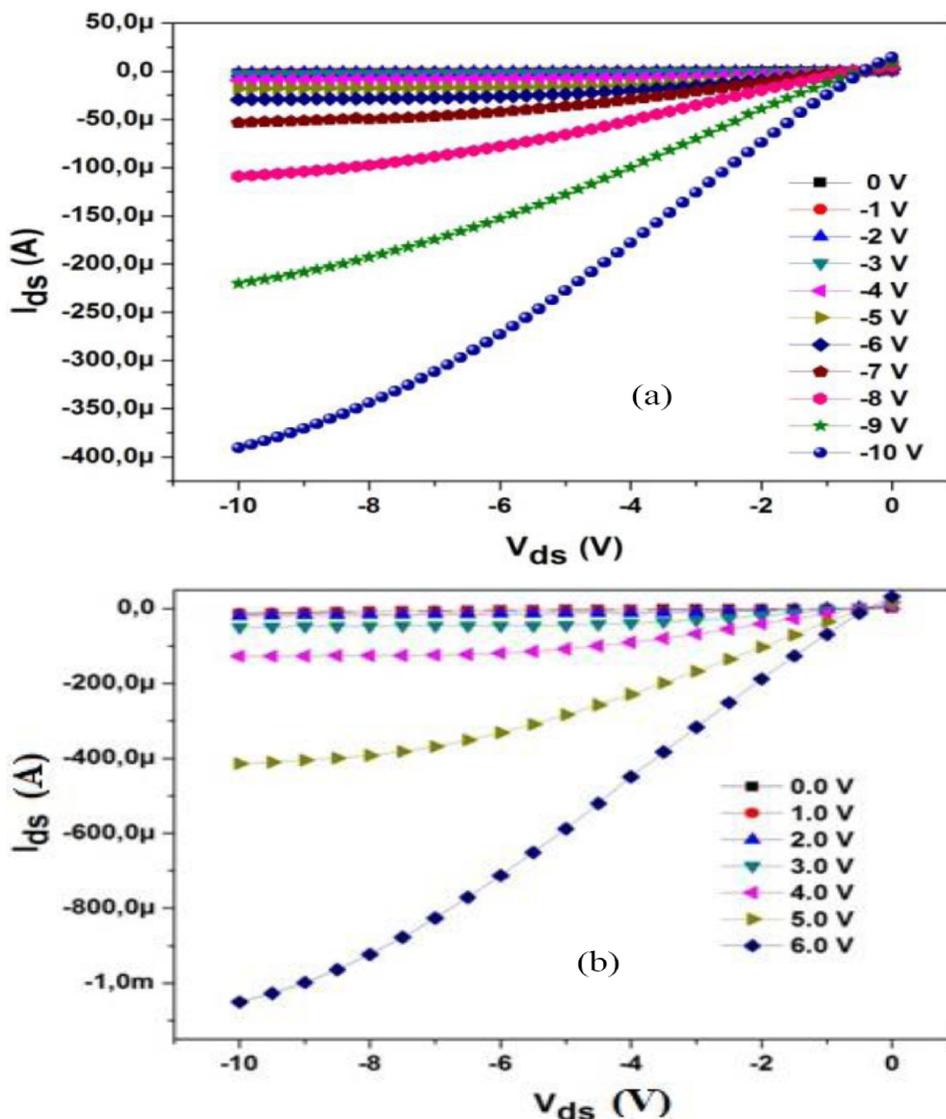


Figure 3 : Output characteristics OFETs using PVA1 in DI-water (a) and DMSO (b).

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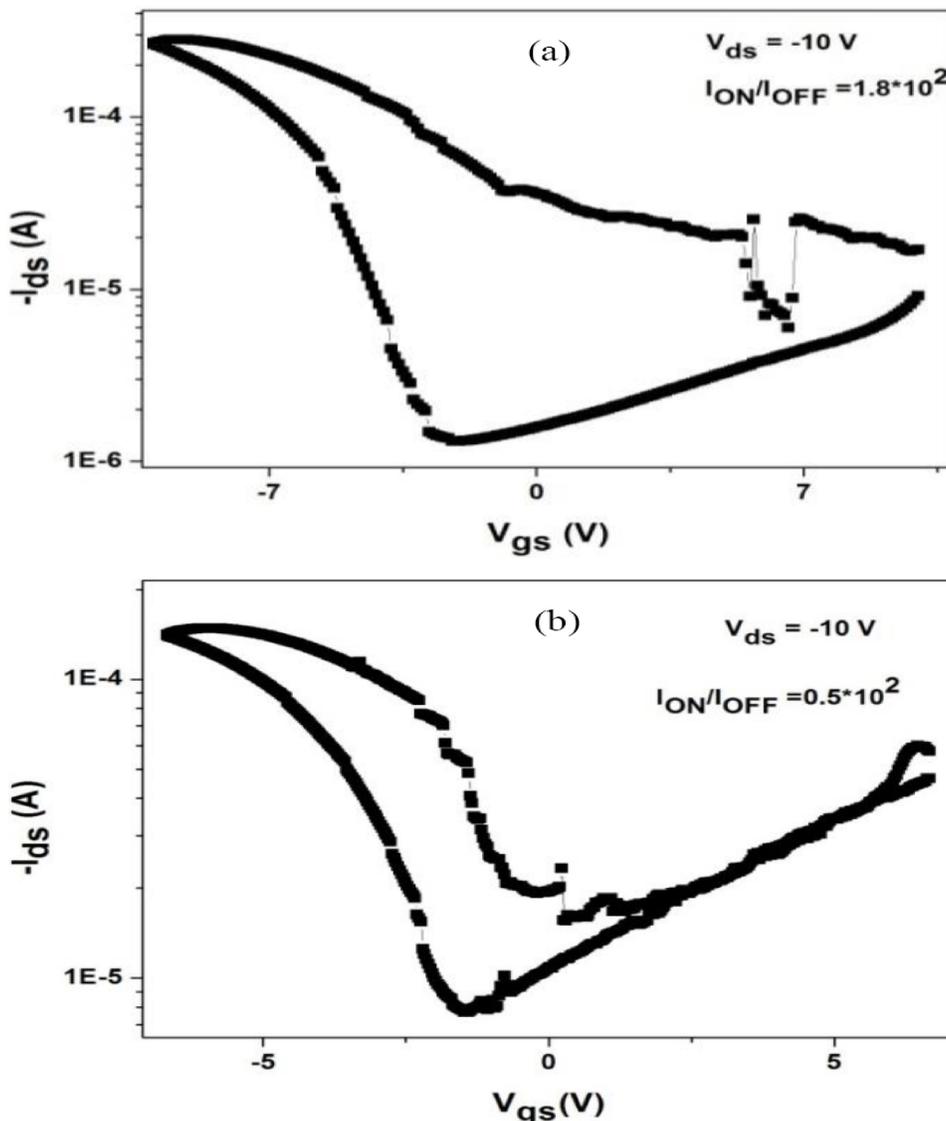


Figure 4 : The effect of the solvents on the transfer characteristics of the PVA1 based OFETs with DI-water (a) and DMSO (b).

the linear and saturation regions can clearly be seen with the increase of drain-source voltage for both devices. At low drain-source voltages, the drain-source current follows Ohm's law, and is proportional to drain-source voltage. As the drain-source voltage increased, the voltage, measured relative to the source, along the channel increases from 0 to V_{ds} . Thus the voltage between the gate and points along the channel decreases from V_{GS} at the source end to $V_{GS} - V_{ds}$ at the drain end. Since the channel is no longer of uniform depth; rather, the channel take the tapered form being deepest at the source end and shallowest at the drain end. As V_{ds} is increased more, the channel becomes more tapered and its resistance increases correspondingly. Thus, the output characteristic ($I_{ds} - V_{ds}$ plot) does not continue as

a straight line. This situation is known as pinch-off of the conductive channel of the transistor.

Therefore it can be said that the observed saturation in I_{ds} is due to pinch-off of the channel. Figure 3 also shows that the drain-source current is effectively modulated by gate voltage and the drain current of both the OFETs increases with gate voltages. It is also noticed that the drain-source current improved significantly in the case of DMSO.

For comparison, the transfer characteristics of the PVA1 based OFETs at fixed V_{ds} voltage of -10 V is given in Figure 4. It is clear that the transfer characteristics of the PVA1 based OFETs are similar to PVA2 based devices. From these investigations, threshold voltage and on/off current ratio of the devices are 2.7

V, 0.7 V and 1.8×10^2 , 0.5×10^2 for the devices where PVA1 dissolved in DI-water and DMSO, respectively.

CONCLUSION

The influence of the molecular weight of polyvinylalcohol, used as gate dielectric layer, and solvents used for gate dielectric deposition on operational stability of the organic field-effect transistors using regioregular poly (3-hexylthiophene) as the active layer was investigated. Due to the considerable improvement in threshold voltage for each molecular weight of PVA, DMSO might be a convenient solvent for PVA based devices. The results of the PVAs based OFET studies revealed that the number of the polar groups inside the PVA has a strong effect on the device characteristics. The selection of the gate dielectric with a proper molecular weight and its solvent is very important in obtaining high performance OFET devices.

ACKNOWLEDGMENTS

This work was supported by The Scientific and Technological Research Council of Turkey, TUBITAK (Grant No: 110T352) and Marmara University BAPKO Project number FEN-E-110411-0104.

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