High mobility polymer gated organic field effect transistor using zinc phthalocyanine

K R RAJESH*, V KANNAN, M R KIM, Y S CHAE and J K RHEE

Millimeter- Wave Innovation Technology Research Centre (MINT), Dongguk University,
Seoul 100-715, Republic of Korea

MS received 15 October 2012; revised 25 April 2013

Abstract. Organic thin film transistors were fabricated using evaporated zinc phthalocyanine as the active layer. Parylene film prepared by chemical vapour deposition was used as the organic gate insulator. The annealing of the samples was performed at 120 °C for 3 h. At room temperature, these transistors exhibit *p*-type conductivity with field-effect mobilities ranging from 0.025–0.037 cm²/Vs and a ($I_{\text{on}}/I_{\text{off}}$) ratio of $\sim 10^3$. The effect of annealing on transistor characteristics is discussed.

Keywords. Organic semiconductor; field effect transistor; phthalocyanine; high mobility.

1. Introduction

Organic field effect transistors (OFETs) are being extensively studied for various applications of electronic circuits (Horowitz 1998; Dimitrakopoulos and Malenfant 2002) including radiofrequency identification (RFID) tags, smart cards, digital paper displays and back planes for flexible active-matrix organic light-emitting diodes (AMOLEDs). The device performances of OFETs have improved dramatically over the past decade. The carrier mobility of OFETs is similar to or even higher than that of typically obtained ones with hydrogenated amorphous silicon TFTs, which have found widespread use in liquid crystal displays (AMLCDs) (Dimitrakopoulos and Malenfant 2002; Sundar *et al* 2004).

Phthalocyanines have been in the limelight due to their promising applications as organic semiconductors. Among them, zinc phthalocyanine (ZnPc) is one of the most important, because of its broad spectral dependence. The basic properties of many metal phthalocyanines have been studied in detail by various researchers (Gould 1985; Belgachi and Collins 1998). They also exhibit strong non-linear optical properties, due to their spatially extended π -electron system (Fang *et al* 1993). In order to utilize the mechanical flexibility inherently possessed by organic materials, many attempts have been made to develop polymeric gate dielectric layers. Recently, a significant amount of effort has been made to deposit organic semiconductors onto polymeric insulators with the ultimate goal of creating all-organic transistors to power flexible display elements (Halik *et al* 2002). The performance characteristics of OFETs, such as their operating voltage, depends critically on the gate dielectric materials and their interfacial properties, because the dielectric surface

is in contact with the channel of OFETs, where the drain current flows (Veres *et al* 2004; Chua *et al* 2005). The interaction between these surfaces and the deposited organic can have a profound effect on thin film growth and the resulting electrical characteristics, since most of the charge transport in these structures occurs near the organic-insulator interface.

We used parylene-C as the gate insulator, which can be deposited by chemical vapour deposition (CVD) on the surface of ITO coated glass at room temperature and can form a parylene/organic interface with a low density of electronic defects (Gershenson *et al* 2006). Parylene forms pin hole free, thin conformal transparent coatings with excellent dielectric and mechanical properties (Podzorov *et al* 2003). It is used to passivate the entire area of the substrate except for ITO contact areas. The application of parylene CVD process to realize ZnPc OFETs has not been reported before. We determined the transistor parameters of the device at room temperature. Comparison of electrical properties of the virgin and annealed devices provides insight into the trap distributions.

2. Experimental

OFETs using ZnPc with a top contact structure were fabricated on ITO coated glass substrates. The cross-sectional structures and bias configurations of OFETs are schematically shown in figure 1. ITO was selectively etched to form electrical contact for the gate insulator. Thoroughly cleaned etched ITO glass substrates with a surface sheet resistance of 10 $\Omega/\square$ were used as the substrates.

The gate dielectric was a 490 nm thick parylene-C layer deposited in a lab coater. The dimer *para*-xylylene was vapourized in the vapourization zone at ~ 135 °C, cleaved in the pyrolysis zone at ~ 695 °C, and polymerized in the

* Author for correspondence (rajthinfilms@yahoo.co.in, rajesh@dongguk.edu)

Figure 1. Schematic of OFETs. Gate is negatively biased to operate in accumulation mode.

deposition zone (the chamber), at room temperature and a pressure of ~ 0.1 Torr.

ZnPc powder (Aldrich Inc.) was evaporated onto the parylene films kept at room temperature using a Hanvac UHV coating plant at a pressure of 10^{-7} Torr. The evaporation rate was kept at $0.1\text{--}0.2$ nm per s and the thickness was ~ 100 nm. Finally, source/drain gold contacts with a thickness of 60 nm were evaporated through a shadow mask. The channel length and width-to-length channel ratio were, respectively, $50\text{ }\mu\text{m}$ and 20 .

Half of the samples were annealed at $120\text{ }^{\circ}\text{C}$ for 3 h in a furnace attached to a programmable temperature controller. The electrical characterizations of OFETs were carried out at room temperature using an Agilent E5272 semiconductor parameter analyser interfaced with a probe station kept in the dark. The capacitance of the parylene film was measured with HP 4294 LCR meter. The atomic force microscope (AFM) images of the samples were recorded by a digital instruments nanoscope.

3. Results and discussion

The fabricated OFETs operate in accumulation mode. The typical transistor characteristics are measured at room temperature in air immediately after device fabrication. Here, we measure the drain current I_d of the as-prepared FETs as a function of the drain voltage V_d , as shown in figure 2.

The voltage is varied from 0 to -80 V in steps of 20 V. The sharp increase of the drain current, I_d , at negative values of the gate voltage, V_g , indicates the formation of p -type conducting channel. Figure 3 shows corresponding transfer curves of the same device, V_g is varied from 20 to -100 V with the application of $V_d = -70$ V.

The field-effect mobility μ and threshold voltage V_t are calculated using (2)

$$I_{d,\text{sat}} = \left(\frac{W}{2L} \right) C_i \mu (V_g - V_t)^2, \quad (1)$$

where $I_{d,\text{sat}}$ is the drain current in the saturation region, C_i the gate capacitance per unit area and V_g the applied gate

Figure 2. Output characteristics of as-deposited OFETs.

voltage. Using (1) and the values, W (width of the channel) = $1000\text{ }\mu\text{m}$, L (length of the channel) = $50\text{ }\mu\text{m}$ and $C_i = 7.2\text{ nF/cm}^2$, we obtain $\mu = 0.012\text{ cm}^2/\text{Vs}$ and $V_t = -34.7\text{ V}$ at $V_d = -40$ V. The maximum on/off current ratio ($I_{\text{on}}/I_{\text{off}}$) is 8.64×10^2 . The sub-threshold swing (SS) is defined as the gate voltage (V_g) required to modulate the drain current (I_d) by one decade as given by

$$\text{SS} = \ln 10 \frac{dV_g}{d(\ln I_d)}. \quad (2)$$

The value of SS is calculated to be 15.29 V/dec . In practice, SS increases with increasing density of trap states at the semiconductor/insulator interface. Also at $V_d = -70$ V, $\mu = 0.025\text{ cm}^2/\text{Vs}$ and $V_t = -47.6\text{ V}$. In this case, on/off current ratio is 1.32×10^3 and SS is 18.95 V/dec . This large value of V_t is due to the trapping of accumulated holes. In pentacene, it has been reported that water molecules are localized between the molecules of pentacene and create trap states in the bandgap (Tsetseris and Pantelides 2007), and that the orientation of the water dipoles changes the local polarization of the organic monolayers, creating trap states in the bandgap (Pernstich et al 2005). The switch-on voltage (V_{so}) corresponding to the flat band potential (Meijer et al 2002) obtained from figure 3 is found to be $+0.51\text{ V}$. Indeed, a positive onset voltage has been reported in some top-gated OFETs (Ling et al 2006). This effect is attributed to the doping of ZnPc with oxygen or moisture. Oxygen was previously shown to create deep acceptor levels and to increase the residual doping level of the organic semiconductor, both of which contribute to the positive shift of the onset voltage (Knipp et al 2006).

Figures 4 and 5 show TFT characteristics of the annealed samples. Using the same procedure, we obtain $\mu = 0.02\text{ cm}^2/\text{Vs}$ and $V_t = 32.06\text{ V}$ at $V_d = -40$ V. $I_{\text{on}}/I_{\text{off}}$ ratio and SS are 3.15×10^3 and 12.87 V/dec , respectively. At $V_d = -70$ V, the values for μ and V_t are $0.037\text{ cm}^2/\text{Vs}$ and 42.56 V , respectively. The corresponding $I_{\text{on}}/I_{\text{off}}$ ratio

Figure 3. Transfer characteristics of as-deposited OFETs. Drain voltage, $V_d = 70$ V.

Figure 5. Transfer characteristics of OFETs annealed at 120 °C for 3 h. Drain voltage, $V_d = 70$ V.

Figure 4. Output characteristics of OFETs annealed at 120 °C for 3 h.

Figure 6. AFM topograph of parylene film deposited on ITO substrate.

and SS are 6.94×10^3 and 14.50 V/dec, respectively. In organic semiconductors, in disordered form, mobility will be a function of the applied field (Brütting 2005). The change in mobility with voltage can be attributed to this. The mobility obtained for ZnPc is the highest among the various phthalocyanines in disordered form. ZnPc with a mobility of $0.32 \text{ cm}^2/\text{Vs}$ has been cited (Liqiang Li *et al* 2008). In this work an ultra-thin buffer layer (para-hexaphenyl) has been utilized between the insulator and semiconductor (Wang *et al* 2007). This structure is slightly different from the present work. The switch-on voltage V_{so} obtained from figure 5 is found to be -4.8 V. This lowering of V_{so} indicates that the annealing process results in the removal of considerable quantities of oxygen acceptor impurities from the sample. Comparing the as-deposited and annealed samples, a decrease in the threshold voltage of the latter can be observed and this can be attributed to the injection improvement at the interface.

Further analysis is possible by finding the interface parameter, $N_{ss}^{\max}$. This corresponds to the maximum number of interface traps present and can be calculated using (3), assuming that the densities of the deep bulk states and interface states are independent of the energy (Rolland *et al* 1993; Unni *et al* 2005):

$$N_{ss}^{\max} = \left[\frac{ss \cdot \log(s)}{kT/q} - 1 \right] \frac{c_i}{q}, \quad (3)$$

where k is the Boltzmann's constant, T the absolute temperature and q the electronic charge. The values of $N_{ss}^{\max}$ calculated for the as-deposited ZnPc and annealed devices are $9.91 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ and $7.57 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, respectively. Hence, annealing process reduces the number of interface traps considerably. This, in turn, would make more carriers available for the conduction process.

Figure 7. Morphology of ZnPc film grown over parylene: (a) as-deposited and (b) annealed at 120 °C for 3 h.

Figure 6 shows a typical AFM topograph of 450 nm thick parylene film. The root-mean square (rms) surface roughness of the film is ~ 7.9 nm over an area of $2 \times 2 \mu\text{m}^2$.

Figure 7 shows morphology of the as-deposited and annealed ZnPc over parylene films. On comparison of these films, we can see larger grains in the annealed samples, which are responsible for their superior electrical properties. It is well established that annealing increases the crystallinity in phthalocyanine thin films. An improvement in crystallinity is observed in CuPc on annealing (Yanagiya 2003). Recently, in vacuum evaporated films of zinc octakis octyloxy phthalocyanine (ZnPcOC₈), it is found that crystallinity increases with increase in annealing temperature (Vinu and Menon 2012). The most plausible explanation for the improved performance of OFETs is, thus, the improvement in their crystallinity and the consequent effective carrier transport through the active layer.

4. Conclusions

Organic field effect transistors were realized using zinc phthalocyanine as the organic active layer and parylene as the organic gate. The measurement of the electrical characteristics of the as-deposited and annealed samples was carried out at room temperature. It was found that the annealed samples exhibit remarkably improved transistor characteristics. The post deposition annealing also improves the crystallinity of the organic layer and in turn the mobility of the device. We also observed a considerable reduction in the number of interface traps for the annealed devices. The mobility observed in this transistor configuration for ZnPc is the highest among the various phthalocyanines. In general, the post-

deposition annealing enhances the transistor characteristics of OFETs based on ZnPc.

Acknowledgement

This work was supported by the Millimeter-Wave Innovation Technology Research Centre (MINT), Dongguk University, Republic of Korea.

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