

The Impact of Capping on the Mobility and Thermal Stability of Organic Thin Film Transistors

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ABSTRACT

We performed temperature-dependent studies on pentacene thin film transistors (TFTs) with and without encapsulation. The capping layer is realized either by a sputtering layer of aluminum oxide (AlO_x) or, alternatively, by a polymeric layer of poly-para-xylylene (PPX). A field-effect can be demonstrated for both capping materials up to temperatures of about 140 - 170 °C, which is about 50 °C above the desorption point of uncapped pentacene thin films on SiO₂ substrates. Complementary studies by thermal desorption spectroscopy and temperature-dependent x-ray diffraction show that the organic layer remains crystalline on the substrate far above the electrical breakdown temperature of the encapsulated device.

INTRODUCTION

In the last years organic electronic devices have found their way into commercial applications. Thereby, devices based on organic materials have to meet certain stability criteria to find their way into commercial products. As many organic materials are sensitive to photo-oxidation, to the exposure to ambient gases and humidity and also to elevated temperatures, new challenges arise concerning the design and stability of organic devices [1, 2]. The exposure of organic semiconducting films to air might lead to doping or oxidation of the organic film, elevated temperatures to a degradation or even to the desorption of the active transport layer. Especially the stability at elevated temperatures under operating conditions is important to guarantee a good long term performance of the device [3, 4]. A possible concept to increase the device stability is the encapsulation of the electronic device, in particular the organic semiconducting layer [5-7].

We have shown recently for the organic semiconductor diindenoperylene (DIP) that by providing the molecular film grown on SiO₂ with an aluminum oxide capping layer, the thermal stability can be strongly enhanced [6, 7]. The DIP remains crystalline on the surface even at temperatures about 200 °C above the desorption point of the uncapped organic layer. In addition, cross-sectional transmission electron microscopy (TEM) and x-ray diffraction have shown that the aluminum oxide layer forms a well defined heterostructure with a sharp interface on the molecular scale on top of the organic film. Hence aluminum oxide shows great promise for a significant enhancement of the stability of organic devices at elevated temperatures.

In this paper we study the structural and electrical properties of pentacene TFTs encapsulated by either a sputtering layer of aluminum oxide (AlO_x) or, alternatively, by poly-para-xylylene (PPX) and their influence on the device performance at elevated temperatures. PPX is widely used in industrial processes as inert, flexible and transparent coating material and therefore, offers promising applications for organic thin film devices. In addition thermal desorption spectroscopy (TDS) and temperature-dependent x-ray diffraction were performed to investigate the desorption process and the structural order of the encapsulated pentacene layer.

EXPERIMENT

Pentacene thin films of a thickness up to 50 nm were deposited by organic molecular beam deposition (OMBD) [8] on transistor structures with bottom gate geometry. These structures consist of a silicon wafer which serves as gate electrode covered by a 290 nm thick thermally grown SiO₂ as gate insulator. Cr/Au electrodes were made by photolithography and amount 5 to 20 μm in length and 2 mm in width. In addition Si(111) wafers with native oxide were evaporated for comparative studies of the structural order and desorption measurements of the pentacene films. The transistors together with the reference substrates were mounted on a sample stage in the vacuum chamber with a base pressure of 1×10^{-7} mbar. After annealing for 12 hours at 120 °C gradient-sublimed pentacene was evaporated at a rate of ~ 0.5 nm/min through a shadow mask while keeping the substrate temperature at 80 °C. The TFTs were electrically characterized in situ at room temperature and in the dark using two Keithley electrometers (Model 617) immediately after thin film deposition. The reference samples were structurally characterized by x-ray diffraction.

In a next step the reference samples and transistors were encapsulated by aluminum oxide or by poly-para-xylylene (PPX). Therefore ~ 100 nm of AlO_x was deposited by HF-magnetron sputtering at 150 W at a rate of ~3 nm/min in a different vacuum system. During sputtering the substrate temperature was kept constant at 18 °C. The PPX deposition was done by polymerization of the source material parylene N in an evacuated heated quartz tube providing a temperature gradient along the tube. The source material was sublimed and pyrolyzed to the monomer in the hottest zone of the tube. The monomerized molecules condensate in the part of the tube kept at room temperature and form a ~ 3 μm thick polymeric film on top of the samples located therein. The encapsulated transistors were reloaded into the vacuum chamber and temperature-dependent electrical measurements were performed after pumping for 12 hours. The TFTs were heated up with a constant heating rate of 1.5 °C/min and the temperature was kept constant for about 1.5 h at each heating step.

We applied thermal desorption spectroscopy (TDS) to analyze the thermal stability of the organic film. Therefore the temperature of the sample is ramped at a constant heating rate of 10 °C/min and the signal of a quadrupole mass spectrometer is recorded which is tuned to single (278 amu) and double ionized (139 amu) pentacene at a resolution of 1 amu.

DISCUSSION

Figure 1 shows the transfer characteristics of an aluminum oxide capped pentacene transistor at different temperatures. Except of a slight shift of the onset voltage to more positive voltages there are no significant changes in the transfer curve characteristics observable up to temperatures of 130 °C.

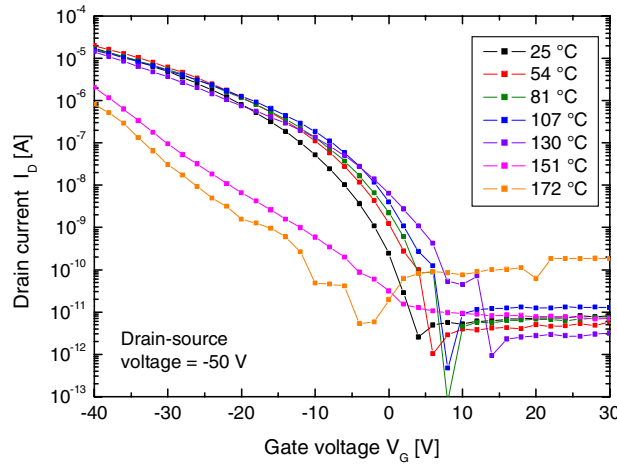


Figure 1. Transfer characteristics at different temperatures of a pentacene thin film transistor encapsulated by aluminum oxide. Changes in the transfer curves occur at temperatures above 130 °C.

For higher temperatures the transistor behavior degrades significantly. This is evident from the deviation of the transfer curves at 151 °C and 172 °C showing a decrease in the source-drain current and in the on/off ratio. To our opinion at these temperatures the charge injection becomes worse due to possible dewetting of pentacene at the interfaces between the conduction channel and the gold contacts [9], leading to the observed decrease of the drain current in the on-state, and the device behavior in the off-state is dominated by thermally induced parasitic effects like surface leakage currents. Nevertheless a field-effect is observable up to these temperatures which are about 70 °C higher than the desorption point of uncapped pentacene on SiO_2 .

Annealing studies under nitrogen atmosphere on pentacene TFTs encapsulated by a parylene layer were for example reported by Sekitani and co-workers in [10]. A field-effect stable over time was demonstrated up to operation temperatures of 140 °C, whereas at higher temperatures a degradation and a decrease of the hole mobility occurred. However, the same group also reported operating pentacene TFTs without encapsulation over the same temperature range up to 160 °C [11], which seems peculiar as desorption of free-standing pentacene layers occurs at about 90 °C.

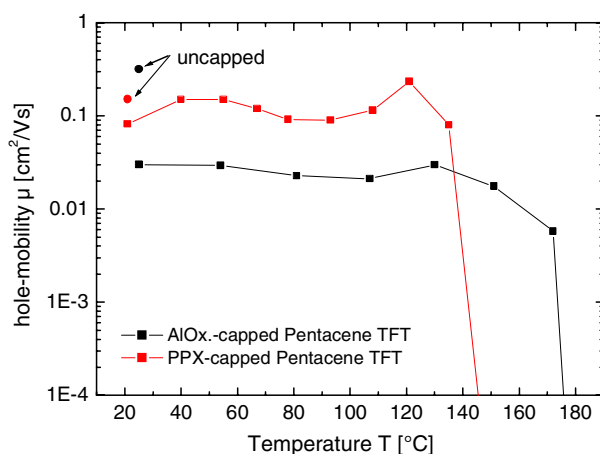


Figure 2. Temperature-dependence of the hole-mobility of an aluminum oxide- (black curve) and PPX-capped (red curve) pentacene thin film transistor. For comparison also the mobilities before encapsulation are shown.

In Figure 2 the hole-mobilities of the aluminum oxide and PPX capped pentacene TFTs are plotted as a function of temperature. In addition the mobilities for the uncapped TFTs are shown. The mobilities are estimated from the transfer characteristics of the TFTs. In the case of the aluminum oxide capped pentacene TFT the mobility is decreasing by one order of magnitude from $0.3 \text{ cm}^2/\text{Vs}$ to $0.03 \text{ cm}^2/\text{Vs}$ by providing the TFT with the capping layer. This observation is presumably due to damaging of the organic transport layer during the sputter process. If the temperature is raised the mobility stays almost constant up to temperatures of $130 \text{ }^\circ\text{C}$ followed by a decrease in the mobility and by the electrical breakdown of the transistors at $175 \text{ }^\circ\text{C}$. Encapsulating the device by PPX does not lead to a change of the device performance at RT, as the mobility is almost similar to that of the uncapped case. This indicates the PPX capping to be more suited to conserve the device performance of the pristine pentacene transistor. If the device is heated up a similar temperature dependence of the hole-mobility can be observed as in the case of the aluminum oxide encapsulated device, the breakdown in case of PPX capping occurs already at $140 \text{ }^\circ\text{C}$.

We analyzed the thermal stability of the pentacene thin films by thermal desorption spectroscopy. In the case of the uncapped pentacene thin film the desorption starts at about $80 \text{ }^\circ\text{C}$, ends at $110 \text{ }^\circ\text{C}$ and indicates desorption kinetic of 0^{th} order. In contrast the thermal stability of the encapsulated organic films is strongly enhanced. The PPX-capped pentacene film starts to desorb at $\sim 160 \text{ }^\circ\text{C}$, for AlOx.-capping the desorption process is shifted even to higher temperatures of $200 \text{ }^\circ\text{C}$. The TDS peaks belonging to the encapsulated films are expanded over a broader temperature range of about $50 \text{ }^\circ\text{C}$, which shows that the desorption-process is kinetically limited by the capping layer.

Complementary studies by x-ray diffraction were performed in order to correlate the observed transport behavior with the structural properties of the pentacene films. The pentacene/ SiO_2 reference samples were examined by x-ray diffraction before and after encapsulation and after heating them simultaneously with the transistors. No changes in the

crystalline order could be observed. In addition, temperature-dependent x-ray measurements were performed, presented in Figure 3, where the relative intensities of the first order Bragg peaks are shown as a function of temperature for uncapped, PPX- and AlOx.-capped pentacene thin films.

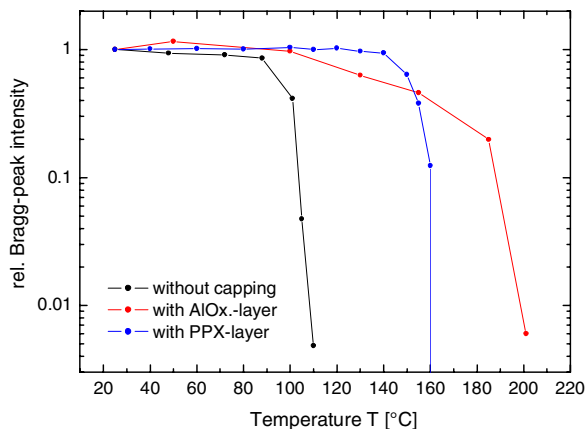


Figure 3. Relative Bragg-peak intensities of pentacene thin films on native SiO₂. without capping and with PPX- or AlOx.-encapsulation as a function of temperature. The capped organic films remain crystalline on the substrate even more than 50 °C above the desorption point of uncapped pentacene.

The crystalline order of the uncapped pentacene film vanishes at about 100 °C, while the thermal stability of the encapsulated films is enhanced to temperatures of 150 °C for PPX- and 190 °C for AlOx.-capping. No changes in the Bragg peaks of the PPX-capped pentacene film can be observed up to temperatures just below the complete breakdown of film crystallinity. In the case of the AlOx.-capped samples a slight decrease in the crystallinity occurs already in a temperature range between 110 °C and 190 °C. Furthermore the breakdown temperatures of the crystallinity are almost in agreement with the desorption temperatures determined by TDS. This indicates that neither decomposition nor desorption of the pentacene film takes place up to these temperatures. These observations together with the temperature-dependent electrical measurements show that the decrease of the device performance at elevated temperatures is not due to a degradation of the organic layer but most probably originates from the encapsulated transistor-structure itself, for example by the dewetting of the organic molecules at the source/drain contacts [9], which might reduce the charge injection or by the migration of gold atoms from the electrodes into the channel [12].

CONCLUSIONS

We have shown by combined thermal desorption spectroscopy, x-ray diffraction and TFT-measurements, that the thermal stability of pentacene thin films can be strongly enhanced by providing them with a capping layer. The point of desorption can be shifted by about 60 °C

for PPX- and 150 °C for AlO_x-capping with respect to the uncapped film. Moreover, the crystalline order of the organic layer is conserved up to these temperatures. For both encapsulation materials a field-effect can be demonstrated for pentacene TFTs upon capping. However, where the mobility is reduced by one order of magnitude in the case of AlO_x., presumably due to effects occurring during the sputter process, the mobility of the polymer capped TFT remains almost unchanged compared to the uncapped TFT. This indicates the PPX-capping to be more suited to conserve the device performance of the pristine pentacene TFTs.

Furthermore, we demonstrated successfully that a field-effect in encapsulated pentacene TFTs is possible up to a temperature of 140 °C for PPX- and 170 °C for AlO_x-capping. The limiting factor on the device performance at these elevated temperatures is the stability of the capped transistor structure rather than that of the organic material itself. We demonstrated that capping offers a universal approach to use OTFTs in applications where the temperature is the limiting factor for device operation.

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