Organic small molecule field-effect transistors with Cytop™ gate dielectric: eliminating gate bias stress effects

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We report on organic field-effect transistors with unprecedented resistance against gate bias stress. The single crystal and thin-film transistors employ the organic gate dielectric Cytop™. This fluoropolymer is highly water repellent and shows a remarkable electrical breakdown strength. The single crystal transistors are consistently of very high electrical quality: near zero onset, very steep subthreshold swing (average: 1.3 nF V/(dec cm²)) and negligible current hysteresis. Furthermore, extended gate bias stress only leads to marginal changes in the transfer characteristics. It appears that there is no conceptual limitation for the stability of organic semiconductors in contrast to hydrogenated amorphous silicon.

Field-effect mobilities in organic thin-films as high as in hydrogenated amorphous silicon (a-Si:H) have been achieved for some ten years now. The main advantage of organic semiconductors is the easy deposition by thermal evaporation or printing. Early works employed Si/SiO₂ substrates for convenience, and the device characteristics significantly improved after Lin et al. suggested to render the SiO₂ surface hydrophilic with the self-assembling agent octadecyltrichlorosilane (OTS). To fully exploit the potential of organic semiconductors, however, it is of great importance to employ easily processable (organic) gate insulators. Thus, the search for suitable organic dielectrics has intensified. Refs. 2 and 3 are recent summaries.

One of the last obstacles to be overcome for a commercialization of organic thin-film transistors is gate bias stress effects. Switching the devices on for some time leads to a reduction in current at a given gate voltage. Gate bias stress effects can result in a significant difference between the forward and reverse sweep and have often been studied by applying a fixed gate voltage for an extended time, followed by a measurement of the shift of the transfer characteristic. The causes of gate bias stress effects are not yet completely identified. The effects are thought to be due to the trapping and release of charge carriers on a time scale comparable to the measurement time. Mounting evidence indicates that water in the dielectric-semiconductor interface region can cause gate bias stress effects. 6

In this letter we report on combinations of small molecule organic semiconductors and an organic spin-on dielectric that yield field-effect transistors with exceptionally high quality characteristics and stability. The transistors have a bottom gate structure with an amorphous fluoropolymer (Cytop™) as gate dielectric. This fluoropolymer is highly transparent, in contrast to ordinary teflon, and its relative permittivity is ε₂ = 2.1 ± 0.2. Cytop™ has previously been used in field-effect transistors with a polymeric semiconductor in a top gate structure. We demonstrate this favorable material in combination with two small molecule semiconductors: rubrene and pentacene. The device stability was evaluated by applying a gate bias for extended periods of time.

The devices were fabricated as follows: ITO coated glass slides served as substrate and gate electrode. For the insulating layer, Cytop CTL-809M (solvent: CT-Solv.180) from Asahi Glass, Japan was spun-coated onto the ITO and dried for one hour at 90°C. The thickness of the insulating layer was determined for each sample with a surface step profiler. The films are 430 to 700 nm thick, which gives a gate capacitance of Cg = 4.4 to 2.7 nF/cm². Leakage current measurements on a typical sample (457±10 nm thick) show current levels below 1 µA up to 450 V, above which the dielectric breaks down. 12 450 V correspond to an applied field of 9.8 MV/cm and the current density at this field is 2.7 x 10⁻⁶ A/cm². This is remarkably good for an organic insulator and is better than the thermally grown SiO₂ that we generally use. The RMS roughness of the insulator was investigated by AFM and is ~ 0.6 nm. Water contact angles are between 110° and 116° (average: 112°).

Rubrene and pentacene single crystal field-effect transistors (SC-FETs) were made by evaporating 30 nm thick gold source and drain contacts onto the fluoropolymer in high vacuum. The single crystals were grown separately by physical vapor transport with argon as carrier gas. 13 The crystals were placed on the prefabricated substrates in air. Pentacene thin-film transistors (TFTs) were made by evaporating a 50 nm thick pentacene film through a shadow mask onto the Cytop™ in high vacuum (base pressure 10⁻⁸ mbar). The thin-film devices were completed by evaporating gold electrodes. All transistor measurements were carried out in a He atmosphere (H₂O, O₂ < 0.5 ppm) with a HP 4155A semiconductor parameter analyzer. The step width was 0.5 V and the integration time was 20 ms (medium) with a zero delay time between the voltage steps. The measurement of a transfer characteristic (forward and reverse sweep) took ~ 70 s.

The excellent performance of the devices is shown in Fig. 1. The transfer characteristics from a rubrene SC-
old regime however, the hysteresis is not increased.

We made 17 rubrene SC-FETs on 7 substrates with Cytop films, and the crystals were grown in 4 different runs. All transistors, except for a pathologic one, have a steep subthreshold swing, a near zero onset voltage and a very small hysteresis. The normalized subthreshold swings from the 16 devices are between 0.75 and 2.6 nF V/(dec cm$^2$) with an average value of 1.3 nF V/(dec cm$^2$). These values are among the best values for an organic transistor obtained to date. In some cases, there is a slightly increased hysteresis in the on-current.

The advantages of the material combinations become striking in gate bias stress studies. We have applied a gate voltage to the three devices in Fig. 1 for a prolonged time. After the initial transfer characteristic measurement, a gate bias of $V_g = -70$ V was applied for two hours. After a two hour relaxation period, a gate bias of $V_g = +70$ V was applied. During the stress periods, the source was grounded and the drain potential was held at 0 V to ensure homogenous gate stress. The drain current depends (approximately) quadratically on the effective gate voltage and is very sensitive to changes induced by a two hour stress period. Bias stress experiments were carried out in the dark.

For the rubrene SC-FET, Fig. 4 shows the initial characteristic, the characteristic measured after 2 hours of negative bias and after 2 hours of positive bias. The device is hardly influenced by the long application of a gate bias. There are only marginal changes in the transfer characteristic. After negative stress, there is a very small shift of the onset voltage to more positive voltages, accompanied by a small increase in current hysteresis and a small decrease in on-current. For the pentacene SC-FET, the observations are similar. When compared to the rubrene device, the shift of the onset voltage due to bias stress is even smaller but the decrease in on-current is somewhat more pronounced (3.8 % at $V_g = -70$ V). In contrast, in similar experiments with single crystals of rubrene or pentacene on OTS-treated SiO$_2$, large shifts
FIG. 3: The rubrene single crystal device is highly stable against gate bias stress. The main panel shows the transfer characteristics measured at $V_g = -80$ V prior to the stress sequence (full black line), after two hours of gate bias stress at $V_g = -70$ V (dashed red line) and after subsequent gate bias stress at $V_g = +70$ V for two hours (dotted green line). The graph includes the forward and reverse sweep in all three cases. The inset shows the drain currents close to the onset voltage.

of the transfer characteristics are observed. For the pentacene TFT, a gate voltage of $V_g = -70$ V applied for two hours leads to a rigid shift of the curve by $-5.2$ V to more negative voltages.

The surface of the amorphous fluoropolymer proves to have a highly desirable quality: essentially no electrically active trap states form in combination with the organic semiconductors. Bias stress effects in SC-FETs are marginal, and thus long-lived states for holes are (almost) non-existent at the insulator surface. The absence of insulator surface states can also account for an improved subthreshold swing. It is remarkable that the insulator works very well with two different semiconductors, i.e., rubrene and pentacene. This may indicate that the absence of surface states is due to the absence (or low density) of a specific chemical species on the insulator surface. Gate bias stress effects in SC-FETs are known to be less severe when the hydrophilic SiO$_2$ is rendered hydrophobic with OTS (water contact angle of $90^\circ - 95^\circ$). The highly hydrophobic Cytop™ surface (water contact angle of $\sim 112^\circ$) leads to an (almost) complete elimination of gate bias stress effects. Water is a known cause of gate bias stress effects which can be eliminated by employing a highly hydrophobic Cytop™ gate insulator. The high reproducibility of the excellent device performance matches the reproducibly high water contact angle of the Cytop™ films.

For the pentacene SC-FET and TFT we have combined the same semiconductor and insulator. However, we observe that the TFT is less stable against bias stress than the SC-FET. Also the onset voltage of the TFT is more negative. These effects cannot be attributed to insulator surface states but should be due to localized states within the pentacene layer close to the dielectric-semiconductor interface.

In conclusion, this study highlights the generically high performance and high stability of small molecule organic semiconductors when combined with a suitable gate dielectric. FETs with rubrene and pentacene in combination with a fluoropolymer show excellent electrical characteristics, and they are hardly affected by long-term gate bias stress. It seems that there is no conceptual limitation for the stability of organic semiconductors in contrast to a-Si:H, where the diffusion of hydrogen leads to gate bias-induced metastable defects.

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