Electrical instabilities in organic semiconductors caused by trapped supercooled water

H. L. Gomes[a] and P. Stallinga
Universidade do Algarve, Faculdade de Ciências e Tecnologia, Campus de Gambelas, 8005-139 Faro, Portugal

M. Cölle and D. M. de Leeuw
Philips Research, Prof. Holstlaan 4, 5656 AA Eindhoven, Netherlands

F. Biscarini
CNR—Istituto per lo Studio dei Materiali Nanostrutturati, Via P. Gobetti 101, I-40129 Bologna, Italy

(Received 31 August 2005; accepted 10 January 2006; published online 21 February 2006)

It is reported that the electrical instability known as bias stress is caused by the presence of trapped water in the organic layer. Experimental evidence as provided by the observation of an anomaly occurring systematically at around 200 K. This anomaly is observed in a variety of materials, independent of the deposition techniques and remarkably coincides with a known phase transition of supercooled water. Confined water does not crystallize at 273 K but forms a metastable liquid. This metastable water behaves electrically as a charge trap, which causes the instability. Below 200 K the water finally solidifies and the electrical traps disappear. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2178410]

There is considerable interest in instability mechanisms in organic field-effect transistors. The most important instability is the threshold voltage shift that is observed after prolonged application of a gate voltage; also known as bias stress. This effect shows up as a continuous decrease in the device current when the gate bias is kept constant. As a consequence, to maintain a constant current level, the gate voltage must be continuously increased, in other words the threshold voltage is constantly increasing.

This instability has been studied extensively because of its practical importance in the envisaged device applications, such as flexible displays and wireless identification transponders. Stress effects are commonly reported in the literature for a variety of transistors prepared using different techniques, different dielectric layers, as well as different organic semiconductors.[1–7] The effect has been explained as due to a slow trapping of charge carriers in defects of unknown origin.[3] It is known that the current degradation is faster when the devices are exposed to water vapor atmosphere,[4] moreover it has been also reported that the device electrical stability improves after heating the devices in high vacuum.[8,9]

Despite this evidence, a clear correlation between water contamination and stress has never been established. The reason lies in the observation that stress is absent below 200 K and starts only above that temperature. Furthermore, there are no pronounced effects near the well-known critical temperature of 273 K. In order to establish a relation between water and stress, we compare the electrical behavior of a sample in its as-grown state, with its electrical characteristics after being deliberately exposed to water vapor. As a sensitive probe, we use the temperature dependence of the device current for a particular stable sample.

Transistor test substrates were heavily n-doped silicon wafers with a thermally grown SiO_2 insulating layer (200 nm) and patterned gold as the source and drain electrodes. These electrodes provide a channel length of 10 μm and a channel width of 10 000 μm. The substrates were passivated by hexamethyldisilazane before deposition of the active layer. Sexithiophene thin films were deposited by thermal sublimation in an ultrahigh vacuum organic molecular beam deposition apparatus, base pressure of 10^{-9} mbar. During the deposition, the sample substrate was held at 150 °C. Poly(3-hexythiophene) and polyarylamine thin films were deposited by spin coating. The polyarlylamine device was subsequently annealed in N_2 environment for 1 h at 100 °C. Film thickness varies between 20 nm for sexithiophene thin films to 57 nm for the polarlylamine film. Electrical measurements were carried out using a Keithley 487 picoammeter/voltage source and an Oxford temperature controller ITC 601. Wet-atmosphere exposure was carried out by bubbling dry N_2 through distilled water poured into a sealed flask. After this, the sample chamber was pumped to high vacuum for 20 min prior to any electrical measurements. The devices do not show contact problems, they have a threshold voltage in the range of 2–4 V and mobilities are of the order 10^{-3} cm^2 V^{-1} s^{-1}.

Figure 1 shows the temperature dependence of the drain-source current measured in the linear region for three different devices. The drain current initially increases exponentially with temperature, as expected. However, just at around 200 K, a change in slope is noticeable for all the devices. In the polyarylamine device the change is abrupt at 200 K causing a pronounced dip. In sexithiophene the slope starts to decrease at around 200 K and slowly continues to change, until finally the current decreases with the temperature giving rise to a maximum in the Arrhenius plot. For the poly(3-heylthiophene) the change is only visible as a decrease in slope starting to occur at 200 K. These changes at 200 K observed in the Arrhenius plots are due to a decrease in the drain-source current for a constant gate bias. The current decrease is caused by strong trapping, which depletes the sample from free charge carriers and is the origin of the

[a]Electronic mail: hgomes@ualg.pt

 © 2006 American Institute of Physics
Downloaded 28 Mar 2006 to 193.136.225.10. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

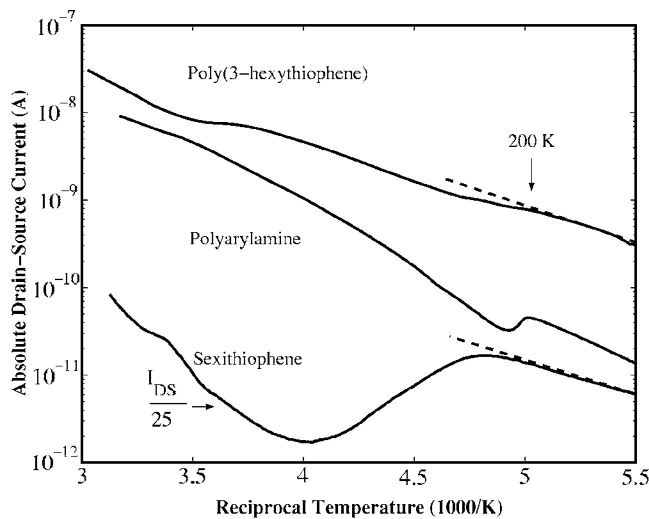

FIG. 1. Temperature dependence of the drain current for three transistor devices fabricated using different active layers. The curves were measured in he linear region (typical bias voltages V_G=−10 V and V_{DS}=−0.5 V). The heating rate was 2 K/min for all the curves. The sexithiophene related curve was shifted for clarity.

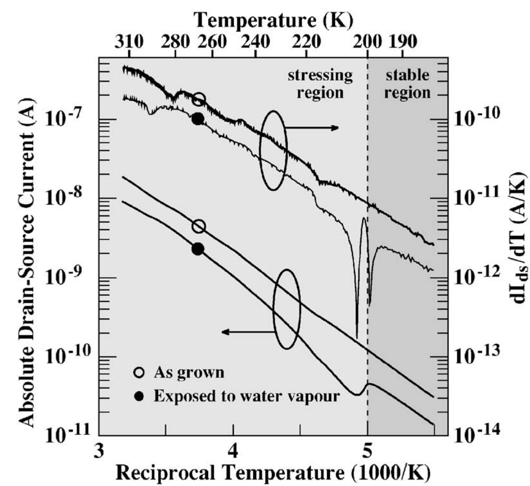

FIG. 2. The temperature dependence of the drain-source current measured in the linear region (V_{DS}=−1 V and V_G=−8 V) and plotted in Arrhenius form. The lines with open circles show the behavior of the as-grown device. The lines with filled circles show the behavior after exposure to water. To highlight the anomaly, the derivatives of the curves are shown in the top part of the figure.

stress effect. Below 200 K the device is stable. It is worth to mention, that the position in temperature (200 K) of the anomaly for a particular sample is independent of the heating rate and gate bias applied.

Near room temperature further changes are observed in the device current, caused again by carrier trapping. These trapping effects usually start to appear above 273 K and can become clearly visible for temperatures around 280–290 K.

It is remarkable that the changes are occurring coincidently at 200 K, for small molecules deposited by vacuum sublimation (sexithiophene) as well as polymers deposited by spin coating [poly(3-hexylthiophene) and polyarylamine]. Furthermore, a similar transition temperature was also reported for poly(3,3‴-dialkyl-quarterthiophene) by Salleo and Street,[10] who observe that the device current exhibits its fastest decay at 220 K.

Although, all the devices show a common anomaly at 200 K, Fig. 1 also shows some differences in the magnitude of the process. While in the sexithiophene device, trapping is quite pronounced, in the poly(3-hexylthiophene) the effect is relatively weak. The difference may be related to different processing and handling conditions (of materials and substrates) as well as due to different morphologies. These effects are under study.

The fact that the transition temperature is relatively independent of the processing methods and materials provides evidence that the transition is related with an extrinsic and very common impurity, which we will show is water.

To prove that water was responsible for the process a particular stable sample of polyarylamine (without anomalous behavior) was selected and deliberately exposed to water vapor. It is important to note that in the as-grown stage, the polyarylamine device was annealed in N_2 environment for 1 h at 100 °C.

Figure 2 shows the experimental data represented again in an Arrhenius plot. The sample in its as-grown state indicated by an open circle exhibits almost a perfect straight line. The absence of anomalies in the temperature dependence of the current reflects a high electrical stability. The curves labelled with filled circles show the behavior of the device after deliberately being exposed to water vapor for 24 h and pumped again in high vacuum prior to the electrical measurements. An anomalous current decrease appears suddenly at around 200 K. To highlight the effect, the same data are plotted as a derivative of the current as a function of temperature, as seen in the upper two lines in Fig. 2

Water molecules, when confined, are unable to form a crystalline structure; thus water remains fluid, well below 273 K. It is then called supercooled water or glassy water. There is a rich and extensive literature about the behavior of supercooled water, for instance see the review in Ref. 11. In the context of the present work, the most relevant is that this metastable form of water has a phase transition at around 200–220 K.[12–17] In between 200 and 273 K the water is a metastable mixture of the two liquid phases.

Apparently, water above 200 K already can trap charge carriers in a very effective way. Furthermore, this means that at critical temperature of 273 K we do not have a conventional solid-liquid phase transition, but something like a change from a metastable liquid form to a liquid form of water and the trapping efficiency is not much altered by this transition. This may explain that at 273 K the changes are not as significant as expected even after water exposure (see Fig. 2). The fact that the agent causing stress is a metastable impurity may explain the complex kinetics of the trapping process, which was tentatively explained by Salleo and Street.[10]

The finding that a water phase transition gives rise to anomalies in the electrical properties may be relevant to other research fields and can possible account for a number of anomalies being published in the literature. Without being exhaustive, examples worth mention are several studies in high T_c superconductors reporting anomalies at 200–220 K and tentatively explained as a phase transition of unknown origin.[18–20]

In summary, we demonstrated that trapped water is likely to be the main source for the electrical instability known as stress as observed in organic based transistors. Liquid forms of water provide efficient traps for charge carriers and water confined in a matrix of an organic semicon-

Downloaded 28 Mar 2006 to 193.136.225.10. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

ductor can remain fluid at temperatures as low as 200 K. This finding is in agreement with observations that stress effects are suppressed or substantially reduced after annealing.[8] We are convinced that research should be oriented to prevent the incorporation of water, either by introducing hydrophobic capping layers or by molecular design of new materials less susceptible to water incorporation.

The authors wish to thank the Portuguese Foundation for Science and Technology (FCT) for financial support of this work (Research Unit 631-CEOT).

[1]W. A. Schoonveld, J. B. Oostinga, J. Vrijmoeth, and T. M. Klapwijk, Synth. Met. **101**, 608 (1999).
[2]A. R. Brown, C. P. Jarret, D. M. de Leeuw, and M. Matters, Synth. Met. **88**, 37 (1997).
[3]R. A. Street, A. Salleo, and M. Chabinyc, Phys. Rev. B **68**, 085316 (2003).
[4]M. Matters, D. M. de Leeuw, P. T. Herwig, and A. R. Brown, Synth. Met. **102**, 99 (1999).
[5]H. L. Gomes, P. Stallinga, F. Dinelli, M. Murgia, F. Biscarini, D. M. de Leeuw, T. Muck, J. Geurts, L. W. Molenkamp, and V. Wagner, Appl. Phys. Lett. **84**, 3184 (2004).
[6]H. L. Gomes, P. Stallinga, F. Dinelli, M. Murgia, F. Biscarini, D. M. de Leeuw, M. Muccini, and K. Müllen, Polym. Adv. Technol. **16**, 227 (2005).
[7]T. Muck, M. Leufgen, A. Lebib, T. Borzenko, J. Geurts, G. Schmidt, L. W. Molenkamp, V. Wagner, and H. L. Gomes, Mater. Res. Soc. Symp. Proc. **771**, L10.3.1 (2003).
[8]T. Sekitani, S. Iba, Yusaku Kato, Y. Noguchi, T. Someya, and T. Sakurai, Appl. Phys. Lett. **87**, 073505 (2005).
[9]P. Stallinga, H. L. Gomes, F. Biscarini, M. Murgia, and D. M. de Leeuw, J. Appl. Phys. **96**, 5277 (2004).
[10]A. Salleo and R. A. Street, Phys. Rev. B **70**, 235324 (2004).
[11]P. G. Debenedetti, J. Phys.: Condens. Matter **15**, R1669 (2003).
[12]O. Mishima and H. E. Stanley, Nature (London) **392**, 164 (1998).
[13]R. Bergman and J. Swenson, Nature (London) **403**, 283 (2000).
[14]L. Liu, A. Faraone, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, J. Phys.: Condens. Matter **16**, S540 (2004).
[15]R. Torre, P. Bartolini, and R. Righini, Nature (London) **428**, 296 (2004).
[16]A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, J. Chem. Phys. **121**, 10843 (2004).
[17]M.-C. Bellissent-Funel, Europhys. Lett. **42**, 161 (1998).
[18]X. H. Chen, T. F. Li, R. P. Wang, Y. M. Qiu, K. Q. Ruan, L. Z. Cao, L. Shi, Y. B. Jia, G. E. Zhou, and Y. H. Zhang, J. Phys.: Condens. Matter **9**, L75 (1997).
[19]K. Fujishiro and Y. Uesu, J. Phys.: Condens. Matter **8**, 6435 (1996).
[20]R. Jin, J. He, J. R. Thompson, M. F. Chisholm, B. C. Sales, and D. Mandrus, J. Phys.: Condens. Matter **14**, L117 (2002).

Downloaded 28 Mar 2006 to 193.136.225.10. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp