

# Mobile Ionic Impurities in Poly(vinyl alcohol) Gate Dielectric: Possible Source of the Hysteresis in Organic Field-Effect Transistors\*\*

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Threshold voltage shifts in organic field effect transistors (OFETs) have been reported frequently.<sup>[1–13]</sup> Cyclic sweeps of the gate voltage in OFETs reveal a hysteresis in the transfer characteristics (drain-source current versus gate-source voltage) thereby unfolding an electrical instability of the transistor element. On the one hand bistable transistors with a non-volatile hysteresis in the transfer characteristics may be used in organic memory elements,<sup>[2,7–9,12]</sup> whereas on the other hand hysteresis free transistors are desired in integrated organic circuits. Therefore understanding the causes of these electrical bi- or instabilities in organic field-effect devices is of primary interest.

OFETs using charged electrets or ferroelectric-like gate dielectrics (e.g., see [7,8,12,14]) show a hysteresis which is normally attributed to the intrinsic properties of these materials. In polymer dielectrics without an intrinsic hysteresis such as poly(vinyl alcohol) (PVA), gate voltage induced hysteresis are often interpreted in terms of electrostatic screening of trapped charge carriers released under the influence of the electric field between the gate and the source/drain electrodes. Experimental results so far revealed a fairly complex picture of this “bias-stress” effect where the detailed mechanisms involved are not yet fully understood. Several publications report evidences of a charge trapping process in the organic

semiconductor close to the semiconductor/dielectric interface.<sup>[5,6]</sup> Lindner et al. supposed that the origin of the hysteresis in organic devices is a combination of slow transport (polarons or mobile ions) with a reaction other than trap recharging, e.g., a direct polaron-bipolaron reaction or a complex formation reaction of polarons / bipolarons with counterions.<sup>[11]</sup> Bias-stress experiments with pentacene on various inorganic dielectrics indicate a reversible structural change of the semiconductor.<sup>[4]</sup> A substantial number of experiments demonstrate an influence of the gate dielectric material on the formation of hysteresis effects. Transistors with a polymer gate dielectric are more likely to show a pronounced hysteresis than transistors with an inorganic gate dielectric.<sup>[3,15]</sup> It has been reported that hydroxyl groups in the form of silanols at the SiO<sub>2</sub>-dielectric/semiconductor interface can work as electron traps<sup>[10]</sup> which can be eliminated by a thin alkane interlayer.<sup>[16]</sup> In many organic dielectrics hydroxyl groups are present in large numbers, either as integral part of the chemical structure and/or as impurities remaining from the process of synthesis. Such hydroxyl groups therefore were suspected of being responsible for the hysteresis effect in many OFET configurations.<sup>[13,16]</sup> Lee et al. conclude that the increase of hydroxyl groups in polymer dielectrics equally increases electron trapping sites which in turn cause a large hysteresis in OFETs, but as they also discussed, the drain current as well as the gate leakage current increased with increasing hydroxyl density, which may be in contradiction with the proposed idea of immobilized carriers.<sup>[13]</sup>

Polymer dielectrics are often hosts for mobile ions. It has been demonstrated for example that mobile Na<sup>+</sup> ions may diffuse from an underlying substrate into organic semiconductors, like pentacene or poly(3-hexylthiophene) under the influence of an applied voltage. Thereby they cause an increase of the current through the semiconductor and, additionally, a current-voltage hysteresis.<sup>[17]</sup> The finding that mobile ions in semiconductors alter their electrical performance is not new.<sup>[18–20]</sup> p-n junction devices, called flexodes, with a variable current-voltage (*I*-*V*) characteristics resulting from a reversible drift of Li<sup>+</sup> ions were suggested in 1963.<sup>[19]</sup> Two years later, small traces of mobile alkali ions in SiO<sub>2</sub> gate dielectrics were reported to cause significant problems in semiconductor devices.<sup>[20]</sup> In fact, the practical application of MOSFETs was delayed in the early 1960s because of severe gate bias instability problems caused by mobile ionic oxide charges like Na<sup>+</sup>,

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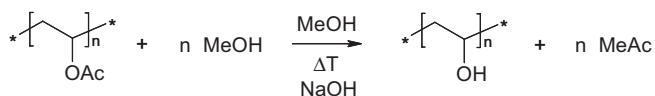
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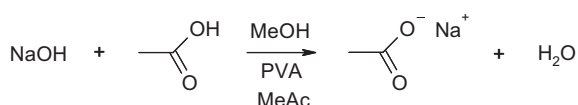
$\text{Li}^+$ ,  $\text{K}^+$  and perhaps  $\text{H}^+$ .<sup>[21]</sup> In OFETs, the presence of ions in the semiconductor can improve charge injection,<sup>[22]</sup> whereas mobile ions in the dielectric might be responsible for the emergence of hysteresis effects.<sup>[23]</sup> While hysteresis effects in dielectrics due to mobile ionic charge carriers have been neglected to a large extent in OFET research, they are well known in the literature on dielectric materials.<sup>[24,25]</sup>

In order to show the importance of mobile ionic impurities for bias voltage instabilities in OFETs we investigated devices with  $\text{C}_{60}$  as the organic semiconductor and poly(vinyl alcohol) (PVA) as the gate dielectric. PVA was chosen because sodium acetate, which provides a source of mobile sodium ions, is a natural by-product in the industrial polymerization reaction of PVA (Scheme 1). Using top contact OFET devices with two different impurity levels in the PVA gate dielectrics we show that the hysteresis is enhanced by increasing the amount of these mobile ionic impurities. By measuring cyclic transfer characteristics at different temperatures and by correlating the results with low frequency dielectric spectra in metal-insulator-metal (MIM) configurations with ion-blocking Al electrodes we observe the clear correlation between ion concentration and the hysteresis in OFETs.

1.) Methanolysis (Transesterification):



2.) Neutralization:



**Scheme 1.** Methanolysis (transesterification) of poly(vinyl acetate) reacting with methanol (MeOH) leads to PVA and methyl acetate (MeAc). Sodium hydroxide (NaOH) catalyzes the reaction and is subsequently neutralized with acetic acid leading to sodium acetate (NaAc) and water [26].

The industrial production of poly(vinyl alcohol) starts with poly(vinyl acetate) dissolved in methanol (MeOH). The poly(vinyl acetate) reacts with MeOH leading to PVA and methyl acetate (MeAc). This reaction is catalyzed by sodium hydroxide (NaOH). After the reaction, the basic solution is neutralized with acetic acid resulting in sodium acetate (NaAc) and water (Scheme 1).

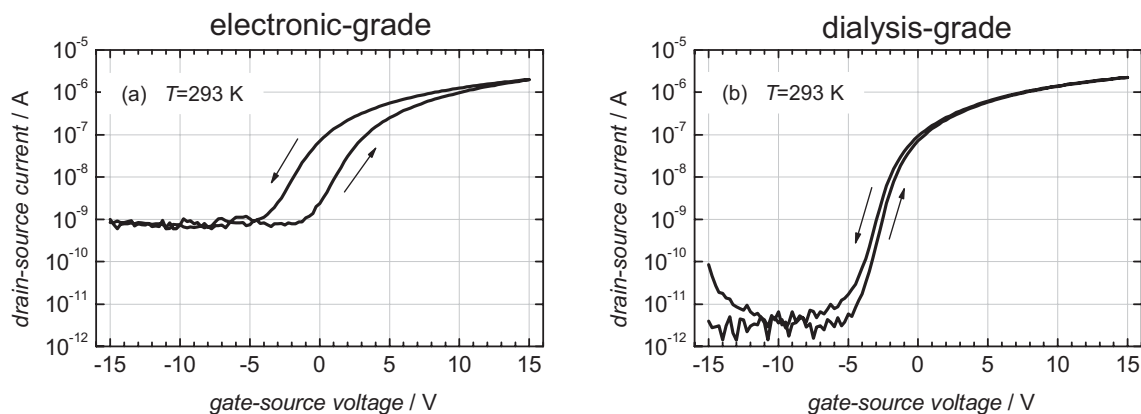
By varying the NaOH concentration, the reaction temperature and the reaction time, it is possible to adjust the residual acetyl group content.<sup>[26]</sup> An important step after the alcoholysis is the removal of the by-product NaAc. The quality of PVA is defined by the concentration of the remaining NaAc ions after purification. We used two different grades of PVA in our experiments. The “electronic-grade” PVA (the cleanest available PVA grade which is produced for microelectronic

applications) with a NaAc content below 0.09 mass % was used as received from the manufacturer. In addition, we purified this electronic-grade PVA by dialysis to a “dialysis-grade” PVA with a NaAc content below 0.004 mass % (detection limit of the atomic absorption spectrometer (AAS) used). The two different grades of PVA were spin cast from aqueous solution to form 1  $\mu\text{m}$  thick gate dielectrics in  $\text{C}_{60}$  based OFETs. Typical transfer characteristics of such transistor devices, measured at room temperature, are depicted in Figure 1. The drain-source voltage of  $V_{\text{DS}} = +10 \text{ V}$  was fixed and starting with a gate voltage of  $V_{\text{G}} = -15 \text{ V}$  the gate voltage was continuously increased up to +15 V in successive steps of 0.25 V and subsequently reduced to -15 V with a decrement of -0.25 V steps. With a cycle period of 847 s the transfer characteristics of most devices stabilize after 3 to 4 cycles. For clarity only a typical transfer characteristic is presented. In these devices the gate leakage current levels were below 10 nA.

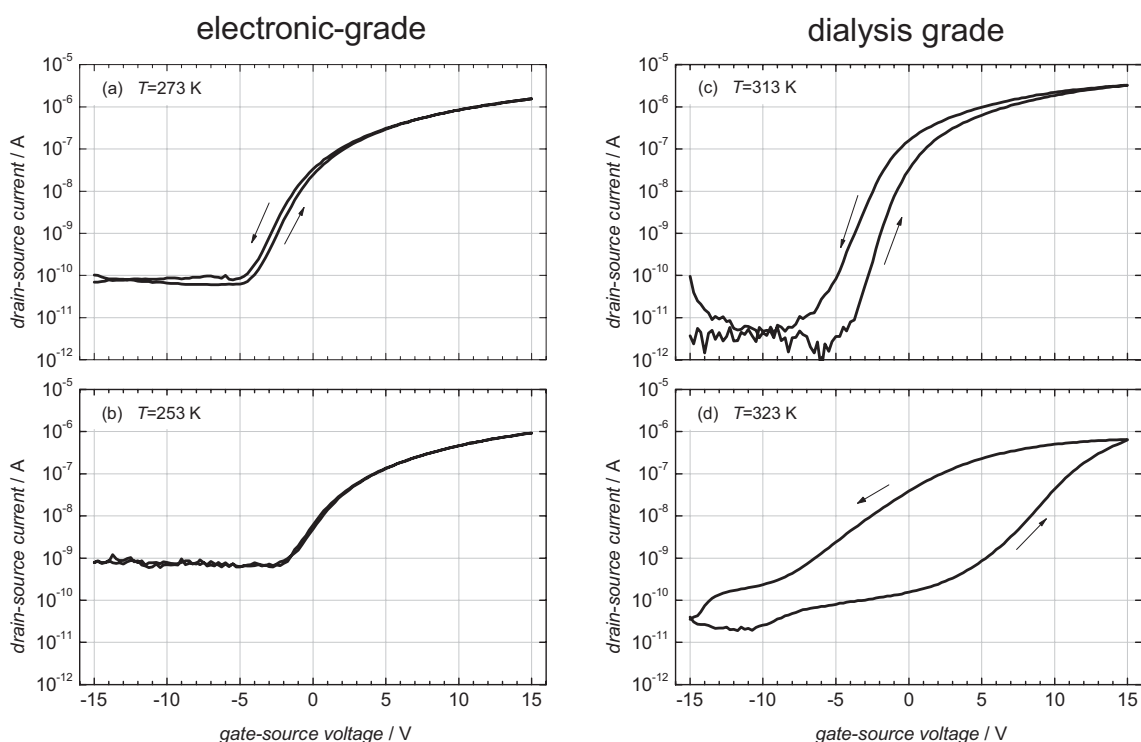
OFETs fabricated with electronic-grade PVA always show a pronounced hysteresis at room temperature. However, transistors built with the dialysis-grade dielectric are almost hysteresis free. Given the structure of PVA (Scheme 1) with many hydroxyl groups we therefore conclude that the presence of hydroxyl groups in the dielectric is not sufficient to explain the appearance of hysteresis effects. Rather the concentration of NaAc in the dielectric has a considerable impact on the threshold voltage and on the hysteresis in the OFET’s transfer characteristics.

Figure 2a and b show measurements at two different temperatures. At 273 K the hysteresis of the electronic-grade transistor substantially decreased and almost disappeared at 253 K. The transfer characteristics of OFETs using a dialysis-grade PVA showed a pronounced hysteresis at 323 K as demonstrated in Figure 2c and d showing cyclic  $I$ - $V$  measurements of the device at 313 and 323 K, respectively.

In order to study the molecular dynamics of ion migration in the gate-dielectric, capacitors with the different PVA grades were prepared in a metal-insulator-metal (MIM) configuration. Dielectric spectroscopy measurements were performed in the low frequency regime from 0.5 mHz up to 10 kHz in an Ar-atmosphere at several temperatures. Figure 3 shows the dielectric spectra of the two PVA grades at room temperature. In order to compare the permittivities of the two devices, the data points in Figure 3a are normalized to unity at a test-frequency of 100 Hz. Thereby slight differences in the sample geometry, especially in the thickness of the dielectric layers are cancelled. Since the film-thickness of the samples varied across the electrode area, a precise determination of the complex permittivity,  $\epsilon = \epsilon' - i\epsilon''$ , is fairly difficult. A good estimation of the real part of the permittivity for such PVA materials is  $\epsilon' \approx 6.1$  at 100 Hz. Between 100 mHz and 10 kHz the dielectric spectra are virtually identical for both PVA grades. Below 100 mHz the dielectric permittivity in both samples increases with decreasing frequency correlated with the impurity levels of the PVA grades: the permittivity of electronic-grade capacitors grows faster than the permittivity of dialysis-grade capacitors at low frequencies.



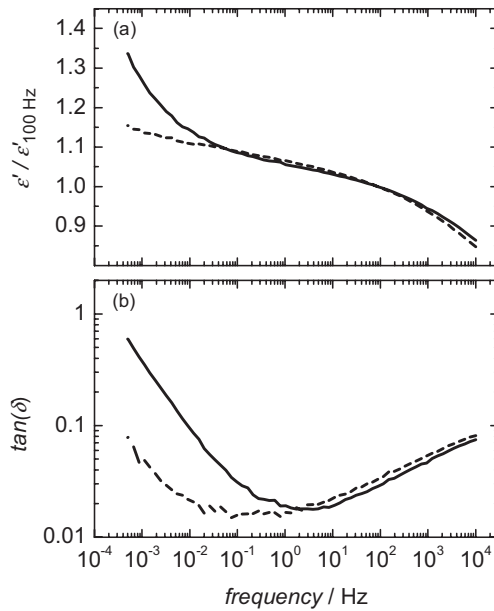
**Figure 1.** Transfer characteristics of  $C_{60}$  field effect transistors with two different grades of poly(vinyl alcohol) gate dielectrics at room temperature. The transistor with the electronic-grade dielectric (NaAc content < 0.09 mass %) shows a clear hysteresis (a). The transistor with the dialysis-grade dielectric (NaAc content < 0.004 mass %) shows almost no hysteresis (b).



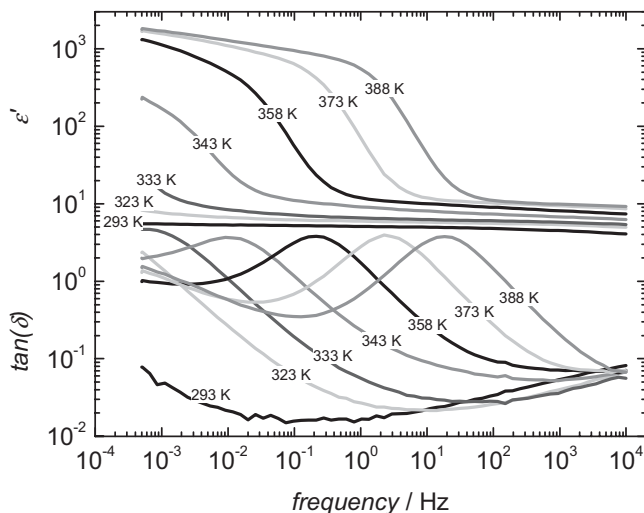
**Figure 2.** Transfer characteristics of  $C_{60}$  field effect transistors with two different grades of PVA gate dielectrics at different temperatures. The hysteresis of the transistor with the electronic-grade dielectric (NaAc content < 0.09 mass %) is significantly reduced at 273 K (a) and almost disappears at 253 K (b). The transfer characteristics of the transistor with the dialysis-grade dielectric opens up and shows a distinct hysteresis at 313 K (c) which becomes very broad at 323 K (d).

Figure 4 shows the dielectric spectra of a dialysis grade PVA capacitor at several temperatures between room temperature and 388 K. The real part of the dielectric permittivity reveals a low-frequency increase by more than two orders of magnitude; the loss angle  $\tan(\delta) = \epsilon''/\epsilon'$  shows distinct maxima and starts to increase again at the lowest frequencies measured. Such a low frequency behavior cannot be explained by a dipolar relaxation mechanism, it clearly demonstrates the presence of charge carriers with low mobility. These carriers move with the applied

electric field leading to charge separation within the electrically neutral dielectric, giving rise to strong electrode effects at the external dielectric-metal interface or Maxwell-Wagner polarization at internal interfaces. Both effects contribute to the increase in the permittivity as described also in other reports.<sup>[27–29]</sup> The increase of both  $\epsilon'$  and  $\tan(\delta)$  at frequencies below the loss maximum, which both appear at sufficient high temperatures, are attributed to ion hopping conductivity with a broad distribution of relaxation frequencies.<sup>[30,31]</sup>

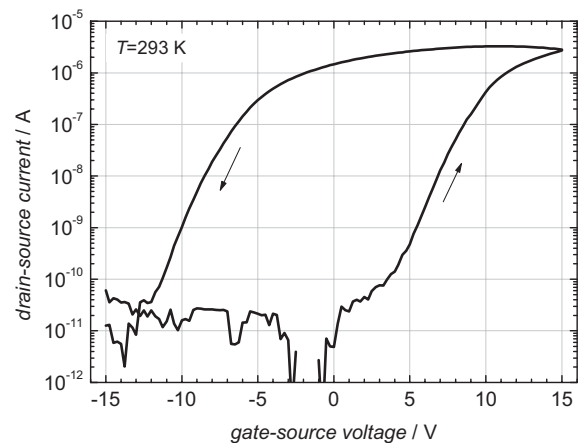


**Figure 3.** Dielectric spectra of the electronic-grade PVA (solid) and the dialysis-grade PVA (dashed) in a MIM configuration with Al electrodes at room temperature. The dialysis-grade PVA has at least a ten times lower NaAc content than the electronic-grade PVA.



**Figure 4.** Dielectric spectra of dialysis-grade PVA in a MIM configuration with Al electrodes at different temperatures (293 K, 323 K, 333 K, 343 K, 358 K, 373 K, 388 K). The dispersion in the real part of the dielectric function and the maximum in the loss angle shifts towards higher frequencies with increasing temperature. The measurements correlate well with the appearance of a hysteresis in dialysis grade PVA transistors at elevated temperatures.

The NaAc content of dialysis grade PVA is below 0.004 mass %, given by the detection limit of the used atomic absorption spectroscope (AAS). We suggest that the experimental results are related to thermally activated  $\text{Na}^+$  ion motion in the PVA dielectric under the influence of applied electric fields. This is further corroborated by measurements of



**Figure 5.** Transfer characteristics of  $\text{C}_{60}$  field effect transistor made with a PVA gate dielectric artificially impurified with 0.5 mass % NaAc.

PVA OFETs with an artificially increased amount of sodium acetate ions, as shown in Figure 5. Here the dialysis grade PVA was artificially impurified with 0.5 mass % NaAc, revealing a very wide hysteresis in the transistor characteristics at room temperature. The size of the hysteresis can be adjusted by artificially impurifying PVA with NaAc. Following the arguments and the results of early investigations in the 60's of the last century regarding the stability problems of Si based MOSFET devices (caused by  $\text{Na}^+$  ions in the  $\text{SiO}_2$  dielectric),<sup>[20]</sup> we further suggest that the change in the volume charge distribution within the PVA gate dielectric as well as the changes in the charge distribution at the organic semiconductor/dielectric interface affect the hysteresis by the field induced polarization of the dielectric. This in turn results in a bistable performance of the OFET device. Thus, it seems reasonable to assume that long-term stability of OFETs fabricated from solution based polymers might only be achieved with extremely high purified materials, especially when they have to operate in thermally fluctuating ambient environments.

### Experimental

We received the “electronic-grade” poly(vinyl alcohol) (PVA) from “Kuraray Specialities Europe GmbH” (Mowiol®40-88). The nominal residual sodium acetate content in this PVA is < 0.09 mass %. For the “dialysis-grade” PVA, a sample of the electronic-grade solution was further purified by dialysis: A dialysis tubing (Sigma–Aldrich, D0530) was filled with a solution of electronic-grade PVA and submerged into 18 MΩ water at room temperature for about 24 hours. Atomic absorption spectroscopy (AAS) measurements revealed a sodium acetate content of less than 0.004 mass % (detection limit) for the dialysis-grade PVA. For the artificially impurified PVA grade 0.5 mass % of sodium acetate (Sigma–Aldrich) were added to the dialysis grade PVA solution. Dielectric thin films with a thickness of approximately 1 μm were prepared from a 5 % solution in  $\text{H}_2\text{O}$  by spin coating on cleaned glass substrates with a bottom aluminum electrode (thickness 100 nm). For the OFETs a 100 nm thick  $\text{C}_{60}$  layer was thermally evaporated onto the PVA dielectric in high vacuum ( $p < 5 \times 10^{-6}$  mbar) at

a rate of  $0.16 \text{ nm s}^{-1}$ . To finalize the MIM and the OFET devices top aluminum electrodes with 100 nm thickness were thermally evaporated through a shadow mask. The channel length  $L$  of the OFETs is  $100 \mu\text{m}$  and the channel width  $W$  is 1 mm. The overlapping electrode area of the MIM capacitors is  $2.5 \text{ mm}^2$ . In the devices the gate leakage current levels typically were below 10 nA. The electrical characterization of all devices was performed in an inert environment: the OFETs were measured inside a nitrogen glove box and the MIM capacitors were mounted into a sealed sample chamber which was purged and filled with argon. An Agilent E5273A instrument was employed for the steady state current-voltage measurements. The dielectric spectroscopy data were obtained with a Novocontrol Alpha Analyzer.

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