Ionic Impurities in Poly(vinyl alcohol) Gate Dielectrics and Hysteresis Effects in Organic Field Effect Transistors

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ABSTRACT

Poly(vinyl alcohol) (PVA) is a water based dielectric often used as a coating layer in paper industry. Due to its water solubility PVA is also interesting as gate insulator in organic field effect transistors. Depending on the preparation of the PVA gate, transistors with and without hysteresis can be produced, with applications in organic electronic circuits or memory elements. In the production of PVA, a major side product is sodium acetate, an ionic salt not completely removed during industrial purification. Such ionic impurities likely influence the hysteresis in PVA based organic field effect transistors. While a hysteresis is desirable in memory elements, it is unwanted in transistors for electronic circuits. Ways to prepare transistors with a desired transfer characteristic are described, for example by using electronic grade products directly from the producer of PVA, or by emplyoing PVA purified by means of dialysis. Measurements are performed with metal-insulator-metal (MIM) structures and organic field effect transistors (OFETs), where Buckminsterfullerene C_{60} is employed as organic semiconductor.

INTRODUCTION

Solution based organic materials may be employed in roll to roll processing of organic field effect transistors [1-2]. Poly(vinyl alcohol) (PVA), a water based dielectric, is interesting as gate insulator in such devices. Depending on the preparation conditions, PVA based transistors have been produced with and without hysteresis in the transistor characteristics [3]. In transistors with as received PVA hysteresis effects are usually observed, while the hysteresis is significantly reduced when chemically cleaned PVA is used. Ionic impurities have been recently proposed to be the source of the hysteresis in PVA based transistors [3-5]. The assumption of mobile ions causing hysteresis in OFETs seems plausible, since polymers as well as many inorganic dielectrics are often hosts of mobile ions. It has been demonstrated for example that mobile Na^+ 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 simultaneously a current-voltage hysteresis [6]. The finding that mobile ions in semiconductors alter their electrical performance is also not new: it has been widely investigated in the 50's and 60's of the last century [7-10]. p-n junction devices, called flexodes, with a variable I-V characteristic resulting from a reversible drift of Li^+ ions were suggested in 1963 [8]. Two years later, small traces of mobile alkali ions in

SiO$_2$ gate dielectrics were reported to cause significant reliability problems in semiconductor devices [9]. In fact, the practical application of MOSFETs was delayed in the early 60s because of severe gate bias instability problems caused by mobile ionic oxide charges like Na$^+$, Li$^+$, K$^+$ and perhaps H$^+$ [10]. The impact of ions on OFETs is still a field of research: ions can improve charge injection [11] and mobile ions within the gate dielectric might be responsible for the emergence of a hysteresis in the transfer characteristics [12].

In this work we demonstrate the influence of mobile ionic impurities on bias voltage instabilities in OFETs. We present measurements of top contact OFETs with C$_{60}$ as the organic semiconductor and poly(vinyl alcohol) (PVA) as the dielectric. PVA is chosen because sodium acetate, which provides a source of mobile sodium ions, is a natural by-product in the polymerization reaction of PVA: the industrial production of PVA starts with poly(vinyl acetate) which is dissolved in methanol and converted to PVA by hydrolysis (alcoholysis). The catalyst for this synthesis is sodium hydroxide. By varying the catalyst concentration, reaction temperature and reaction time, it is possible to adjust the residual acetyl group content [13]. Important after the alcoholysis is the removal of the by-product sodium acetate. The final quality after cleaning is given by the remaining Na-acetate content which defines the grade of the PVA.

EXPERIMENT

We used four different grades of PVA for our experiments: We received the "normal grade" and the "electronic grade" PVA from "Kuraray Specialities Europe GmbH" (Mowiol®40-88). The nominal residual sodium acetate content in these PVAs is < 0.5 mass% and < 0.09 mass%, respectively. For the "dialysis grade" PVA, a sample of the electronic grade solution was further purified by dialysis (dialysis tubing Sigma Aldrich, D0530, submerged into 18 MΩ water at RT). 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 ("ionic grade"), sodium acetate (Sigma Aldrich) was added to the dialysis grade PVA solution. Dielectric thin films with a thickness of approximately 1 µm were prepared from a 5 % solution in H$_2$O by spin coating on cleaned glass substrates with a 100 nm bottom aluminum electrode. For the OFETs a 100 nm thick C$_{60}$ layer was thermally evaporated onto the PVA dielectric in high vacuum (p < 5x10^{-6} mbar) at a rate of 0.16 nm/s. 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 µm and the channel width W is 1 mm (Fig. 1). The overlapping electrode area of the MIM capacitors is 2.5 mm². The electrical characterization of all devices was performed in an inert atmosphere. An Agilent E5273A instrument was employed for the steady state current-voltage measurements. The dielectric spectroscopy data were obtained with a Novocontrol Alpha Analyzer.
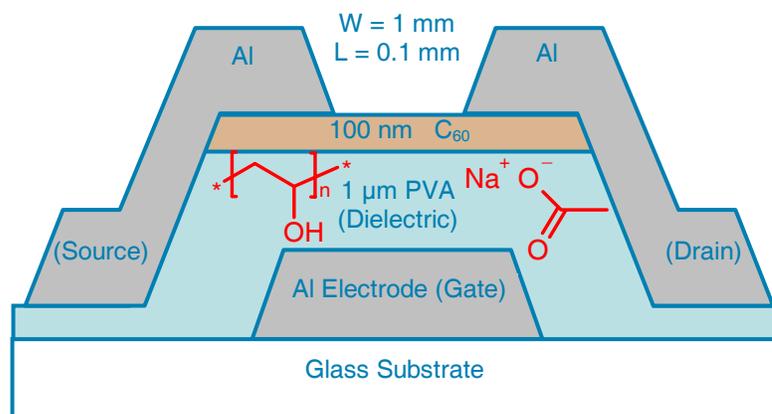
FIGURE 1: The structure of the investigated OFET.

DISCUSSION

Transistors fabricated with "normal grade" PVA always show (Fig. 2) a very pronounced hysteresis in the transfer characteristic at a certain sweep rate (in these investigatins 200 mV/s). Transistors with the same geometry using "electronic grade" PVA show a less pronounced hysteresis at the same sweep rate. Cleaning the "electronic grade" PVA by dialysis drastically decreases the amount of sodium acetate in the PVA solution below our detection limit and transitors built from this solution show almost no hysteresis at room temperature.
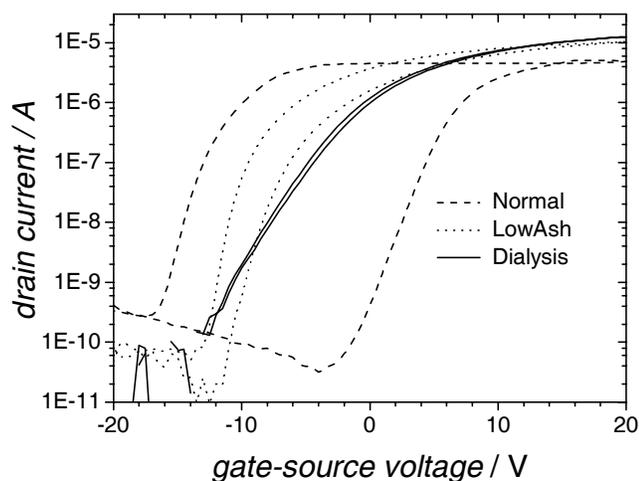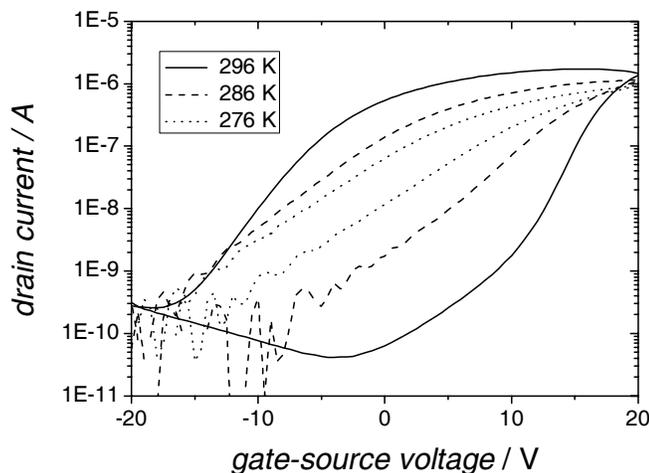

FIGURE 2: Transfer characteristics at RT of OFETs using different PVA grades (normal, electronic and dialysis) incorporating different amounts of sodium acetate (ions) in the dielectric.

Reducing the hysteresis by dialysis raises the question whether artificial impurification (putting ions into the PVA) will increase the hysteresis. Figure 3 (recorded at 296 K) shows a

OFET built from an "ionic grade" PVA which is a dialysis grade PVA having 10 mass% of sodium acetate added to the solution.

Dielectric spectroscopy measurements showed a strong temperature dependence of the mobility of the ions in the PVA [3]. Therefore we investigated the temperature dependence of the "ionic grade" OFET (Fig. 3): reducing the temperature only by a few degrees drastically decreases the hysteresis. This process is completely reversible: heating the OFET back to room temperature increases the hysteresis again.

FIGURE 3: Transfer characteristics of an OFET using an "ionic grade" PVA (dialysis grade PVA with 10 mass% sodium acetate added to the solution) at RT and at lower temperatures.

The main applications of organic electronics shall operate at room temperature, nevertheless the devices shall stand normal heating as can occur due to sunlight. Therefore we investigated the "dialysis grade" OFET at slightly elevated temperatures (Fig. 4): Raising the temperature just by 20 °C already opens the hysteresis. Further heating drastically increases the hysteresis. The temperature dependence of the hysteresis is reversible, but operating the OFET at higher temperatures causes some degradation (reduced "on" current and reduced mobility).
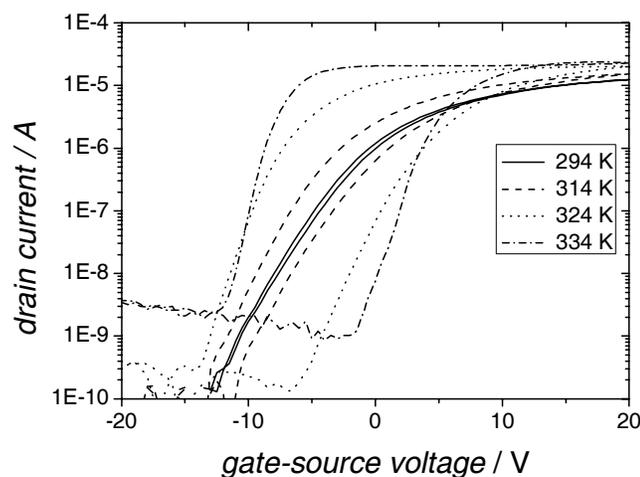
FIGURE 4: Transfer characteristics of an OFET using dialysis grade PVA at RT and at elevated temperatures.

CONCLUSIONS

Our measurements prove that ions in the dielectric have a strong influence on the hysteresis in OFETs. The mobility of these ions shows a strong temperature dependence. Further investigations are necessary to clear the different influence of the cation and the anion. It is also not yet clear whether large ions will show the same effect as small sodium ions.

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