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Water as Origin of Hysteresis in Zinc Tin Oxide Thin-Film Transistors

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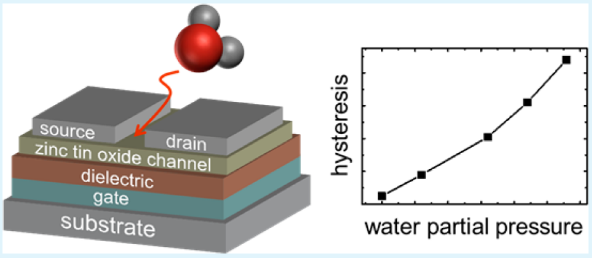
Ⓢ *Supporting Information*

ABSTRACT: The hysteresis behavior of transparent zinc tin oxide (ZTO) thin film transistors (TFTs) is identified to be a result of short-term bias stress induced by the measurement. The related density of shallow defect states can be adjusted by the amount of water in the ambient. Time-resolved studies of the TFTs under varied ambient demonstrate that hysteresis can be immediately switched on and off by the adsorption and desorption of water, respectively. These findings are expected to be of general importance also for other oxide-based TFTs.



KEYWORDS: *oxide thin-film transistor, zinc tin oxide, water, oxygen, hysteresis, ambience*

INTRODUCTION

Transparent thin film transistors (TTFT) based on oxide semiconductors have gained increasing interest within the past few years.[1−7] The high electron mobility and the possibility to process TTFTs at moderate temperatures are some benefits of transparent amorphous oxide semiconductor (TAOS) based channels. These advantages make them attractive for a variety of applications like pixel drivers for displays and flexible electronics.[8,9] However, stability of oxide TFTs under bias stress and illumination is a serious challenge.[10−12] Specifically, the hysteresis in current−voltage characteristics of these devices is a substantial issue and its origin has not yet been thoroughly understood. Recent studies have claimed that hysteresis is caused by trapping of charge carriers into states at the dielectric/semiconductor interface.[13−16] Conversely, the importance of adsorbates on the characteristics of TAOS based TFTs is well-known and has to be taken into account.[17−20] Current reports have described a relation between defect states induced by surface adsorbates and hysteresis.[21,22] In this report, we unambiguously demonstrate the dominating effect of water adsorption at the semiconductor surface as origin of hysteresis in zinc tin oxide (ZTO) TFTs. A study of the time dependent response of the TFT to changes in the ambient humidity reveals that water exposure immediately leads to hysteresis in the TFT characteristics. Thereby, the adsorbed water acts as a shallow acceptor-like trap, which affects the transfer characteristic of TFTs.

The staggered bottom gate TFTs used in this study are composed of an indium−tin-oxide gate electrode and an AlO_x-TiO_x (ATO) nanolaminate dielectric. The ZTO channel semiconductor is prepared by magnetron sputtering. The channel width to length ratio is 1 mm/200 μm with a thickness of 50 nm. Finally the devices have been annealed in air at 400 °C for 20 min. A detailed preparation procedure of the investigated devices is given in ref 23. Generally, the transfer characteristics are measured by a forward and reverse sweep of the gate voltage. A typical transfer curve of a ZTO TFT measured at a moderate speed $v_{measurement}$ of 1 V/s is shown in Figure 1. In this sense, the TFT is subjected to a gate bias stress on a short time scale inflicted by the sweep of the transfer curve. Typically, the impact of bias stress is increased with the bias voltage and also with the duration of the stress. Hereby, the stress duration is determined by the speed of the measurement $V_{measurement}$. The dynamical bias voltage is given by the measurement voltage range (here: −5 V...10 V) and the voltage increment (here 1 V). Commonly, oxide-based TFTs are sensitive to gate bias stress, which is known to result in a drift of the threshold voltage V_{th}.[10,24] Hence, a shift of the transfer curve can be observed between forward and reverse sweep as a result of the bias stress during the measurement sweep. Thereby, one can define the hysteresis voltage V_h as the difference in gate voltage at a constant drain-source current

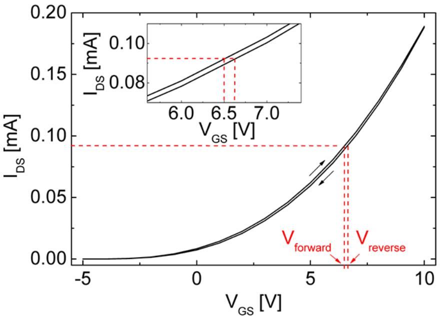


Figure 1. Evaluation of the hysteresis voltage V_h from the typical transfer characteristics of our devices. The inset shows a magnified view of the transfer characteristics near $V_{forward}$ and $V_{reverse}$.

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between forward trace V_{forward} and reverse trace V_{reverse} (see Figure 1):

$$V_{\mathrm{h}} = (V_{\mathrm{reverse}} - V_{\mathrm{forward}})|_{I_{\mathrm{DS}}=\mathrm{const.}} \qquad (1)$$

while $I_{\mathrm{DS}} \gg 0$ has to be chosen in order to obtain reasonable results for V_{h} (in this work $I_{\mathrm{DS}} = I_{\mathrm{DS,max}}/2$; where $I_{\mathrm{DS,max}}$ corresponds to the current flow at the maximum gate voltage $V_{\mathrm{GS,max}} = 10$ V of the measurement range). In addition, a simultaneous shift of both V_{forward} and V_{reverse} can be induced by a shift of the threshold voltage V_{th} of the TFT. In this work, we focus on the investigation of V_{h} and V_{th}. Although V_{h} is indicative for the separation between the forward and reverse trace (hysteresis), V_{th} usually denotes the absolute position of the transfer characteristics. In the following the relation between observed hysteresis voltage V_{h} and varied speed of the measurement $v_{\mathrm{measurement}}$ between 0.25 and 250 V/s is studied by characterizing the TFT in pure water vapor ambient (partial pressure of water, $p_{\mathrm{H_2O}} = 22$ mbar) or in vacuum ($p = 1 \times 10^{-7}$ mbar) as reference. Figure 2 illustrates the dependence of V_{h} on the measurement speed. In general, a high measurement speed $v_{\mathrm{measurement}} > 10$ V/s only causes a short bias stress during the measurement. In case of a water vapor ambient this results in a transfer characteristic which shows a considerably reduced hysteresis compared to V_{h} observed at slower measurement speed $v_{\mathrm{measurement}} < 1$ V/s. In contrast, the V_{h} of the device in vacuum reveals no significant dependence on $v_{\mathrm{measurement}}$. Moreover, the hysteresis of the devices in vacuum is almost zero (within the sensitivity of the measurement). Therefore, we can confirm that hysteresis is due to water induced trap states, which are negatively charged during the measurement sweep. In our further experiments, a very high measurement speed of $v_{\mathrm{measurement}} = 250$ V/s is chosen in order to focus on short-term effects which are addressed during a measurement sweep of the transfer characteristic. Moreover, a fast $v_{\mathrm{measurement}}$ prevents a potential measurement induced pile-up of charges trapped into the dielectric which would permanently shift V_{th}.

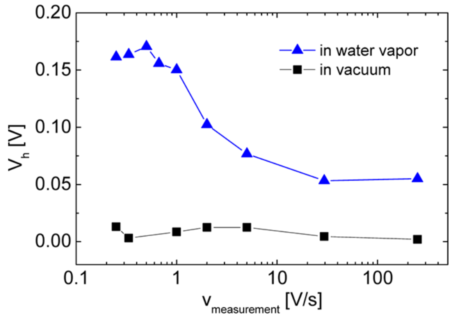

Figure 2. Dependence of observed hysteresis voltage V_{h} on measurement speed $v_{\mathrm{measurement}}$ for TFTs studied in vacuum and water vapor atmosphere ($p_{\mathrm{H_2O}} = 22$ mbar).

To investigate the influence of adsorbed species on the formation of trapping states, we have characterized the TFTs in various atmospheres. As already discussed, the V_{h} is significantly reduced when the transistors are transferred from water vapor ambient ($p_{\mathrm{H_2O}} = 22$ mbar) to vacuum (1×10^{-7} mbar). The TFTs have subsequently been re-exposed to pure oxygen ($p_{\mathrm{O_2}} = 210$ mbar) or water ambient ($p_{\mathrm{H_2O}} = 22$ mbar), respectively. Table 1 unambiguously shows that the hysteresis only recovers upon exposure to water vapor atmosphere. Even though oxygen is known as an electron trap, our results clearly show that oxygen adsorption is not a cause for hysteresis as it remains absent in pure oxygen atmosphere. The mobility and subthreshold swing remain vastly unaffected ($\mu_{\mathrm{sat}} \approx 10$ cm^2/(V s), SS ≈ 0.6 V/dec). It is essential to note, that a similar series of experiments with TFTs using a $\mathrm{SiO_2}$ dielectric instead of ATO verifies that the hysteresis in our devices does not depend on the choice of dielectric material. This particular finding is in contrast to recent studies, where the dielectric has been accounted for the hysteresis in the TFT characteristics.[15,25,26]

Table 1. Change of Hysteresis Voltage ΔV_{h} Measured in Water Vapor, Vacuum, and Oxygen

from	to	ΔV_{h} (mV)
water vapor ($p_{\mathrm{H_2O}} = 22$ mbar)	vacuum	−60
vacuum	oxygen	0
vacuum	water vapor ($p_{\mathrm{H_2O}} = 22$ mbar)	60

To study the time-resolved variation of the TFT characteristics upon an abrupt change of the ambient conditions, the TFTs are first transferred into vacuum ($p = 1 \times 10^{-7}$ mbar) and are subsequently exposed to water vapor with a partial pressure of $p_{\mathrm{H2O}} = 22$ mbar. Figure 3 illustrates the resulting change of hysteresis voltage V_{h} and threshold voltage V_{th}. The moment of water exposure is indicated by an arrow. V_{h} is immediately increased after introducing water vapor into the measurement chamber, whereas V_{th} is lowered simultaneously. In addition, a retarded further reduction of V_{th} is observed on a substantially longer time scale of several hours. Obviously, the influence of water on the TFT can be divided into two effects. On the one hand, water induces shallow trap states. Former studies have already demonstrated the capability of polar media like water to form acceptor-like trap states.[21,27] Hence, the measurement of the transfer curve in forward direction leads to trapping of electrons into these shallow states which partially depletes the channel and therefore, results in a reverse transfer characteristic shifted toward higher voltages and according to eq 1 to an increase of V_{h}. Obviously, the hysteresis is observed because the trapping happens somewhat faster than the detrapping/emission. Notably, the time constant of water adsorption is below a minute, because the abrupt change of V_{h} occurs within a time interval smaller than the time between two subsequent

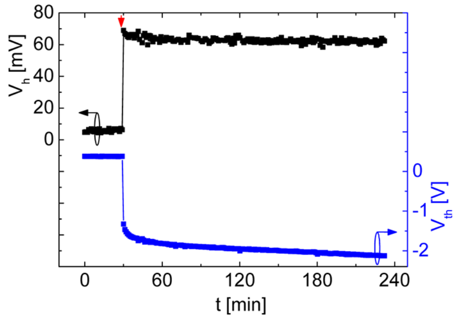

Figure 3. Time-dependent evolution of the hysteresis voltage V_{h} and the threshold voltage V_{th} upon change of the ambient from vacuum to water vapor $p_{\mathrm{H_2O}} = 22$ mbar. Start of water exposure is indicated by an arrow.

measurements (Δt = 1 min). In addition to hysteresis, the polarization of the oxide surface due to the dipole moment of water leads to an enhancement layer,[28] which in turn immediately reduces the overall threshold voltage V_{th}, in our case, by approximately 2 V. A further slow decrease of V_{th} with a saturating behavior can be observed on a time scale of several hours, which may be related to the ongoing process of water adsorption/desorption due to incomplete water coverage at accessible surface states of the ZTO channel semiconductor.

After the exposure of the TFTs to water atmosphere, now the change of the hysteresis upon transfer to vacuum is investigated. To this end, the chamber is evacuated to $p = 1 \times 10^{-7}$ mbar. Figure 4 illustrates the resulting time dependent change of V_h and V_{th}. Interestingly, the hysteresis is almost instantaneously eliminated, which hints a fast desorption time constant similar to that of the adsorption process. A full recovery of V_h is reached after an hour of evacuation, which is associated with a retarded evaporation rate of water. Simultaneously, the threshold voltage is also increased toward the initial value before water exposure. As above, the rate of this process is also limited by the evaporation rate of water. Notably, the effect of water exposure on V_{th} appears to be not fully reversible, because the magnitude of V_{th} after exposure to water and subsequent transfer to vacuum (V_{th} = 0.14 V) is about 0.2 V lower than the initial value of V_{th} for the device in vacuum before water exposure (V_{th} = 0.38 V). We explain this reduced value of V_{th} as being due to desorption of adsorbed oxygen from the surface of the transistor as a consequence of the water exposure. The phenomenon of water induced oxygen desorption from the surface of an oxide semiconductor has been already demonstrated in recent studies.[29] Adsorbed oxygen is known to capture an electron from the TFT channel and leads to an increased threshold voltage in an n-channel device.[18] Thus, water induced oxygen desorption can explain the reduced value of V_{th}.

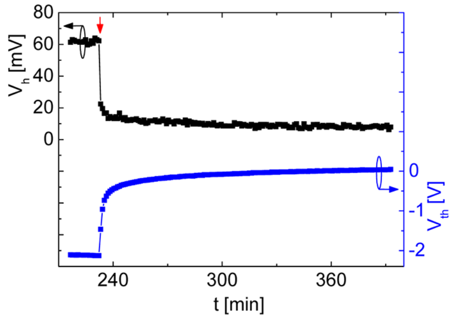

Figure 4. Reduction of hysteresis V_h and recovery of the threshold voltage V_{th} after evacuation from a water vapor atmosphere of p_{H_2O} = 22 mbar (time point indicated by an arrow) to 1×10^{-7} mbar.

Remarkably, a subsequent addition of oxygen to a pure water vapor ambient leads to a reduction of the hysteresis V_h demonstrating the competitive adsorption of O_2 and H_2O at the surface of zinc−tin-oxide in a mixed ambience of oxygen and water which leads to a balancing process between adsorption and desorption of both species.[29,30] For more details please refer to the Supporting Information.

Figure 5 shows the resulting dependence of hysteresis voltage V_h on a varied water vapor partial pressure p_{H_2O}. The selected range of p_{H_2O} corresponds to a humidity of 0−90% in air at 25 °C. The relation between V_h and p_{H_2O} is found to be almost linear within the range of 0−28 mbar. We can therefore conclude that sufficient adsorption sites at the semiconductor surface exist as no saturation of water coverage is observed. The density of water induced trap states at the TFT surface is certainly related to the amount of water in the ambient. Therefore, a more humid ambient allows for the formation of more trap states and consequently leads to an increased hysteresis voltage V_h of the TFTs under an identical speed of the measurement.

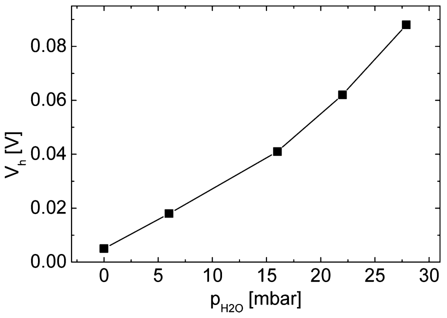

Figure 5. Relation between hysteresis voltage V_h and partial pressure of water p_{H_2O} in the ambient (measured at a speed of 250 V/s).

In conclusion, we have shown that the hysteresis in the transfer characteristics of oxide-based TFTs is a result of measurement speed and the charging of trap states during the measurement. Moreover, we have demonstrated that the origin of hysteresis in zinc tin oxide TFTs is associated with shallow trap states created by adsorbed water at the semiconductor surface. These states are immediately eliminated when the devices are transferred to vacuum. Selective analysis of the devices in various ambient conditions, unambiguously shows that these trap states are due to water molecules adsorbed on the TFTs channel. Thus, aside from the speed of the measurement, the accurate knowledge of the humidity is of particular importance for a meaningful characterization of oxide based TFTs. Our findings are expected to have a broad implication for oxide-based TFTs in general.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Influence of oxygen on the hysteresis of TFTs in a water vapor ambient (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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