Humidity effect on electrical performance and bias stability of solution-processed $\text{In}_2\text{O}_3$ thin film transistor

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**ABSTRACT**

Relative humidity (RH) in storage environment has a great impact on the electrical performance of thin film transistors (TFTs), and the RH is critical for semiconductor manufacturing and device packaging. In this work, solution-processed indium oxide ($\text{In}_2\text{O}_3$) TFT is fabricated, and the electrical performance of the device is investigated after being exposed to various RH conditions. It is found that the threshold voltage ($V_{th}$) and the mobility of $\text{In}_2\text{O}_3$ TFT exhibit clear responses to the RH ranging from 23% to 85%. The inherent mechanism about the humidity effect on the electrical performance is elaborated, and this is due to the "donor effect" from the absorbed water molecules. In addition to the effect on $V_{th}$ and mobility, RH also exhibits a significant effect on the electrical stability of the TFT. The experimental result indicates that the $\text{In}_2\text{O}_3$ TFT exposed to RH <50% exhibits excellent stability with an applied positive bias stressing for 2000s.

**1. Introduction**

Solution-processed metal oxide (MO) semiconductor-based thin film transistor (TFT) shows a great potential in the next-generation display technology [1,2]. During the conventional sol–gel process, the precursors such as metal alkoxide and metal acetate are easily reacted with water molecules [3]. Therefore, the relative humidity (RH) during the coating process has a great impact on the quality of thin film and the device properties [4–6]. It is reported that the device fabricated under RH <50% exhibits high device performance [7]. However, the RH in storage environment also has a strong influence on the conductivity of the channel layer [8], the saturation current, the off-current ($I_{off}$), the voltage threshold ($V_{th}$), and the subthreshold slope (SS), exhibiting responses to the humidity [9,10]. In addition, the RH is critical for the semiconductor manufacturing and device packaging, and it is also necessary to monitor the RH in moisture-sensitive environments (such as cleaning rooms and glove boxes) [11]. In this regard, it is essential to investigate the effect of RH in storage environment on the device property.

In order to realize the practical application of oxide TFT, the electrical stability is a critical index to be considered. For the unpassivated device, the water and oxygen in environment are responsible for the instability of the device [12]. Especially, the semiconductor layer in the solution-processed TFT will provide more gas absorption/desorption sites, leading to the deteriorated stability [13,14]. The O$_2$ effect on the device stability has been investigated in the previous reports, and it is reported that the O$_2$ is responsible for the positive shift of $V_{th}$. However, the role of water molecules in the device stability is still ambiguous. Therefore, it is valuable to investigate the humidity effect on the stability of the solution-processed TFT.

In this work, $\text{In}_2\text{O}_3$ TFTs are fabricated by the solution process, and the effect of RH on the electrical properties of the $\text{In}_2\text{O}_3$ TFTs is investigated. It is observed that the saturation current ($I_{sat}$) of the device is increased with the RH, and the $V_{th}$ and mobility ($\mu_{FE}$) of the TFT are linearly dependent on the RH. Furthermore, the electrical stability of the TFTs was tested under different RH, by applying the positive bias stress (PBS) on the gate electrode. It is found that the $V_{th}$ variation under lower RH is smaller than that under higher RH, which is due to the donor effect from the adsorbed H$_2$O molecules.

**2. Experimental**

**2.1. Precursor solution preparation and thin film deposition**

The mixture of In(NO$_3$)$_3$·$9$H$_2$O and $10$ mL 2-methoxyethanol (2-ME) was employed as $\text{In}_2\text{O}_3$ precursor solution, and the solution was stirred overnight until a transparent and homogeneous solution (0.1 M) was formed. For the thin film deposition, the heavy-doped p-Si with $200$ nm thermal-grown SiO$_2$ was employed as a substrate. The Si/SiO$_2$ substrate was subjected to ultrasonic cleaning, in the sequence of acetone,
ethanol, and deionized water. In order to increase the hydrophilicity of the substrate, O2 plasma (80 W) treatment was carried out for 5 min. The In2O3 thin film was prepared by spin-coating the In(NO3)3·9H2O precursor solution on the top of Si/SiO2 substrate. After being prebaked at 150°C for 15 min, the as-spun thin film was annealed at 280°C in air for 2 h.

2.2. Integration of In2O3 TFT

In this study, In2O3 TFT was fabricated by a facile solution process, the RH of the spin-coating environment is kept at 23%, and the detailed process is shown in Figure 1. The In2O3 precursor was spin-coated on the Si substrate with thermal-grown SiO2 as dielectric. After thermal annealing treatment at 280°C, aluminum source/drain electrodes were evaporated on the top of In2O3 thin film using a shadow mask, and the channel width (W) and length (L) are 1000 and 100 μm, respectively.

2.3. Investigation of humidity effect on In2O3 TFT

For the investigation of the humidity effect on the electrical performance of In2O3 TFT, the fabricated device was placed on the top of the saturated solution, with the RH ranging from 30% to 85%. The RH is controlled by the saturated vapor pressure of the saturated solution, respectively, as shown in Table 1. After 30 min exposure, the electrical performances of the In2O3 TFTs were investigated by means of a semiconductor parameter analyzer (Keithley 2634B) in a dark box. The field-effect mobility (μFE) of the device could be calculated by Equation (1):

\[ I_{DS} = \frac{W}{2L} \mu_{FE} C_s (V_{GS} - V_{th})^2 \]  

where \( C_s \) and \( V_{GS} \) represent the areal capacitance of the dielectric and the gate voltage, respectively; \( V_{th} \) is the threshold voltage, which can be obtained from the intercept of the fitting line used to extract the mobility in the saturation regime \( I_{DS}^{1/2} \) vs. \( V_{GS} \) characteristics.

3. Results and discussion

3.1. Humidity effect on morphology of In2O3 thin film

After exposed to ambient atmosphere, the morphology evolution of the In2O3 thin film with RH was examined by the atomic force microscopy (AFM). Figure 2(a–c) illustrates the morphologies of In2O3 thin films at various RH of 30%, 50%, and 70%, respectively. It is found that the In2O3 thin film at low RH exhibits the smooth surface with a small RMS of 0.611 nm. However, some needles are observed and become more and more with the increment of RH, and the RMS value is increased accordingly. The RMS evolution is shown in Figure 2d, and the increase in RMS is due to the swelling of the In2O3 thin film at higher RH [15].

3.2. Electrical performance of In2O3 thin film transistor

The transfer characteristics of the In2O3 TFT exposed to various RH environments are shown in Figure 3a. It is found that both the on-current \( I_{on} \) and off-current \( I_{off} \) of the In2O3 TFTs increase with the RH from 23% to 85%. This result indicates that the conductivity of the semiconductor layer has been improved after its exposure to higher RH. In addition, the \( V_{th} \) of the TFT is negatively shifted with the RH, and this further confirms the improved conductivity of the channel at higher RH. By extracting electrical parameters, the relationships between the electrical parameters \( (V_{th}, \mu) \) and RH are summarized in Figure 3b,c. It is found that

![Figure 1. Fabrication process of solution-processed In2O3 TFT. (a) Spin-coating; (b) Thermal Anneal and (c) Humidity treatment](image-url)
Figure 2. AFM images of In$_2$O$_3$ thin films exposed to various RH: (a) 30%, (b) 50%, and (c) 70%. (d) RMS evolution with increment of RH.

Figure 3. (a) Transfer characteristics of In$_2$O$_3$ TFT exposed to various humidity. (b) $V_{th}$ and (c) mobility response of In$_2$O$_3$ TFT to RH variation.
the electrical property of In$_2$O$_3$ TFT is strongly dependent on the RH variation. Figure 4 shows the corresponding output characteristics of the In$_2$O$_3$ TFTs exposed to various RH, the devices exhibit typical n-channel transistor behavior with the distinct pinch-off and current saturation. The electrical performance and the saturation current are varied with the RH, which make it possible for the In$_2$O$_3$ TFT employed as an RH sensor.

It is assumed that partial net charges originated from the absorbed H$_2$O molecule are donated to the In$_2$O$_3$ surface, and this is called the “donor effect” [16,17]. With the aim at investigating the humidity effect on the conductivity of the semiconductor layer, the I–V relationship of the In$_2$O$_3$ semiconductor is tested. The result is shown in the inset of Figure 5. Figure 5 shows the corresponding resistance of In$_2$O$_3$ under different RH. It is found that with the RH, the resistance of the In$_2$O$_3$ semiconductor is decreased accordingly, indicating the enhanced conductivity. This result is consistent with the transfer characteristics of the In$_2$O$_3$ TFT, as shown in Figure 3a.

### 3.3. Influence mechanism of humidity on TFT performance

From the transfer characteristics, it can be concluded that the electrical property of In$_2$O$_3$ TFT is closely related to the RH variation. Hoshino et al. reported that the moisture incorporation prior to channel layer deposition will not lead to the variation of the TFT electrical performance [18]. The effect of the RH on the substrate could be excluded; that is, the RH is responsible for the conductivity of the channel layer. The mechanism on the surface conductivity change in the presence of water has been explained in few reports [19]. From the literature, the water molecules are adsorbed on the oxide surface by physisorption or hydrogen bonding. In general, at higher temperature (>100°C), the adsorbed H$_2$O is dissociated and reacts with the oxide lattice as shown in Equation (2) [20]:

$$H_2O + O\_In \leftrightarrow In - OH + V\_O + e^- \quad (2)$$
Subsequently, the chemisorption of water molecules is induced by the ionic $\text{In}^{3+}$ with strong electrostatic field. During the process, the depletion layer is formed beneath the active surface and the thickness is decreased, and the conductivity of the $\text{In}_2\text{O}_3$ channel layer is increased accordingly. Another explanation for the increase in conductivity is that the oxygen is absorbed on the semiconductor surface, leading to the formation of negative-charged $\text{O}^-$ as shown in Equation (3). In the presence of the water molecule, $\text{H}_2\text{O}$ is accumulated on the surface of channel layer through physical adsorption, and the pre-adsorbed oxygen is replaced to form terminal hydroxyl group as shown in Equation (4), and this reaction process is reversible [21].

$$O_2(\text{gas}) + e^- = O_{\text{ad}}^- \quad (3)$$

$$\text{H}_2\text{O} + O_{\text{ad}}^- + 2\text{In} \rightarrow 2(\text{In} - \text{OH}) + e^- \quad (4)$$

In order to reveal the mechanism of the humidity effect on the electrical property of $\text{In}_2\text{O}_3$ TFT, the recovery of the $\text{In}_2\text{O}_3$ TFT is investigated. The as-prepared TFT (RH = 23%) is exposed to the ambient atmosphere with high humidity (RH = 85%) and then placed in dry air with different time intervals. The transfer characteristics are shown in Figure 6, and it is observed that the electrical performance is recovered to the original value, with the recovery time of 2 min. This indicates that the effect of RH on the conductivity of oxide is dominated by the physisorption of $\text{H}_2\text{O}$ molecule, while the chemical adsorption plays a minor role [21]. And the excellent recovery indicates the reproducibility of the solution-processed $\text{In}_2\text{O}_3$ TFT, which further confirms the great potential of the fabricated TFT as an RH sensor.

The schematic illustration of the TFT exposed to various RH conditions is proposed, as shown in Figure 7. When the TFT is exposed to the ambient environment, $\text{O}_2$ is pre-absorbed on the oxide surface to form the ionosorbed oxygen atoms. As a result, the
depletion region is formed and the energy band of semiconductor is bended upwards (Figure 7a). With the humidity increasing, the water molecule is accumulated on the metal oxide channel layer and reacted with the pre-adsorbed oxygen, accompanied by the formation of hydroxyl groups (-OH), and an

![Figure 7. Mechanism of humidity effect on the electrical performance of In$_2$O$_3$ TFT.](image)

![Figure 8. Positive bias stress tests for In2O3 TFTs under various RH conditions: (a) RH=23%; (b) RH=50%; (c) RH=70%. (d) Vth shift of In2O3 TFT under various RH conditions.](image)
3.4. Bias stress stability of In$_2$O$_3$ TFT

Except for the electrical parameters, electrical stability of the TFT is also an important indicator to estimate the device performance. It is well known that the ambient atmosphere has a great impact on the electrical stability of the device [16]. The dependence of the bias stability on RH is investigated by applying a bias stress of +30 V for 2000s. Figure 8(a–c) shows the evolution of the transfer characteristics of the In$_2$O$_3$ TFT after being exposed to various RH (23%, 50%, and 75%). The variations of the $V_{th}$ ($\Delta V_{th}$) of the devices with the bias stress time are shown in Figure 8d. It is found that with the increasing RH, the $\Delta V_{th}$ of TFT is increased accordingly, while the variation in SS value is negligible. It is reported that the parallel shift in $V_{th}$ without apparent SS change is attributed to the trapped charge at the interface of channel and dielectric and/or in the dielectric [25,26]. As one knows that the interface quality is closely related to the maximum areal density of states ($N_s^{\text{max}}$), which can be calculated by Equation (5).

$$N_s^{\text{max}} = \frac{\text{SS} \log(e)}{kT/q} - 1 \cdot \frac{C_i}{q}$$  (5)

where $k$, $T$, and $q$ are Boltzmann’s constant, absolute temperature, and charge quantity, respectively. The SS and corresponding $N_s^{\text{max}}$ values for In$_2$O$_3$ TFTs exposed to various RH are listed in Table 2. It is found that with the increase in RH, the SS and $N_s^{\text{max}}$ are increased accordingly, indicating the poor quality of the dielectric/channel interface [2]. And the larger SS value indicates the worse quality of the semiconductor layer in the device and the more interface defect states in FET [27], which account for the deteriorated stability for the TFT exposed to high RH.

During the bias stress, the interaction between the back channel and atmosphere is responsible for the $V_{th}$ variation. It is well known that the electrons are captured by the O$_2$ molecules, and oxygen species (such as O$_{ad}$) are formed following the chemical reaction shown in Equation (3) [28,29]. The negatively charged species will be overcome by additional gate voltage, and this leads to the positive shift of $V_{th}$ during the PBS test. However, in the presence of H$_2$O molecules, the mechanism on the $V_{th}$ variation is complicated. In the literature, the water-assisted O$_2$ absorption model is proposed, which explains the role of H$_2$O in the variation of $V_{th}$ [30]. The detailed mechanism is shown in Figure 9. It is found that upon the exposure to the lower RH, the negatively charged O$_{ad}$ is generated and the energy band of semiconductor is bended upwards, as shown in Figure 9a. As a result, the energy barrier is formed at the surface of the oxide, which impedes the continuous capture of electrons. However, when exposed to higher RH, H$_2$O is absorbed on the back channel, and the energy barrier is bended downwards due to the donor effect of H$_2$O (Figure 9b). This leads to the conductivity enhancement of the back channel, and the $I_{on}$ is increased at higher RH.

Based on the above analysis, when exposed to higher RH, more electrons are donated in the channel for the TFT, and more O$_2$ could be adsorbed on the back channel. As a result, a depletion layer beneath the
surface of In$_2$O$_3$ is formed, leading to the positive shift of the $V_{th}$ [16]. The equilibrium constant ($K$) in the above reaction is denoted as $[O_2^-]/P_{O_2}$, and the $V_{th}$ is shifted in the positive direction due to the increase in $P_{O_2}$ [31,32]. This leads to the large $\Delta V_{th}$ of the In$_2$O$_3$ TFT at higher RH during the positive bias stressing. In order to improve the device stability, the incorporation of passivation layer is considered as an effective strategy [33].

4. Conclusion

In summary, the effect of the RH in storage environment on the electrical property of the In$_2$O$_3$ TFT is investigated. From the transfer characteristics of the In$_2$O$_3$ TFT under various RH conditions, the clear responses of $V_{th}$ and $\mu$ to the RH are observed. The inherent mechanism of the electrical performance of In$_2$O$_3$ TFT dependent on RH is also explained, which is due to the donor effect of the water molecules. Furthermore, the electrical stability depending on the RH is investigated, and it is confirmed that the higher humidity is responsible for the $V_{th}$ instability during the bias stressing.

Disclosure statement

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