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Effects of humidity on performance of electric-double-layer oxide-based thin-film transistors gated by nanogranular SiO_2 solid electrolyte

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Electric-double-layer oxide-based thin-film transistors gated by nanogranular SiO_2 solid electrolyte have been fabricated at room temperature. The effects of humidity on performances are investigated. At the relative humidity of 65 %, the measured capacitance is 10 μF/cm^2, and the device shows $I_{on/off}$ ratio of 8.93×10^7, field-effect mobility of 5.9 cm^2/Vs. As relative humidity declines, the measured capacitance decreases, which gives rise to the degradation in performance. Especially, at the relative humidity of 0 %, the capacitance of 0.01 μF/cm^2 is measured, so the device cannot be turned off. The reason may be that humidity can promote H_2O molecules to permeate into solid electrolyte, which can cause charges accumulation. © *2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4815970]

I. INTRODUCTION

Low voltage oxide based thin film transistors (TFTs) are ideal to build blocks for sensor applications. Low voltage operation of such TFTs can be accomplished by using high-*k* materials as gate insulators, such as Al_2O_3, HfAlO and polycrystalline Y_2O_3, etc.[1–3] Recently, due to extraordinarily high capacitance,[4,5] electrolytes have been commonly used as the gate dielectric layer. Electrolytes are polarized by application of a gate potential, leading to the formation of a electric double layer (EDL) layer which is virtually independent of the thickness of the electrolyte at the electrolyte-semiconductor interface.[6] Therefore, the rapid formation and the extremely strong electrostatic coupling effect of an EDL with a large capacitance at the conjugated polymer/electrolyte interface results in a fast and robust field effect transistors, which are capable of operating at low voltages.[7,8] In our previous work, low voltage (<1.5 V) oxide-based EDL TFTs, which is gated by microporous SiO_2 solid electrolyte films after being soaked in phosphoric acid, have been demonstrated.[9] However, Indium Zinc Oxide (IZO) EDL TFTs need to be exposed to the environment for proper operations. In many cases, electrical characteristics of oxide based EDL TFTs will be affected by the relative humidity (RH), but the reasons and the mechanism are still not very well known. Therefore, it is necessary to further investigate effect of operating environments on device characteristics for explaining the unclear operating mechanism.

In this paper, in order to investigate reasons and the mechanism, IZO EDL TFTs gated by nanogranular SiO_2 solid electrolyte have been characterized at different levels of relative humidity. Nanogranular SiO_2 solid electrolyte sandwiched between (Indium Tin oxide) ITO electrodes and IZO electrodes forms a capacitor, which is measured by Solartron 1260 impedance analyzer. In closed rooms, where a humidity controller with a hygrometer is used for controlling humidity environment,

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the electrical characteristics of IZO EDL TFTs are analyzed by Keithley 4200 semiconductor parameter analyzer at room temperature in the dark.

II. EXPERIMENTAL DETAILS

The devices are fabricated on ITO glasses substrates and the whole process is performed at room temperature. To reduce pollution sources, the substrates are cleaned firstly by ultrasonic cleaning in alcohol and deionized water for 15 min before deposition in sequence. Then, nanogranular SiO_2 solid electrolyte used as the gate dielectric of oxide-based EDL TFTs are fabricated by PECVD, using SiH_4 (94% SiH_4 + 6% PH_3) and O_2 as reactive gases. The flow rate of SiH_4 is 10 sccm and that of O_2 is 60 sccm. The deposition pressure, radio frequency power, and deposition time are 30 Pa, 100 W, and 60 min, respectively. Finally, IZO film, which is used as channel layer, drain electrode and source electrode of oxide-based EDL TFTs, is deposited by radio-frequency magnetron sputtering. IZO patterns are deposited by using an IZO ceramic target (In_2O_3: ZnO = 10:90 wt.%) through a shadow mask.[10] The radio frequency magnetron sputtering conditions are performed with a power of 100 W, a deposition pressure of 0.5 Pa and Ar (14 sccm) as protective gases. The deposition rate of IZO film is estimated to be 10 nm/min. The channel length of IZO TFTs is 80 μm, and the channel width is 1000 μm. In order to obtain the cross-sectional SEM image, some samples are deposited on n^{++} (100) Si substrate.

Figure 1(a) shows schematic diagram of oxide-based EDL TFTs gated by nanogranular SiO_2 solid electrolyte. The cross-sectional SEM image of nanogranular SiO_2 solid electrolyte is obtained by scanning electron microscope (SEM). In a closed room, a humidity controller with a hygrometer is used for humidity controlled environment. With the relative humidity increasing from 0% to 65%, the capacitance of nanogranular SiO_2 solid electrolyte is measured by Solartron 1260 impedance analyzer. The electrical characteristics of IZO EDL TFTs are analyzed with Keithley 4200 semiconductor parameter analyzer at room temperature.

III. RESULTS AND DISCUSSION

The cross-sectional SEM image of nanogranular SiO_2 solid electrolyte on Si (100) substrate deposited at room temperature by PECVD is shown in Figure 1(b). It can be seen clearly that the section of nanogranular SiO_2 solid electrolyte is the vertical and porous shape. This indicates that nanogranular SiO_2 solid electrolyte fabricated at room temperature by PECVD method features the micro pore structure, which is desirable for proton conduction.[11,12] The important advantages of this micro pore structure include that it can provide a larger specific surface area and that it can be capable of adsorbing many water molecules, which will take place capillary condensation effect in the micro pores,[13] even make it like a pondlet.[14,15]

The measured serial capacitance and phase angle as a function of the frequency of the applied voltage (0.2 V) for a capacitor based on nanogranular SiO_2 solid electrolyte are shown in Figure 2. Based on the phase angle mechanism,[16] the component can be classified as being either capacitive ($\theta < -45^\circ$) or resistive ($\theta > -45^\circ$) at a certain frequency. At the relative humidity of 65 % as shown in Figure 2(a), we can see that two regions can be identified: a resistive behaviour at high frequencies (2×10^5 Hz $< f$), and a capacitive behaviour at low frequencies ($f < 2 \times 10^5$ Hz). The two regions can be associated with ionic relaxation and the EDL formation, respectively. In the EDL formation regions, as the frequency becomes higher, the measured capacitance decreases. This is mainly determined by the physical transport mechanism of protons in nanogranular SiO_2 solid electrolyte. To understand the physical transport mechanism better, the micro pores are supposed to columnar structure. Then, each micro pore and solution in micro pore composes a cylindrical solid electrolytic capacitor. When applied a voltage, a great number of protons can move along the direction of electric field, but proton could be adsorbed by hydroxyl groups on the wall of micro pores at intervals during proton transport, as shown in Figure 3. This proton transport mechanism is called as “hopping conduction”. Because the proton conduction is promoted through the hopping of the protons between hydroxyl groups and water molecules[17] and in most cases of high frequency regions, protons will be kept of conjugated status in the middle position, so the component can be

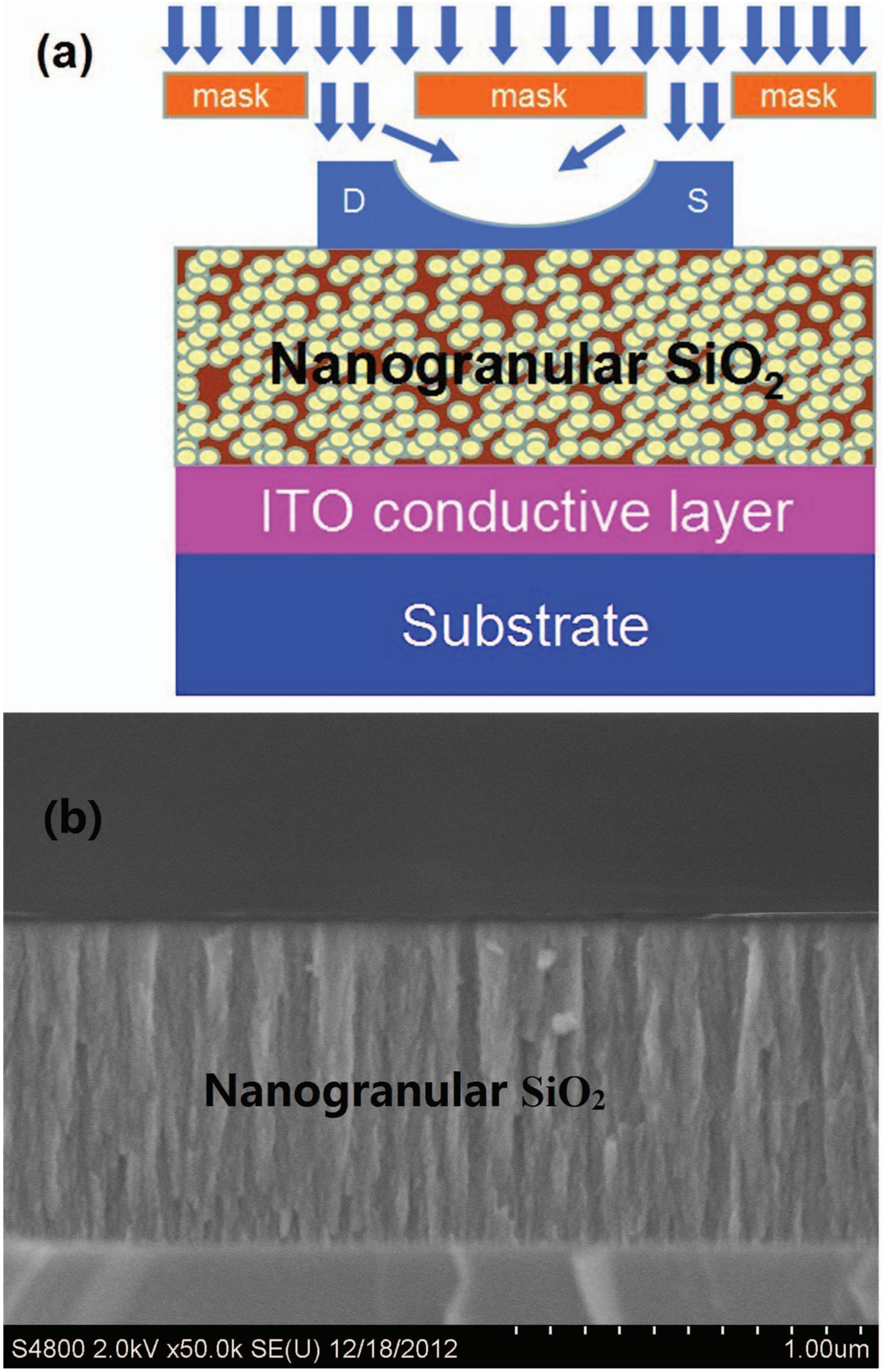

FIG. 1. (a) Schematic diagram of oxide-based EDL TFTs gated by nanogranular SiO_2 solid electrolyte and (b) A cross-sectional SEM image of nanogranular SiO_2 solid electrolyte on n^{++} (100) Si substrate.

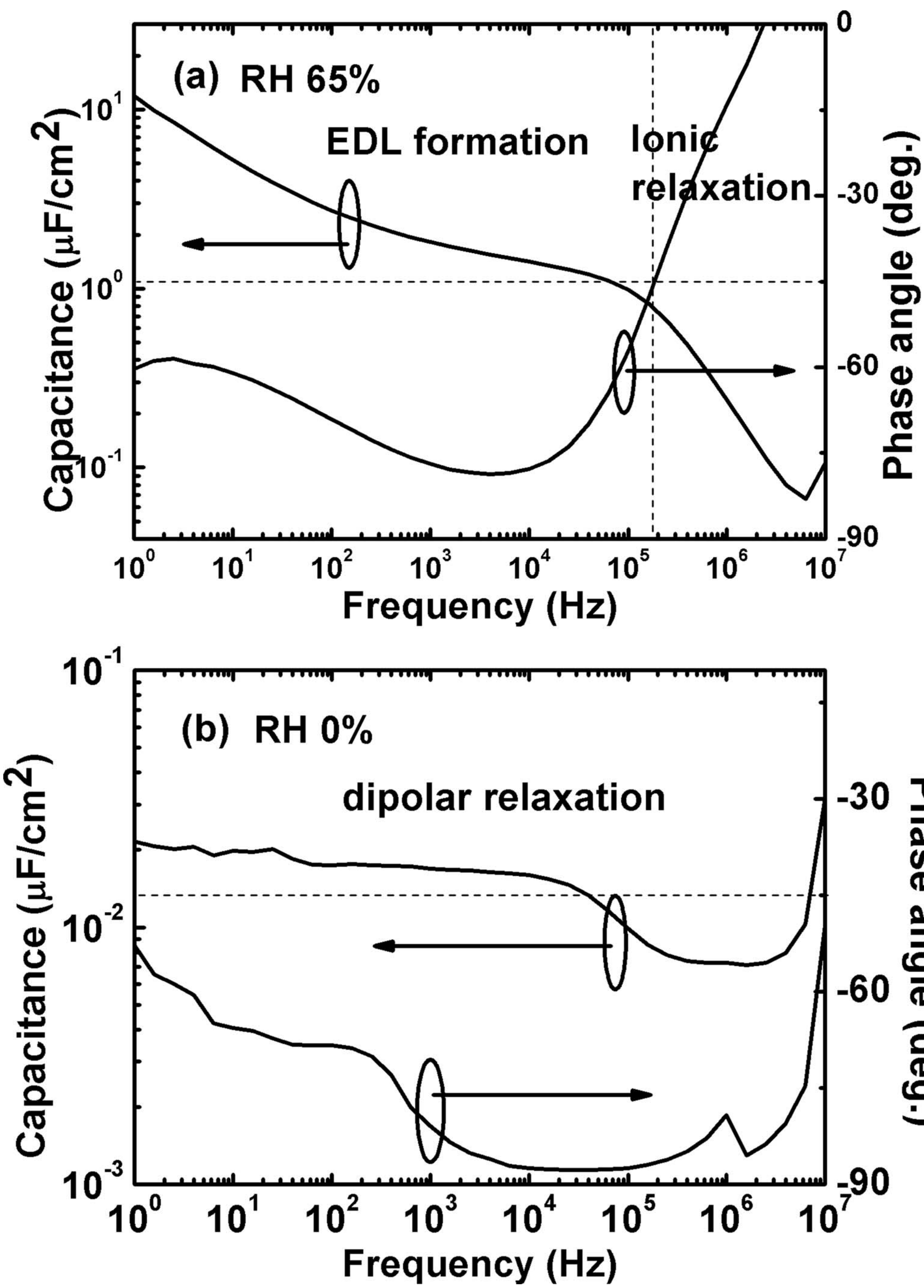

FIG. 2. The measured serial capacitance and phase angle versus the frequency of the applied voltage (0.2 V) for a capacitor based on nanogranular SiO_2 solid electrolyte (a) RH 65% (b) RH 0%.

classified as being resistive. When the frequency decreases, protons have enough time to move to the opposite interface of nanogranular SiO_2 solid electrolyte, causing more and more protons to accumulate. Finally, the measured capacitance increases, which is conducive to the EDL formation. However, when in low frequency regions at relate humidity of 0 %, as shown in Figure 2(b), the measured capacitance is only about 0.01 μF/cm^2. The above behavior indicates that the capacitance is also dependent of the relate humidity.

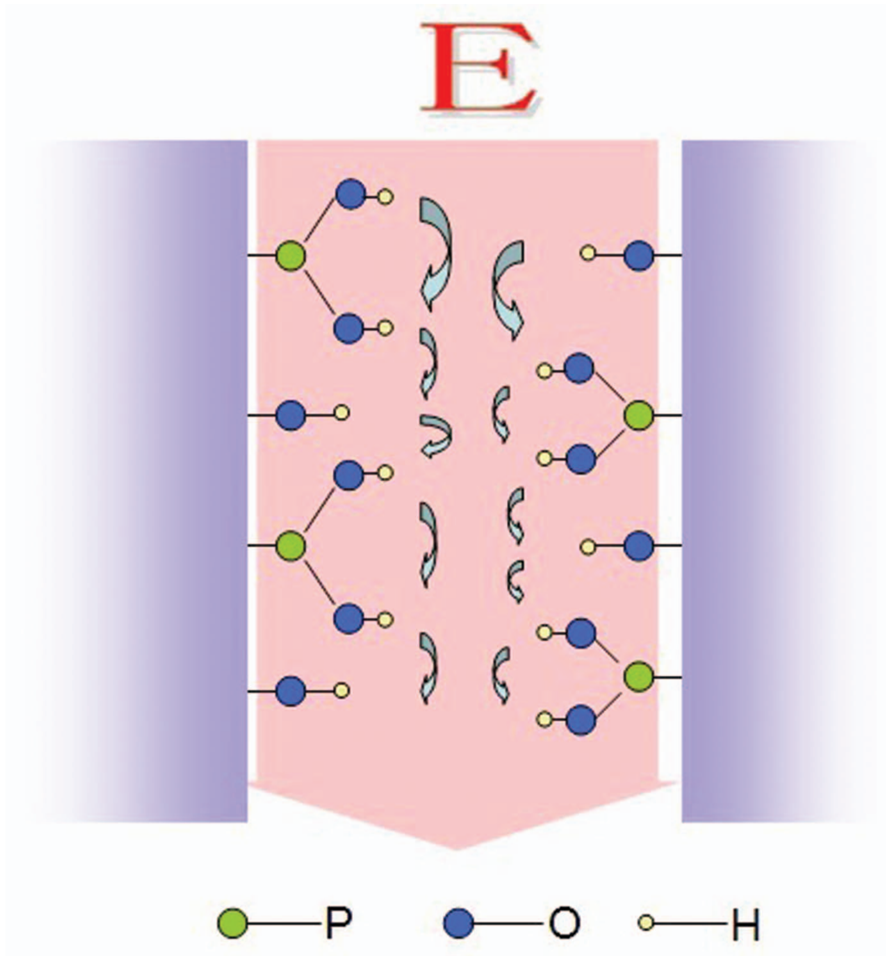

FIG. 3. Proton conduction in micro pores of nanogranular SiO_2 solid electrolyte.

In order to further study the relationship between relative humidity and specific gate capacitance, the measured gate capacitance of a capacitor based on nanogranular SiO_2 solid electrolyte is plotted as a function of the relative humidity, as shown in Figure 4. It can be seen that as the relative humidity goes down from 65 % to 45 %, specific gate capacitance decreases from 10 μF/cm^2 to 4.8 μF/cm^2. The relative capacitance decreasing with the decrease in humidity can be explained by taking types of the densities into account,[18] which suggesting that the density of charge is reducing gradually. Because when in high relative humidity environment, hydroxyapatite groups (-OH)[19] are formed in nanogranular SiO_2 solid electrolyte by chemisorptions of H_2O molecules, so the proton concentration and the speed of proton conduction could be improved, leading to the augment in the density of charge. To the contrary, with the relative humidity decreasing, less and less H_2O molecules permeate to the nanogranular SiO_2 solid electrolyte, which gradually leading to less protons accumulation and electrochemical reaction, so the density of charge is reducing gradually.

We use nanogranular SiO_2 solid electrolyte as gate dielectric of IZO EDL TFTs and measured transfer characteristic curves with different relative humidity, as shown in Figure 5. The operating voltage is only 1.0 V. When the relative humidity is 65 %, the current on/off ratio, threshold voltage and subthreshold swing are estimated to be 8.93×10^7, 0.13 V and 97.8 mV/decade, respectively. Very small leakage current (<4 nA) is observed. The hysteresis phenomena between the forward and reverse sweep typically is observed in the transfer curves when reducing the gate voltage as shown in Figure 5(a), which is mostly due to the slow ionic response of the mobile protons in nanogranular SiO_2 solid electrolyte.[20] Actually, when a gate voltage is imposed, the proton will move to the

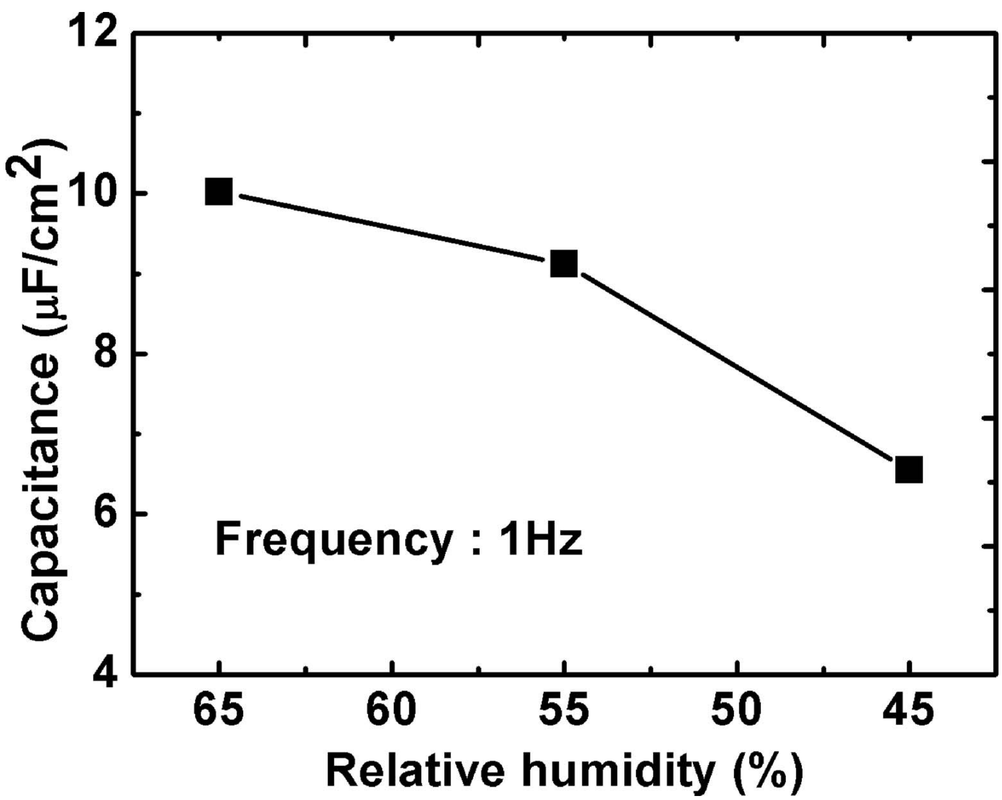

FIG. 4. The measured capacitance as a function of the relative humidity for a capacitor based on nanogranular SiO_2 solid electrolyte.

dielectric/channel interface, as a result, the equal density negative charges are induced underneath of the channel layer. At that humidity the amount of absorbed water is so large that percolation paths are formed, in which proton transport takes place via hopping between absorbed molecules.[21] The devices exhibit excellent electrical characteristics. While when the relative humidity is 0 %, the transistor can not be switched off, as shown in Figure 5(b), which indicates that the relative humidity plays an important role in the electrical characteristics of the devices.

In order to give detailed evidence, the electrical characteristics of EDL TFT gated by nanogranular SiO_2 solid electrolyte are measured with different humidities, as shown in Figure 5(c) and 5(d). From Figure 5(c) and 5(d)., it can be seen that with the relative humidity decreasing from 65 % to 45%, the threshold voltage, mobility, and current on/off ratio decreases to 0.03 V, 4.37 cm^2/Vs, and 3.82×10^6 ($V_{ds} = 1.0$ V), while the subthreshold swing increases to 139 mV/dec., respectively.

As we all know, the charge density equals to the product between capacitance and voltage. For oxide-based EDL TFT, the capacitance function is regulatory the charge density of the channel layer. As the relative humidity reduces, the charge density of the channel layer is limited by the gradually decreasing capacitance, which will lead the channel layer to provide a smaller on current. Therefore, with the relative humidity reducing, the current on/off ratio gradually diminishes. On the other hand, the concentration and the number of protons will dwindle, with water molecules lessening. A small number of protons need only a smaller gate voltage to achieve operation; while the small concentration restricts protons transport freely and the speed of protons in nanogranular SiO_2 solid electrolyte. Those factors make the threshold voltage to drift toward positive direction.[22] It indicates that reducing the relate humidity makes the operation mode of the devices changing from enhance mode to depletion mode. Moreover, protons need a longer time to move from the gate electrode-electrolyte interface to the electrolyte-semiconductor interface with the lower humidity due to the low speed, which results in changes in field-effect mobility and subthreshold swing.[23] When reducing the relative humidity to 0%, there are few protons which are absorbed firmly on the

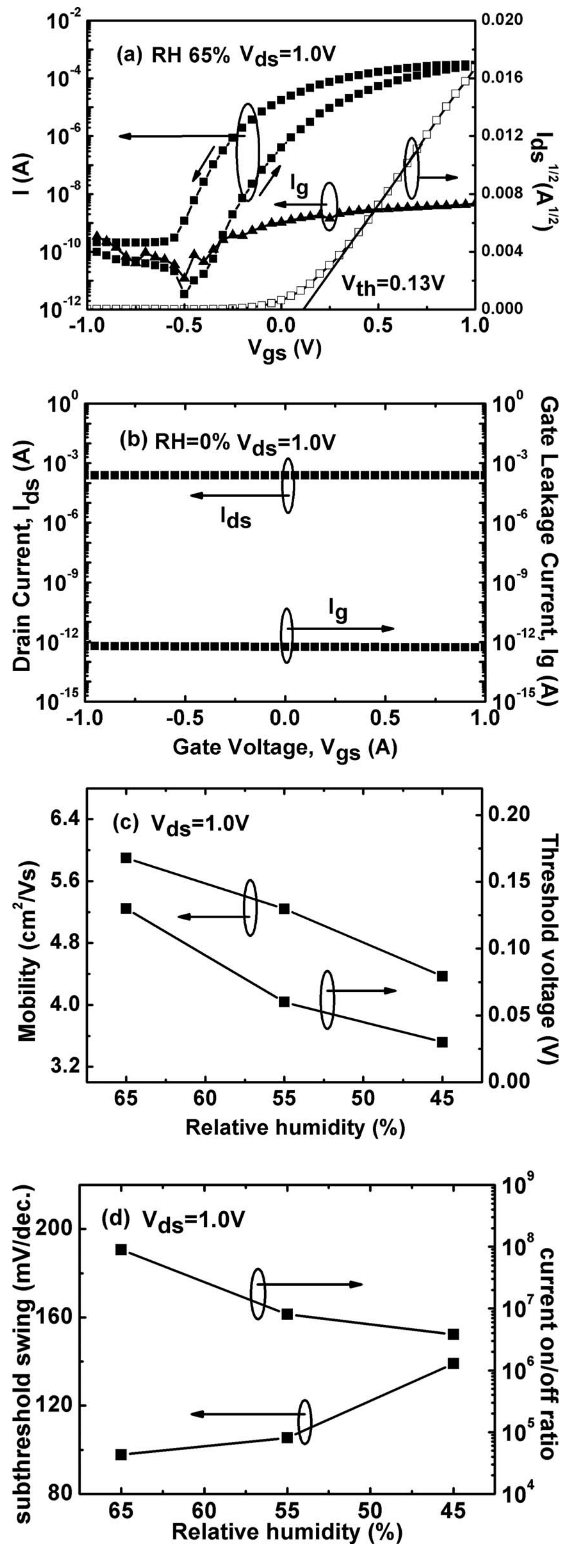

FIG. 5. The transfer curves of IZO EDL TFTs gated by nanogranular SiO_2 solid electrolyte. (a) RH 65%, (b) RH 0%; (c) and (d) the electrical characteristic of IZO EDL TFTs gated by nanogranular SiO_2 solid electrolyte as function of the relative humidity.

wall of micro pores in nanogranular SiO_2 solid electrolyte, and nanogranular SiO_2 solid electrolyte has no regulation; as a result, the big source-drain current is come into being by applying source-drain voltage as shown in Fig. 5(b). Due to electron induced effect, a hole layer also forms at the under surface of the channel closed to source electrode, and it will eliminate barrier potential difference between drain electrode and source electrode. Because of the above effect, the devices can not be turned off. Since electrical performances of our devices are highly dependent on the relative humidity greatly, such devices are highly desired for applications in humidity sensors.

IV. CONCLUSION

In summary, we have fabricated IZO EDL TFTs gated by nanogranular SiO_2 solid electrolyte and investigated the effects of the relative humidity on the electrical characteristics of devices. Proton migration, which plays an important role in the formation of EDL, is dependent on the relative humidity of surrounding environment. As the relative humidity decreases, the concentrate, the speed and the number of protons are restrained which give rise to the degradation in electrical properties of the devices. Such behaviors exhibit the excellent potential of IZO EDL TFTs as high-sensitive humidity sensors.

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