Effects of NaCl treatment on the performance and environmental stability of microporous SiO$_2$-based thin film transistors

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In this letter, we report the effects of NaCl treatment on the performance and environmental stability of microporous SiO$_2$-based thin film transistors (TFTs). It was found that appropriate amounts of NaCl treatment significantly improved the electric double layer (EDL) capacitance of such composite solid electrolytes from 1.9 to 4.7 $\mu$F cm$^{-2}$. A highest field effect mobility of 42.8 cm$^2$ V$^{-1}$ s$^{-1}$ was found for 1% NaCl treated microporous SiO$_2$-based TFTs. However, 10% and 26.5% NaCl treated microporous SiO$_2$-based TFTs showed good environmental stability of the $I_{on}/I_{off}$ ratio with reasonable field effect mobility.

Experimental

The entire process of the microporous SiO$_2$-based TFTs fabrication was performed at room temperature. First of all, microporous SiO$_2$ gate dielectric with the thickness of 2 $\mu$m was deposited by plasma-enhanced chemical vapor deposition (PECVD) method on ITO glass and Si (100) substrates using SiH$_4$ and O$_2$ mixture as the reactive gases. Then, the samples were immersed in 0.1%, 1%, 10% and 26.5% NaCl aqueous solution, respectively. After 3 hours, these samples were taken out and dried in air ambient. Then, a 40 nm-thick ITO layer was deposited by RF magnetron sputtering method with a RF power of 100 W in Ar/O$_2$ (4 : 1) mixed ambient of 0.5 Pa as active channel. At last, highly conductive ITO layers were deposited by dc sputtering methods in pure argon ambient at 1.0 Pa as source and drain electrodes. The channel length and width-to-length ratio of the shadow mask were 80 $\mu$m and 12.5 : 1, respectively. The structural characterization of the microporous SiO$_2$ electrolyte film was investigated by field emission scanning electron microscopy (Hitachi S-4800 SEM). The electrical characterizations of the microporous SiO$_2$ dielectric and EDL transistors were investigated by an impedance analyzer (WK 6500B) and a semiconductor parameter analyzer (Keithley 4200 SCS) at room temperature in dark with a relative humidity of 60%.

Results and discussion

Fig. 1(a) shows the schematic picture of ITO-based TFTs gated by microporous SiO$_2$ treated by NaCl. On account of immersing into NaCl aqueous solution for 3 hours, some protons enter the microporous SiO$_2$ and some anions adhere to the surface of the microporous SiO$_2$, these anions induce image charges of equal density and opposite sign in the dielectric layer, which is similar to the case of EDL organic transistors gated by ionic liquids or...
solid state electrolytes. Its transformation may be driven by proton transfer to and from a water molecule with very little permittivity temperature dependence. The major advantage of the EDL effect is that the specific capacitance is exceptionally large which results in an ultrahigh current throughput at an ultralow operating voltage of 0.5 V. Fig. 1(b) shows the density dependence of the specific capacitance versus frequency of the microporous SiO₂ with and without NaCl treatment in the frequency range from 20 Hz to 5 MHz. Compared with the SiO₂ without NaCl treatment, the specific capacitance of microporous SiO₂ with 10% and 26.5% NaCl treatment has increased to 4.7 μF cm⁻² at 20 Hz and remains about 1 μF cm⁻² at 1 kHz. However, the specific capacitance of microporous SiO₂ with 1% NaCl treatment is about 2 μF cm⁻² and decreases rapidly. It is expected that this behavior is mainly due to the changing of Na⁺ ions concentration in the films, which is similar to the incorporation of Na⁺ ions into gate dielectrics. The out-put characteristics of all the TFTs with and without NaCl treatment showed typical transistor behavior. Fig. 2 shows the transfer characteristics of the TFTs with and without NaCl treatment measured after different time interval of fabrication. The fresh measurement refers to the TFTs fabrication after 3 h of SiO₂ film deposition and the electrical properties were measured within 1 h of the device fabrication. To study the environmental stability of the TFTs with and without NaCl treatment, the devices were exposed to air without surface passivation and their electrical properties were measured after 1 week and 1 month of air exposure. The mobility and the drain current ratio for the freshly prepared TFT without NaCl treatment were 12 cm² V⁻¹ s⁻¹ and 3.4 × 10⁶, respectively. The threshold voltage (Vth) was −0.1 V and it was shifted in the positive direction with exposure to air. The Ion/Ioff ratio of the TFT without NaCl treatment measured after 1 week and 1 month of air exposure were 1.8 × 10⁵ and 6 × 10⁴, respectively. The mobility was significantly decreased with exposure to air. The TFT with 1% NaCl treatment showed a mobility of 41.8 cm² V⁻¹ s⁻¹ and the mobility was decreased to 15 cm² V⁻¹ s⁻¹ with an Ion/Ioff ratio of 3.1 × 10⁶ after 1 week aging. From Table 1 it is noted that after 1 month aging the TFT with 1% NaCl treatment showed a lower stability than the TFT without NaCl treatment. The mobility and Ion/Ioff ratio for the freshly prepared TFT with 10% NaCl treatment was 64.5 cm² V⁻¹ s⁻¹ and 2.5 × 10⁸, respectively. In this case, the mobility was decreased to 29.3 and 12 cm² V⁻¹ s⁻¹ after 1 week and 1 month aging, respectively. The TFT with 26.5% NaCl treatment showed a mobility and Ion/Ioff ratio of 36.5 cm² V⁻¹ s⁻¹ and 3.5 × 10⁶, respectively, and the Ioff/Ion ratio measured after 1 month aging was 1.2 × 10⁴, which is about three orders of magnitude higher than the Ioff/Ion ratio of TFT without NaCl treatment. It is noted that, the threshold voltage of the TFTs was shifted in the positive direction after 1 month aging, which may be attributed to the reduction of defect or trap density at the gate dielectric and channel interface.

To understand the effect of air exposure on the stability of the TFTs, the subthreshold slope was calculated using the following function: $S = \delta V_g / (\delta \log I_d)$. From Table 1, it is clearly seen that the subthreshold slope rapidly increased with air exposure duration in case of the TFT without NaCl treatment.
and a moderate increase of subthreshold slope was also observed for the TFTs with 1% and 10% NaCl treatment. However, almost constant subthreshold slope was observed for the TFTs with 26.5% NaCl treatment.

In order to further investigate the stability and reproducibility of the TFTs with and without NaCl treatment, the bias stress measurements have been performed. Fig. 3 shows the bias stress curves for transistors gated by microporous SiO$_2$ with and without NaCl treatment. After 10 minutes bias with $V_{gs} = 0.5$ V and $V_{ds} = 0.5$ V, transistor gated by 26.5% NaCl-treated microporous SiO$_2$ shows a small on current loss of 1.7%. While the transistor gated by microporous SiO$_2$ without NaCl treatment shows an on current loss of 9.3%. For dynamic stress test (inset in Fig. 3), the transistor was repeatedly cycled between on and off states (period square wave pulses of $V_{gs} = +0$ V to $-1.0$ V and $V_{ds} = 0.5$ V). TFT gated by NaCl-treated microporous SiO$_2$ maintained a current on/off ratio of $10^6$ and without obvious current degradation after more than 2000 seconds operation. These results suggest that no chemical doping (i.e. Na$^+$ penetrate into the ITO channel) or chemical reaction occurs at the electrolyte/ITO channel interface when the gate potential is biased. As we know, if chemical doping or a chemical reaction occurs, $I_{ds}$ will not return to its original value after gate scanning.$^{17}$

![Graphs showing transfer characteristics of TFTs with and without NaCl treatment.](image-url)

**Fig. 2** Transfer characteristics of TFTs (a) without and with (b) 1%, (c) 10% and (d) 26.5% NaCl treatment measured after different durations of air exposure.

| NaCl content | Fresh | 1 week aging | 1 month aging |
|--------------|-------|--------------|---------------|
|              | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $I_{on}/I_{off}$ | $V_{th}$ (V) | $S$ (mV per decade) | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $I_{on}/I_{off}$ | $V_{th}$ (V) | $S$ (mV per decade) |
| 0            | 12    | $3.4 \times 10^5$ | $-0.1$ | 110 | 4.3 | $1.8 \times 10^5$ | 0.04 | 120 | 3.6 | $6 \times 10^4$ | 0.05 | 180 |
| 1%           | 41.8  | $1.1 \times 10^5$ | $-0.2$ | 100 | 15 | $3.1 \times 10^6$ | $-0.28$ | 150 | 5.7 | $1.3 \times 10^3$ | $-0.35$ | 160 |
| 10%          | 64.5  | $2.5 \times 10^6$ | $-0.17$ | 100 | 29.3 | $7 \times 10^5$ | $-0.2$ | 130 | 12 | $6 \times 10^4$ | $-0.11$ | 180 |
| 26.5%        | 32.6  | $3.5 \times 10^6$ | $-0.35$ | 90 | 36.5 | $9.2 \times 10^6$ | $-0.37$ | 90 | 24 | $1.2 \times 10^7$ | $-0.16$ | 90 |
Conclusions

In conclusion, we have investigated the effects of NaCl treatment on the performance and environmental stability of microporous SiO$_2$-based TFTs. The results showed that an appropriate amount of NaCl treatment can enhance the EDL capacitance of the microporous SiO$_2$ dielectric, which are the key factors for obtaining high performance TFTs. Further, with an optimized amount of NaCl treatment, the environmental stability of $I_{on}/I_{off}$ ratio and on current of the NaCl treated microporous SiO$_2$-based TFTs can be improved with a reasonable field effect mobility which is very important for switching applications.

Conflicts of interest

There are no conflicts to declare.

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