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<td><strong>Citation</strong></td>
<td>IEEE Transactions On Device And Materials Reliability, 2012, v. 12 n. 2, p. 520-528</td>
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<tr>
<td><strong>Issued Date</strong></td>
<td>2012</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10722/155767">http://hdl.handle.net/10722/155767</a></td>
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Improved Performance of Pentacene OTFTs With HfLaO Gate Dielectric by Using Fluorination and Nitridation

L. F. Deng, Y. R. Liu, H. W. Choi, Senior Member, IEEE, C. M. Che, and P. T. Lai, Senior Member, IEEE

Abstract—Pentacene organic thin-film transistors (OTFTs) with fluorinated high-κ HfLaO as gate insulator were fabricated. The dielectrics were prepared by sputtering method and then annealed in N₂ or NH₃ at 400 °C. Subsequently, the dielectrics were treated by fluorine plasma for different durations (100, 300, and 900 s). The N₂ and NH₃-annealed OTFTs with a 100-s plasma treatment achieve a carrier mobility of 0.62 and 0.66 cm²/V·s, respectively, which are higher than those of the OTFTs without plasma treatment (0.22 and 0.41 cm²/V·s). Moreover, the plasma-treated OTFTs realize better 1/f noise characteristics than those without plasma treatment. The improved performance is due to passivation of the dielectric surface by plasma-induced fluorine incorporation. However, for longer time (300 and 900 s) of plasma treatment, the performance of the OTFTs deteriorates in terms of carrier mobility and 1/f noise characteristics due to increased plasma-induced damage of the dielectric surface. The morphology of the pentacene film grown on the HfLaO gate insulator was characterized by SEM. It reveals that the pentacene film has larger grain size and smoother surface on the HfLaO dielectric (for both annealing gases) than the others (0, 300, and 900 s). Finally, AFM characterization of the HfLaO film also confirms the damaging effect of excessive plasma treatment on the dielectric.

Index Terms—Dielectric, HfLaO, high-κ, organic transistor, 1/f noise.

I. INTRODUCTION

ORGANIC thin-film transistors (OTFTs) have emerged as an important electronic device since the electrical conductivity of organic material was discovered [1]–[3]. Though semiconductor devices based on inorganic materials (e.g., Si, Ge, GaAs, InP, et al.) opened up the great era of information technology, organic electronic devices should have a significant role to play [2]. In comparison with their inorganic counterparts, organic devices have their own advantages. First of all, organic devices could be easily realized on flexible substrate such as plastics due to low fabrication temperature [4]–[6]. Moreover, they could be fabricated in large area [7]. Both points mean that organic devices are inherently good candidates for large-area flexible displays [8], [9], which can likely make a mobile phone function like a computer in the future. Besides, without lithography, it is cheaper to manufacture organic electronic products. Furthermore, organic devices are lightweight, which is especially suitable for mobile applications. In addition, evaporation [10], spin coating [11], solution processing [12], and inkjet printing technology [13]–[16] are feasible to realize organic electronic devices. OTFT is a key member in the family of organic electronic devices, and it could be applied to large-area flat-panel displays [17], radio frequency identification card (RF-ID) [18], [19], electronic paper, electronic textile [20], sensors [21]–[24], and so on. Pentacene OTFTs have achieved a performance comparable to that of amorphous-silicon transistors as far as carrier mobility is concerned [19], [25]. However, the operating voltage of OTFTs is usually high (> 15 V for most cases), which imposes extra requirements on the power source as well as leads to heat dissipation problems. The operating voltage can be reduced by scaling down the dielectric thickness, but large gate leakage may result. An alternative is to use high-κ dielectric as the gate insulator [26]–[28], instead of the conventional SiO₂. Hafnium-based oxides with high dielectric constant have been studied extensively due to their good interfacial characteristics with silicon [29]–[31]. Among them, HfLaO is promising as incorporation of La could reduce Fermi-energy pinning [32], [33]. Therefore, organic thin-film transistors with hafnium-based oxides as gate insulator have been reported recently [28], [34]. Also, HfLaO applied to pentacene OTFTs was demonstrated to be very promising [10], [35], [36]. In this paper, high-κ HfLaO prepared by sputtering method is treated in a fluorine plasma before pentacene deposition so as to passivate the traps at the dielectric surface and hence reduce their effects on the carriers in the channel of OTFTs. It is found that treating the HfLaO film in a fluorine plasma for an appropriate time could enhance the performance of OTFTs.

II. EXPERIMENTAL DETAILS

First, n-type silicon substrate was treated by the standard RCA method to achieve clean surface. The silicon was <100> type and its resistivity was 0.5 ~ 0.7 Ω·cm. Next, the samples were kept in hydrofluoric acid (concentration of 5%) for...
1 minute to remove the native oxide, and then washed by de-ionized water. Then, the wafer was inserted into the chamber of a sputterer (Denton Vacuum LLC Discovery 635) to deposit a layer of HfLaO film. The target was HfLa alloy with an atomic ratio 6:4 for Hf and La. Radio frequency sputtering mode was used at a power of 33 W and a pressure of $2.0 \times 10^{-6}$ torr. During the sputtering process, argon and oxygen were injected into the chamber with a gas flow rate of 24 and 6 sccm, respectively. After sputtering, the samples were annealed in N$_2$ or NH$_3$ to improve the surface and bulk qualities of the HfLaO dielectric. Then the samples were divided into three groups to incorporate fluorine in the dielectric for different times (100, 300, and 900 s). In the fluorination process, CHF$_3$ and O$_2$ (to remove carbon due to CHF$_3$) were injected into the chamber, and the flow rate was 10 and 1 sccm, respectively. The pressure of the chamber was 105 mtorr and RF power was 20 W. The substrate was kept at 5 °C. For comparison, control samples without fluorine incorporation were used to check the effects of fluorination. After the fluorination, hydrofluoric acid with a concentration of 20% was used to remove the back oxide on the substrate. Then, the samples were put into the chamber of an evaporator Edwards Auto 306, and a layer of pentacene (purchased from Sigma-Aldrich) was evaporated on the dielectric at a vacuum of $4.0 \times 10^{-6}$ torr through sublimation. The growth rate of pentacene film was 1.2 nm/min, which was monitored by a quartz-crystal oscillator. The thickness of pentacene film was 30 nm. Finally, gold drain and source electrodes were formed through a shadow mask at a vacuum of $8.0 \times 10^{-6}$ torr. The channel length and channel width of the devices were measured by a digital microscope, while the value was 30 and 200 µm on the mask, respectively.

To characterize the quality of the HfLaO dielectric, dummy wafer was prepared. Aluminum was evaporated on the dielectric at a vacuum of $8.0 \times 10^{-6}$ torr. Silicon MOS capacitors (Si-HfLaO-Al) were fabricated by lithography method.

HP 4145B semiconductor parameter analyzer, Berkeley Technology Associates FET Noise Analyzer Model 9603 and HP 35665A Dynamic Signal Analyzer were used to measure the I–V characteristics and noise characteristics of the OTFTs. The C–V characteristics of the silicon MOS capacitors were recorded by HP 4284A Precision LCR Meter. All the electrical measurements were conducted in a shielded probe station. The thickness of HfLaO film was gotten by an ellipsometer Wvase 32 made by J. A. Woollam Co., Inc. Morphology of the pentacene film was obtained by scanning electron microscope (SEM). Surface morphology of the HfLaO film was characterized by atomic force microscope (AFM).

### III. RESULTS AND DISCUSSIONS

Figs. 1–8 show the output characteristics of the eight OTFTs, whose gate dielectric is annealed in N$_2$ or NH$_3$ and then plasma treated for 0, 100, 300, and 900 s, respectively. All of the OTFTs can operate at a voltage as low as 5 V, and exhibit good field-effect characteristics. For both the N$_2$ and NH$_3$ annealings, the drive current of the OTFT is increased after a plasma treatment for 100 s. However, with the plasma treatment time increased to 300 s or over, the drive current decreases.

Figs. 9 and 10 show the transfer characteristics of the OTFTs annealed in N$_2$ and NH$_3$, respectively with different plasma treatment time. According to the current–voltage expression (1) of a field-effect transistor operating in the saturation region, carrier mobility can be derived as (2), where $I_d$ is the drain current; $\mu$ is the carrier mobility; $C_{ox}$ is the capacitance per unit area of the gate dielectric; $W$ is the channel width; $L$ is the
channel length; $V_{gs}$ is the gate voltage relative to the source; and $V_{th}$ is the threshold voltage [37]

$$I_d = -\frac{1}{2} \mu C_{ox} \frac{W}{L} (V_{gs} - V_{th})^2 \quad (1)$$

$$\mu = \frac{2L}{WC_{ox}} \left( \frac{\partial \sqrt{-I_d}}{\partial V_{gs}} \right)^2 \quad (2)$$

After calculation, the carrier mobility of the OTFTs annealed in $N_2$ or $NH_3$ without fluorination is 0.22 and 0.41 cm$^2$/V · s, respectively. The latter is larger than the former because nitrogen and hydrogen atoms decomposed from $NH_3$ could passivate the surface of HfLaO film (next to the conduction channel of OTFT), and hence decrease the traps there. Consequently, trap-related carrier scattering is reduced, and the OTFT annealed in $NH_3$ realizes a higher carrier mobility.
As far as the fluorination time is concerned, the OTFTs plasma treated for 100 s obtain a higher carrier mobility than their corresponding counterpart without fluorination. In the case of N₂ annealing, the plasma-treated OTFT gets a higher mobility (0.62 cm²/V·s) than that without plasma treatment (0.22 cm²/V·s). Similarly for NH₃ annealing, the plasma-treated OTFT acquires an enhanced mobility (0.66 cm²/V·s) when compared to the one without fluorination (0.41 cm²/V·s). This should be due to incorporation of fluorine at the surface of HfLaO surface, hence passivating the traps at/in the channel of OTFTs [39]. The plasma-induced fluorination can passivate the traps (dangling bonds) at the surface of the HfLaO gate dielectric because the highly reactive fluorine atoms can form bonding with the dangling bonds at the HfLaO surface, thus reducing the trap-related scattering on the charge carriers in the conduction channel. In contrast, with plasma treatment time increased to 300 s or longer, the carrier mobility of the OTFTs (annealed in N₂ or NH₃) decreases. This is because RF plasma could damage the HfLaO film through ion bombardment if the treatment time is too long. As a result, it leads to higher defect density at the surface of the HfLaO film, and thus more traps in/at the channel of OTFTs.

Sub-threshold swing (SS) is a key parameter to evaluate the switching characteristics of a field-effect transistor. It reflects the speed of a field-effect transistor transiting between “off” state and “on” state. Usually, the smaller, the better when a field-effect transistor is used as a switch [40]. It could be calculated according to

$$SS = 1/\left(\frac{\partial (\log_{10} |I_d|)}{\partial V_{gs}}\right).$$  (3)
As shown in Tables I and II, the sub-threshold swing of the OTFTs treated by various conditions fluctuates around 0.65 V/dec. The small sub-threshold swing is related to the utilization of high-κ material as the gate dielectric of OTFTs. As the dielectric constant increases, the capacitance per unit area of the gate dielectric becomes larger. Hence, the devices display small value of sub-threshold swing [35].

Noise is related to the fluctuation of current in the channel of OTFTs. It becomes a concern if OTFTs are applied commercially, as the ratio of signal to noise is of importance for circuits [41]. Because of the low carrier mobility of organic devices in comparison with their inorganic counterparts, OTFTs are mainly for low-frequency applications. Consequently, $1/f$ noise is especially significant as the noise power spectral density is inversely proportional to the frequency. In this paper, the $1/f$ noise spectra of the OTFTs were measured, and are displayed in Figs. 11 and 12. In Fig. 11, the OTFT with plasma treatment for 100 s presents the lowest power spectra among all the $N_2$-annealed samples. Similarly in Fig. 12, the OTFT with plasma treatment for 100 s shows the lowest power spectra among all the $NH_3$-annealed devices. Furthermore, the Hooge’s parameter $\alpha$ can be used to quantitatively characterize the $1/f$ noise. It can be calculated from equation (4), where $f$ is the measurement frequency; and $S_{id}$ is the noise power spectral density [42].

$$\alpha = \frac{f^2 S_{id}(f) L^2}{\epsilon \mu V_{ds} I_d}.$$  \hspace{1cm} (4)

The Hooge’s parameter is calculated and summarized in Tables I and II. For both annealing gases, the OTFT treated by plasma for 100 s gets smaller Hooge’s parameter than that without plasma treatment. With the increase of plasma treatment time over 100 s, the Hooge’s parameter becomes larger and thus the noise characteristics become poorer. This indicates that after incorporation of fluorine through the plasma treatment, the OTFT acquires improved noise characteristics than that without plasma treatment. In contrast, the noise characteristics deteriorate with longer plasma treatment, illustrating that excessive plasma treatment damages the dielectric surface (next to the channel of OTFTs) and leads to increased trap-related noise. For both annealing gases, the Hooge’s parameter exhibits the same trend with the plasma treatment time.

SEM image on the surface morphology of pentacene film deposited on the dielectric can provide further information to understand the performance of OTFTs. For the two annealing gases, SEM images are shown in Figs. 13 and 14, respectively. The pentacene film deposited on HfLaO treated in plasma for 100 s has larger grain size and smoother film than that without plasma treatment. However, the surface morphology of pentacene becomes poorer for longer plasma treatment (300 s or over). Larger grain size means less grain boundaries in the organic film, hence less carrier scattering in the grain boundaries. This can further explain the enhanced performance of the OTFTs treated by plasma for appropriate time (100 s in this work).

In order to evaluate the effect of plasma treatment on the surface of the HfLaO film, AFM characterization was done to obtain the surface morphology and roughness of the dielectric. The AFM images are displayed in Figs. 15 and 16 for the $N_2$ and $NH_3$-annealed HfLaO films, respectively. The roughness of the surface is listed in Tables I and II for the two annealing gases, respectively. In the case of HfLaO film annealed in $N_2$, the roughness almost does not change with the plasma treatment time. On the other hand, the $NH_3$-annealed samples
Fig. 14. SEM image of pentacene morphology on HfLaO annealed in NH$_3$ (northwest: 0-s plasma; northeast: 100-s plasma; southwest: 300-s plasma; southeast: 900-s plasma).

show a smaller roughness than their N$_2$-annealed counterparts, further supporting the benefits of using NH$_3$ for annealing the gate dielectric. However, the roughness of the NH$_3$-annealed HfLaO film increases slightly for plasma treatment time longer than 100 s, providing good evidence on the damaging effects of excessive plasma treatment on the surface of the HfLaO film.

Fig. 15. AFM image of HfLaO surface annealed in N$_2$ (northwest: 0-s plasma; northeast: 100-s plasma; southwest: 300-s plasma; southeast: 900-s plasma).
The quality of the HfLaO film can be evaluated by means of leakage measurement. To characterize the leakage of the dielectric, the $I-V$ characteristics of relevant MOS capacitors (with Al-HfLaO-Si structure and patterned by lithography) are measured. In Fig. 17, the six dielectrics treated with plasma for less than 900 s display a leakage current around $10^{-7}$ A/cm$^2$ at an electric field of 1 MV/cm. By contrast, the two dielectrics treated with plasma for 900 s show a much larger leakage current of about $10^{-1}$ A/cm$^2$, even at lower electric field, thus further proving the damaging effect of excessive plasma treatment on the HfLaO film.

**IV. CONCLUSION**

Pentacene OTFTs with fluorinated high-$\kappa$ HfLaO as gate dielectric were fabricated. The HfLaO film was annealed in N$_2$ or NH$_3$ at 400 $^\circ$C, and then treated in a fluorine plasma. For both annealing gases, OTFT treated in the plasma for 100 s achieves higher carrier mobility, improved $1/f$ noise characteristics, and larger drive current than that without plasma treatment. This should be due to fluorine incorporation at dielectric surface which passivates the traps there. However, for longer plasma treatment, the performance of the OTFT deteriorates because excessive plasma treatment damages the dielectric, and thus the channel of the OTFT. SEM image of the pentacene film grown on HfLaO indicates that suitable time (100 s in this work) of plasma treatment could obtain smoother film and larger grain size. On the contrary, plasma treatment for excessive time causes poor morphology of the organic film. AFM characterization of the HfLaO film also supports the damaging effect of excessive plasma treatment on the surface of the dielectric. In conclusion, this work proves that HfLaO film with the incorporation of fluorine through appropriate plasma treatment can act as the gate dielectric of high-performance OTFTs.
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