<table>
<thead>
<tr>
<th>Title</th>
<th>Effects of annealing temperature and gas on pentacene OTFTs with HfLaO as gate dielectric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Deng, LF; Liu, YR; Choi, HW; Xu, JP; Che, CM; Lai, PT</td>
</tr>
<tr>
<td>Citation</td>
<td>IEEE Transactions on Device and Materials Reliability, 2012, v. 12 n. 1, p. 107-112</td>
</tr>
<tr>
<td>Issued Date</td>
<td>2012</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10722/155741">http://hdl.handle.net/10722/155741</a></td>
</tr>
<tr>
<td>Rights</td>
<td>©2012 IEEE. Personal use of this material is permitted. However, permission to reprint/republish this material for advertising or promotional purposes or for creating new collective works for resale or redistribution to servers or lists, or to reuse any copyrighted component of this work in other works must be obtained from the IEEE; This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.</td>
</tr>
</tbody>
</table>
Effects of Annealing Temperature and Gas on Pentacene OTFTs With HfLaO as Gate Dielectric

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

Abstract—Pentacene organic thin-film transistors (OTFTs) with high-κ HfLaO as gate insulator were fabricated. HfLaO film was prepared by sputtering method. To improve the film quality, the dielectric was annealed in N2, NH3, or O2 at two temperatures, i.e., 200°C and 400°C, respectively. The I–V characteristics of the OTFTs and C–V characteristics of corresponding organic capacitors were measured. The OTFTs could operate at a low operating voltage of below 5 V, and the dielectric constant of the HfLaO film could be above ten. For all the annealing gases, the OTFTs annealed at 400°C achieved higher carrier mobility than their counterparts annealed at 200°C (with the one annealed in NH3 at 400°C showing the highest carrier mobility of 0.45 cm2/V·s), which could be supported by SEM images which indicate that pentacene tended to form larger grains on HfLaO annealed at 400°C than on that annealed at 200°C. The C–V measurement of the organic capacitors indicated that the localized charge density in the organic semiconductor/oxide was lower for the 400°C annealing than for the 200°C annealing. Furthermore, through the characterization of gate current leakage, HfLaO film annealed at 400°C achieved much smaller leakage than that annealed at 200°C. Since the maximum processing temperature of ITO glass substrates is around 400°C, this study shows that 400°C is suitable for the annealing of HfLaO film in high-performance OTFTs on glass substrate.

Index Terms—Dielectric, HfLaO, high κ, organic thin-film transistor (OTFT).

I. INTRODUCTION

O RGANIC thin-film transistors (OTFTs) have emerged as an important electronic device since the electrical conductivity of organic material was discovered [1]–[3]. In comparison with their inorganic counterparts, organic devices are advantageous in many aspects. First of all, they can be easily manufactured in large area, and so, this makes them particularly suitable for the application of displays [4]. Moreover, the fabrication temperatures of organic devices are usually much lower than those of inorganic devices, and hence, the former can be realized on flexible plastic substrate. Furthermore, organic products are often light. The advantages mentioned previously are helpful for organic devices to be applied in portable equipment. Moreover, lithography is usually not needed for the fabrication of OTFTs. Consequently, it costs less to fabricate organic devices than inorganic devices. In a word, OTFTs have high potential to be applied in large-area flexible display [5], [6], radio-frequency identification card [7], electronic paper, sensors [8]–[10], and so on.

Carrier mobility is a significant parameter to evaluate the performance of OTFTs, because it decisively influences the speed of the device and relevant circuit. Pentacene OTFTs based on silicon dioxide gate dielectric prepared by oxidation have a mobility comparable to that of amorphous silicon thin-film transistors [11]. However, the operating voltage of the OTFTs is usually too high, and typical value is often larger than 15 V. The high operating voltage leads to excessive power consumption, as well as complicated power supply. As a result, organic devices add extra cost and also are not suitable for low-voltage portable equipment. The high operating voltage of OTFTs originates from the small capacitance of their gate dielectric. A straightforward way to solve this problem is to scale down the thickness of the gate insulator. However, too thin insulator may cause large gate current leakage. An alternative is to replace the gate insulator of low dielectric constant with material of high dielectric constant (high κ). Dimitrakopoulos et al. [12], [13] pioneered in 1999 the use of high-κ oxides as the gate dielectric of OTFTs. By this way, the operating voltage of OTFTs was reduced to as low as 5 V. Several dielectric films were synthesized through sputtering method. There were barium zirconate titanate (BZT; κ = 17.3), barium strontium titanate (BST; κ = 16), and Si3N4 (κ = 6.2). Pentacene OTFTs based on these dielectrics had a carrier mobility higher than 0.3 and 0.5 cm2/V·s for the BZT and BST dielectrics, respectively, while for the Si3N4 case, the mobility of the pentacene OTFT could amount to 0.6 cm2/V·s. Kang et al. in 2004 reported pentacene OTFTs using Gd2O3 as the gate insulator [14], with the Gd2O3 film grown by ion-beam-assisted deposition. The operating voltage of the OTFTs was
10–20 V, and the mobility was 0.1 cm²/V · s. In 2003, Lee et al. [15] reported pentacene OTFTs based on Al₂O₃, which was deposited by magnetron radio-frequency sputtering. The mobility was 0.14 cm²/V · s, and the device could operate at a voltage of 30 V. Hf-based dielectric applied in OTFTs was first reported by Tardy et al. in 2007 [16]. Pentacene-based OTFT with HfO₂ (κ = 22 for anodic oxidation and κ = 11 for sol-gel) gate dielectric was grown by anodic oxidation method and sol-gel method, respectively. The maximum mobility was around 0.12 cm²/V · s, and the device could operate at about 2.5 V. HiLaO is a promising gate dielectric to be applied in inorganic MOSFETs because Fermi-energy pinning could be reduced by adding lanthanum (La) into hafnium oxide [17], [18]. Also, OTFTs with HiLaO gate dielectric had been reported and demonstrated high performance [19]–[22].

The carrier transport of OTFTs occurs at the interface between the organic semiconductor film and the gate dielectric film. Therefore, treatment of the gate dielectric film can significantly affect the performance of the devices [23]. In the case of OTFTs with HiLaO gate dielectric, the effects of annealing temperature, together with annealing gas, on their performance have not been reported. This is a major concern for devices fabricated on glass substrate or plastic substrate, because there usually exists a tradeoff between device performance and maximum processing temperature. Therefore, this study concentrates on how the annealing temperature of the gate dielectric affects the quality of HiLaO film itself and the performance of relevant OTFTs.

II. EXPERIMENTAL DETAILS

First, n-type silicon substrate was treated according to 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 min to remove the native oxide and then washed up by deionized water. Then, the wafer was inserted into the chamber of a sputterer (Denton Vacuum LLC Discovery 635) to deposit a layer of HiLaO film. The target was HiLa alloy with an atomic ratio of 6:4 for Hf and La. Radio-frequency sputtering mode was used at a power of 35 W and a pressure of 2.0 × 10⁻² torr. During the sputtering process, argon and oxygen were injected into the chamber with gas flow rates of 24 and 6 sccm, respectively. After sputtering, the samples were annealed in N₂, NH₃, or O₂ to improve the surface and bulk qualities of the HiLaO dielectric. To study the effects of annealing temperature on the performance of the devices, 400 °C and 200 °C were chosen for all the annealing gases because they are roughly the upper limit for the processing temperature of ITO glass and plastic substrates, respectively. For all the aforementioned combinations, the annealing time was 10 min, and the gas flow rate was 1000 mL/min. After the annealing, 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 × 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 × 10⁻⁶ torr. The channel length and channel width of the devices were measured by a digital microscope, and the values were 30 and 200 μm on the mask, respectively.

To characterize the quality of the HiLaO dielectric, a dummy wafer was prepared. Aluminum was evaporated on the dielectric at a vacuum of 8.0 × 10⁻⁶ torr. Silicon MOS capacitors (Si–HiLaO–Al) were fabricated by lithography method. Organic MOS capacitors are on the same wafer of OTFTs with a structure of Au–pentacene–HiLaO–Si.

An HP 4145B semiconductor parameter analyzer was used to measure the output characteristics and transfer characteristics of the OTFTs and the I–V characteristics of the silicon MOS capacitors. C–V characteristics of the silicon MOS capacitors and the organic MOS capacitors (Au–pentacene–HiLaO–Si) were characterized by HP 4284A Precision LCR Meter. All the electrical measurements were conducted in a shielded probe station. The thickness of HiLaO film was gotten by an ellipsometer Vyase 32 made by J. A. Woollam Co., Inc. Morphology of the pentacene film was obtained by a scanning electron microscope.

III. RESULTS AND DISCUSSIONS

Figs. 1–3 show the output characteristics of the six OTFTs with gate dielectric annealed in N₂, NH₃, or O₂ at 200 °C and 400 °C, respectively. According to these graphs, all the OTFTs can operate with a supply voltage below 5 V and display good field-effect characteristics. The drive current for the OTFTs exceeded 1 μA. Among them, OTFT annealed in NH₃ at 400 °C achieves the largest drive current of 5 μA, while OTFT annealed in N₂ at 200 °C has the smallest drive current of 1.3 μA. For each annealing gas, OTFT annealed at 400 °C obtains larger drive current than that annealed at 200 °C.

Figs. 4–6 show the comparison of transfer characteristics of the OTFTs annealed at 400 °C and 200 °C, respectively. Transfer characteristics can be used to extract the major parameters of a field-effect transistor. Carrier mobility is one significant parameter for the evaluation of OTFTs, because it affects the speed of the devices. According to the current–voltage

![Fig. 1. Output characteristic comparison of OTFTs annealed in N₂.](Image)
DENG et al.: EFFECTS OF ANNEALING TEMPERATURE AND GAS ON PENTACENE OTFTs

Fig. 2. Output characteristic comparison of OTFTs annealed in NH$_3$.

Fig. 3. Output characteristic comparison of OTFTs annealed in O$_2$.

Fig. 4. Comparison of transfer characteristics of OTFTs annealed in N$_2$.

For each annealing gas, the carrier mobility of the OTFT annealed at 400 $^\circ$C is larger than that annealed at 200 $^\circ$C. Hence, the interface characteristics between the 400 $^\circ$C annealed HfLaO film and pentacene are better than those of the 200 $^\circ$C annealed counterpart. The OTFT annealed in NH$_3$ at 400 $^\circ$C got the highest mobility of 0.45 cm$^2$/V $\cdot$ s, while the OTFT annealed in O$_2$ at 200 $^\circ$C has the lowest mobility of 0.13 cm$^2$/V $\cdot$ s. For NH$_3$ annealing, nitrogen atoms are incorporated at the gate dielectric surface and can passivate the traps at the surface and, thus, trap-related carrier scattering, resulting in higher carrier mobility [23], [24].

The interface characteristics between HfLaO and pentacene can be further analyzed through the measurement of $C$–$V$ characteristics of the organic MOS capacitors (Au–pentacene–HfLaO–Si units). Fig. 7 shows the $C$–$V$ characteristics of the organic MOS capacitors measured at 100 kHz. According to the Mott–Schottky equation (3), the localized charge can be extracted from the capacitance variation in the depletion region [25], [26]

$$\frac{\partial(1/C^2)}{\partial V_g} = -\frac{2}{q\varepsilon_0\varepsilon_s N_A}.$$  

In (3), $C$ is the capacitance per unit area of the organic MOS capacitor, $V_g$ is the voltage between the Au electrode and the substrate, $q$ is the electron charge, $\varepsilon_0$ is the vacuum permittivity, $N_A$ is the concentration of localized charge, and $\varepsilon_s$ is the relative permittivity of pentacene (3.0 is chosen for the calculation).
The value of \( N_A \) can be derived by calculating the slope of the \( C^{-2} - V_g \) curve in the depletion region. The localized charge density in the organic MOS capacitor with HfLaO annealed at 400 °C is much lower than that for HfLaO annealed at 200 °C for all three annealing gases. In the case of \( \text{NH}_3 \) or \( \text{O}_2 \), the organic MOS capacitor annealed at 400 °C acquires a localized charge density one order lower than that at 200 °C. Carrier transport in the channel of OTFTs is influenced by the localized charge in the organic semiconductor. Less localized charge can explain why OTFTs annealed at 400 °C got higher mobility than those annealed at 200 °C for all three annealing gases.

The morphology of pentacene film on HfLaO can further help to explain why OTFTs annealed at 400 °C exhibit higher carrier mobility than those annealed at 200 °C for the annealing gas \( \text{N}_2 \), \( \text{NH}_3 \), or \( \text{O}_2 \). Figs. 8–10 show the morphology of pentacene on HfLaO dielectrics by using scanning electron microscopy. By comparing these photographs, the grains of pentacene on HfLaO annealed at 400 °C are larger than those annealed at 200 °C for the same annealing gas \( \text{N}_2 \), \( \text{NH}_3 \), or \( \text{O}_2 \). The larger the grain, the fewer the grain boundary in the organic semiconductor film, thus resulting in less scattering between the carriers and grain boundaries. Consequently, OTFTs annealed at 400 °C obtain a higher carrier mobility than OTFTs annealed at 200 °C.

Generally, the mobility of OTFTs is also influenced by the grain boundaries of the organic film in addition to the localized charge, as scattering by the defects at the grain boundaries affects the transport of carriers. The larger the grains, the lower the density of grain boundaries, thus less carrier scattering. In this paper, we concentrate on the comparison of samples annealed at 200 °C and 400 °C for the same annealing gas. In the case of annealing gas, higher annealing temperature results in lower density of localized charge and larger grain size than lower annealing temperature, hence higher mobility for the former. However, lower density of localized charge does not necessarily mean higher mobility for different annealing gases due to the other important factor—grain size.

In the case of the same annealing temperature, OTFT with the dielectric annealed in \( \text{NH}_3 \) achieves a higher carrier mobility than those annealed in \( \text{N}_2 \) or \( \text{O}_2 \) (the latter two have almost the same value). This could be explained as follows. Nitrogen and hydrogen atoms decomposed from \( \text{NH}_3 \) could passivate the surface of the HfLaO film (next to the conduction channel of the OTFT) and hence decrease the traps there [23], [24]. Consequently, trap-related carrier scattering is reduced, and the OTFTs annealed in \( \text{NH}_3 \) realize a higher carrier mobility.

For the same annealing gas (\( \text{NH}_3 \), \( \text{N}_2 \), or \( \text{O}_2 \)), the samples annealed at 400 °C have an enhanced performance in comparison with their respective counterparts annealed at 200 °C. This is because the HfLaO dielectric treated at higher temperature is denser than that annealed at lower temperature. This is supported by the ellipsometry results shown in Table I.
Densified dielectric film could have less defects and, thus, less traps hindering the carrier flow in the channel of the OTFTs. As a result, the OTFTs annealed at 400 °C obtain an improved performance than those annealed at 200 °C.

The enhanced quality of the HfLaO film annealed at 400 °C could be further proved by means of leakage measurement. To characterize the leakage of the dielectric, the \( I-V \) characteristics of the Si MOS capacitors (Al–HfLaO–Si) are measured. The applied voltage is divided by dielectric thickness to transform to electric field in Fig. 11. In the graphs, the dielectric annealed at 400 °C shows less leakage than that annealed at 200 °C for \( \text{N}_2 \), \( \text{NH}_3 \), or \( \text{O}_2 \) annealing. It indicates that the HfLaO film gets enhanced electrical characteristics through annealing at a higher temperature of 400 °C. This can be attributed to better densification of the dielectric film and, thus, decrease of defects. For all the films, the leakage is on the order of \( 10^{-7} \ \text{A/cm}^2 \), with the exception of annealing at 200 °C in \( \text{N}_2 \) or \( \text{O}_2 \), whose larger leakage is on the order of \( 10^{-6} \ \text{A/cm}^2 \).

In the case of leakage current, defects in the dielectric film play an important role. HfLaO film annealed at 400 °C displays less leakage than that annealed at 200 °C for each gas because more thermal energy at higher temperature can remove defects more effectively. According to Fig. 11, all the three samples annealed at 400 °C have about the same leakage because, at this higher temperature, the three films can densify to achieve roughly the same bulk quality. However, at the lower temperature of 200 °C with little densification, nitrogen atoms dissociated from \( \text{NH}_3 \) can passivate the defects at the surface of the film and thus give a lower leakage for the \( \text{NH}_3 \)-annealed sample as compared to the \( \text{N}_2 \)- and \( \text{O}_2 \)-annealed samples. Other major parameters of the OTFTs and capacitors are listed in Table I.

## IV. CONCLUSION

Pentacene OTFTs with high-\( \kappa \) HfLaO as gate dielectric were fabricated. The dielectric films were prepared by sputtering method and annealed in \( \text{N}_2 \), \( \text{NH}_3 \), or \( \text{O}_2 \) at 200 °C and 400 °C, respectively, to improve the surface/bulk qualities of the dielectric films. The output characteristics and transfer characteristics of the OTFTs were measured. The devices could operate at a supply voltage as low as 5 V and presented good field-effect characteristics. OTFTs annealed at 400 °C displayed higher carrier mobility than those annealed at 200 °C for all the three gases. OTFT annealed in \( \text{NH}_3 \) at 400 °C obtained the highest carrier mobility of \( 0.45 \ \text{cm}^2/\text{V} \cdot \text{s} \), while that annealed in \( \text{O}_2 \) at 200 °C acquired the lowest carrier mobility of \( 0.13 \ \text{cm}^2/\text{V} \cdot \text{s} \). The \( C-V \) characteristics of the organic capacitors were measured. Organic capacitors with HfLaO annealed at 400 °C achieved less localized charges than those annealed at 200 °C. SEM images indicated that the pentacene film intended to grow larger grains on HfLaO film annealed at 400 °C than on HfLaO film annealed at 200 °C. Moreover, for all the three annealing gases, HfLaO film annealed at 400 °C exhibited smaller current leakage than that annealed at 200 °C. Since the maximum processing temperature for ITO glass substrate is around 400 °C, this study shows that 400 °C is suitable for the annealing of HfLaO gate dielectric used in high-performance OTFTs.

## REFERENCES


