Surface-State Modification of OTFT Gate Insulators by Using a Dilute PMMA Solution

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(Received 7 August 2003)

A new technique using a dilute poly-methylmethacrylate (PMMA) solution is proposed for the surface state modification of a gate insulator for organic thin film transistors (OTFTs). After the surface modification of a low pressure chemical vapor deposition (LPCVD) oxide and a nitride by using a dilute PMMA solution, the electrical performance parameters of the OTFTs were dramatically improved in view of mobility, subthreshold slope, on-off current ratio, and off-state current. The improvements were due to a reduction in the surface energy by the hydrophobic ending group ($-\text{CH}_3$). OTFTs with a low temperature oxide (LTO) and a silicon nitride gate insulator treated with a 3:1 dilute PMMA solution showed a 2~25 times larger mobility and one two order of magnitude lower off-state current than those of an OTFT without surface modifications, even though the resistivity of pentacene after a 9:1 dilute PMMA insertion was 1.5 times larger than that before treatment.

PACS numbers: 85.45.Db
Keywords: PMMA, OTFTs, Surface modification

I. INTRODUCTION

For the fabrication of OTFTs, the surface state modification of gate insulators and/or electrodes by self-assembly monolayers (SAMs) such as octadecyltrichlorosilane (OTS) and 1-hexadecanethiol is indispensable to the high performance of OTFTs [1–3]. Even though the treatment of gate insulators by SAMs results in a drastic improvement of performances, the procedures in the treatment are very tedious jobs to be executed in an inert-gas ambient to prohibit reactions with oxygen and moisture.

We propose a new technique to modify the surface state of the gate insulators by using a dilute poly-methylmethacrylate (PMMA) solution on the basis of a spin-coating process. The solution does not have any dependency on surface state of gate insulators, i.e., hydrophobic or hydrophilic, like OTS does. Furthermore, the modification process requires neither an inert-gas ambient nor a high baking temperature because of the stable characteristics of PMMA.

In this paper, we report the performance improvement of pentacene OTFTs with a low pressure chemical vapor deposition (LPCVD) oxide and a silicon-nitride gate insulator after surface treatment as well as the mechanism for the improvement by means of static contact angles, atomic force microscopy (AFM) images, and X-ray diffraction (XRD) spectra. Also, the ohmic contact characteristics for Ni electrodes with a dilute PMMA layer were investigated for applications of OTFTs with bottom electrodes.

II. EXPERIMENTAL PROCEDURES

Oxide and silicon-nitride with thickness of 30 nm were deposited on a p-type wafer with a resistivity of 15 Ωcm by using LPCVD at temperatures of 450 °C and 650 °C, respectively. After the low-temperature oxide (LTO) and the silicon-nitride had been patterned, the wafers were cut to sizes of 2 × 2 cm. Each sample with an LTO gate dielectric was coated with a dilute PMMA solution by using a spin-coating process and then baked in a convection oven at a temperature of 110 °C. Treatment conditions are no treatment, 3:1 and 9:1 dilute PMMA solution, and monochlorobenzene on an LTO, respectively. X:Y dilute PMMA is a mixed solution of monochlorobenzene and 1 % PMMA. The volume ratio of monochlorobenzene to 1 % PMMA is X to Y. After the surface state modifications by using dilute PMMA and monochlorobenzene, pentacene was deposited by using a thermal evaporator with a pressure in the range of 3 × 10$^{-8}$~5 × 10$^{-7}$ torr. During the deposition, the temperature of the substrate holder and the deposition rate were maintained at 80 °C and under 0.3 Å/sec, respectively [4]. Pentacene was purchased from Aldrich Company, and its purity was about 98 % based on a CHN (carbon, hydrogen, and nitrogen)
elemental test. All pentacene sources in this experiment were used without purification. Finally, a 50-nm-thick Ni film was deposited through a shadow mask for the source, the drain and the gate electrodes by using an e-gun evaporator at a base pressure of $5 \times 10^{-6}$ torr.

Static contact angles were measured to analyze the surface energy changes of the LTO insulators after various surface treatments. Also, the deposited pentacene was studied by using atomic force microscopy (AFM) and x-ray diffraction (XRD) to investigate the surface morphology and the crystallographic structure. In addition, devices for the investigation of ohmic contacts were fabricated. The device had the structure of Ni(50 nm)/pentacene(50 nm)/dilute PMMA/Ni(50 nm), as shown in Fig. 8(a). After fabrication of the OTFTs and the ohmic contact devices, I-V characteristics were measured using an HP4155B semiconductor parameter analyzer at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the results for the transfer characteristics of OTFTs with surfaces modified by using dilute PMMA solutions. For the case of an OTFT with an LTO gate insulator, the electrical performance characteristics of the OTFT, such as mobility, subthreshold slope, and on/off current ratio, are very inferior to those of OTFTs after surface modifications. As shown in Table 1, the mobility of OTFTs after treatment with the 3:1 and 9:1 PMMA solutions was $23\sim25$ times better than that of an OTFT without the treatment. The improved mobility can be explained by changes in the surface energy of the treated insulators, as shown in Table 2. Lowering the surface energy on a gate insulator is identified as a key factor to increase the grain size during the growth of pentacene [2]. The one liquid method combined with Young’s equation usually allows the evaluation of the surface free energy of a solid ($\gamma_s$) from a single measurement of the contact angle of a liquid with a known surface tension ($\gamma_L$) [5]. Therefore, we used the following equation obtained from both Young’s equation [5] and the equation of state [5] for solid-liquid interfacial tension in order to investigate the surface energy of treated gate insulators:

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_L\gamma_s}e^{-\beta(\gamma_L-\gamma_s)^2},$$

where $\gamma_L$, $\gamma_s$, $\theta$, and $\beta$ are the surface tension of water, the surface energy of the solid, the contact angle, and an empirical constant with an average value of 0.0001057 (m$^2$mJ$^{-1}$)$^2$, respectively. In the calculation of surface energy of a solid ($\gamma_s$), the surface tension of water is adopted as 72.8 mJ/m$^2$ [5]. As shown in the Table 2, the mobility of OTFTs is correlated with the surface energy of the gate insulators. The surface energy data show that the OTFTs of a gate insulator with low surface energy have a tendency to have the high mobility due to the large pentacene grain size and good crystallographic structure.

The AFM images in Fig. 2 give good agreement for the relationship between the surface energy and the grain size. The average grain size in Fig. 2(b) is in the range of 2 $\sim$ 3 $\mu$m, whereas the size in Fig. 2(a) is a few hundred of nanometers. Figure 3 shows that the crystallographic structure of pentacene depends on the surface treatment condition for a gate insulator. The XRD spectra in Fig. 3 show that pentacene deposited on LTO treated with 3:1 PMMA has a better crystallographic structure than that grown on the untreated LTO. The pentacene on the treated LTO has thin-film phases ($d_{001} = 15.66$, $d_{002} = 7.78$, $d_{003} = 5.17$, and $d_{004} = 3.86$), whereas the pentacene on the untreated LTO does not have any crystallographic peaks. The results indicate that the dilute-PMMA coating process to the lower surface energy of
Table 1. Summary of electrical performance parameters for the OTFTs with different surface treatments of gate insulators.

<table>
<thead>
<tr>
<th></th>
<th>mobility (V/sec/cm²)</th>
<th>SS (V/dec)</th>
<th>V_T(V)</th>
<th>I_on/I_off</th>
<th>off-state current</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTO only</td>
<td>0.01</td>
<td>3.2</td>
<td>−2</td>
<td>10²</td>
<td>1.2 × 10⁻⁵</td>
</tr>
<tr>
<td>3:1 PMMA</td>
<td>0.25</td>
<td>0.45</td>
<td>−2.35</td>
<td>1.8 × 10⁵</td>
<td>8.0 × 10⁻¹¹</td>
</tr>
<tr>
<td>9:1 PMMA</td>
<td>0.23</td>
<td>0.5</td>
<td>−0.5</td>
<td>1.8 × 10⁴</td>
<td>1.8 × 10⁻⁹</td>
</tr>
<tr>
<td>monochlorobenzene</td>
<td>0.02</td>
<td>1.3</td>
<td>−0.55</td>
<td>9.6 × 10²</td>
<td>3.2 × 10⁻⁹</td>
</tr>
</tbody>
</table>

Table 2. Static contact angle and surface energy for gate insulators with various surface state treatments.

<table>
<thead>
<tr>
<th></th>
<th>LTO only</th>
<th>3:1 PMMA</th>
<th>9:1 PMMA</th>
<th>monochlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>static contact angle</td>
<td>21°</td>
<td>69°</td>
<td>74°</td>
<td>28°</td>
</tr>
<tr>
<td>surface energy (γ_s)</td>
<td>68.1 mJ/m²</td>
<td>33.9 mJ/m²</td>
<td>29.9 mJ/m²</td>
<td>64.6 mJ/m²</td>
</tr>
</tbody>
</table>

Fig. 3. X-ray diffraction (XRD) spectra from pentacene thin films deposited on an LTO and on an LTO treated with 3:1 PMMA.

Fig. 4. Output characteristics of OTFTs with LTO gate insulators coated with different dilute PMMA solutions. Gate insulators are summarized as (a) LTO only and (b) 3:1 dilute PMMA, (c) 9:1 dilute PMMA, and (d) monochlorobenzene on an LTO.
V_{DS} = −10 V are different for each devices, as shown in Fig. 4. The main difference in the saturation current level is thought to arise from differences in the grain size of pentacene.

For the investigation of the surface modification effects for other gate dielectrics by using a dilute PMMA solution, the surface modification technique was applied to OTFTs with a silicon-nitride gate insulator. Figure 5 shows the transfer characteristics for OTFTs with a silicon-nitride insulator with and without a 3:1 PMMA treatment. Even though the gate dielectric thickness after 3:1 PMMA treatment is about 20 nm thicker than it was before treatment, the current level after treatment remained at the same current level. This result was due to an enlarged grain size after treatment, as shown in Fig. 6. The mobility is proportional to the pentacene grain size. In addition, other electrical parameters, such as the subthreshold slope, the on/off current ratio, and the threshold voltage, are improved, as shown in Table 3. The mobility and the on/off current ratio were improved about 2.7 times and 2.5 times than those before surface treatment, respectively. The threshold voltage was reduced from −1.5 V to −2.2 V. These results indicate that surface-state modification by using a dilute PMMA can be universally applied for other gate insulators due to the spin-coating process.

On the other hand, the structures of OTFTs need to have bottom electrodes for mass production, which requires conventional photolithography, instead of a shadow mask. Even though the thickness of a dilute PMMA layer is very thin under 20 nm, an ohmic contact is a prerequisite for high-performance bottom-electrode OTFTs in view of hole injection. Before fabricating pentacene OTFTs with a bottom-electrode structure, we investigated ohmic contact characteristics. Figure 8 shows the device structures for the investigation of ohmic characteristics and the current density characteristics versus the applied anode-cathode voltage. The inset shows the two structures; a 9:1 PMMA buffer layer was (a) inserted
or (b) not. From the characteristics in Fig. 8, ohmic behaviors were confirmed for the two structures. The resistivity of pentacene with and without a dilute 9:1 PMMA layer was extracted from the I-V characteristics and the device dimension. In the calculation of the resistivity, the error range was based on the size of the contact area, 1 ∼ 1.5 mm² and a dilute 9:1 PMMA with thickness variation of 5 ∼ 10 nm. The thickness of the pentacene was taken as 50 nm on the basis of a thickness monitor in the thermal evaporator. The resistivity of pentacene without the PMMA layer was in the range of 2.1 × 10⁴ Ωcm ∼ 3.1 × 10⁴ Ωcm, whereas that with the layer ranged from 2.3 × 10⁴ Ωcm to 5.3 × 10⁴ Ωcm. Taking the middle value in the range, ρ₁ (pentacene with PMMA) and ρ₂ (pentacene only) were 3.8 × 10⁴ Ωcm and 2.6 × 10⁴ Ωcm, respectively. The pentacene resistivity of 2.6 × 10⁴ Ωcm is thought to be a reasonable value compared with the values in the literature [8]. Even though the ohmic contact characteristics were obtained after PMMA insertion, the resistivity with PMMA was increased by up to 46 % compared to that without PMMA. The increased resistivity is thought to be not serious, considering the improved I-V characteristics.

IV. CONCLUSIONS

A surface modification technique by coating with a dilute PMMA solution is proposed for surface-state modification of gate insulators and electrodes, instead of SAMs such as OTS and 1-hexa-decanethiol. The method can be simply applied to gate insulators by using a spin-coating process in air. Furthermore, OTFTs having an LTO and a silicon-nitride gate insulator coated with a dilute PMMA solution show performance improvements in terms of the mobility, the subthreshold slope, and the on-off current ratio, compared with OTFTs without surface modification. The noticeable improvement in the performance is attributed to an increase in the hydrophobicity due to ending groups of methyl radicals (−CH₃). In addition, a dilute PMMA solution has a high potential for application to all gate insulators because the surface states of the gate insulators are independent. Even though the resistivity after the insertion of a 9:1 dilute PMMA layer is 1.5 times larger than that before treatment, ohmic contact characteristics were confirmed. The increased resistivity may have an effect on the reduction in the saturation drain current level.

ACKNOWLEDGMENTS

This work was supported by a contract of the inter-university semiconductor research center (ISRC), 2002-X-5505, with electronics and telecommunications research institute (ETRI) and ministry of information and communication (MIC) to carry out the Advanced Technology Project.

REFERENCES