Organic-inorganic hybrid dielectrics with low leakage current for organic thin-film transistors

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Using a thermally cross-linkable organosiloxane-based organic-inorganic hybrid material, a solution-processable gate dielectric layer for organic thin-film transistors has been fabricated. The hybrid dielectric was synthesized by a sol-gel process, followed by heat treatment at below 190 °C. Dielectric strength of 1.4–1.65 MV/cm was measured and it was confirmed that the leakage current is governed by the Poole-Frenkel emission mechanism in which the silanol groups act as trap sites. An organic thin-film transistor utilizing the hybrid dielectric shows similar electrical performance to a transistor fabricated using surface-modified thermally grown SiO₂.

Organic thin-film transistors have received considerable attention of late because of their flexibility, light weight, low cost, and easy processability. They are considered potential candidates for a wide variety of applications such as large-area displays and low-end electronic devices such as smart cards and electronic identification tags as well as large-area sensing devices. However, relative to the impressive advances that have been made towards the overall improvement of organic thin-film transistors (OTFTs), little work has been reported on the gate dielectrics, a critical factor in OTFT electrical performance. Most gate dielectrics reported thus far are based on thermally grown silicon dioxide, plasma-enhanced chemical-vapor-deposited silicon nitride, sputtered aluminum oxide, or sputtered tantalum pentoxide, and hence are typically brittle and expensive to prepare. The poor mechanical properties of these materials pose a major obstacle to their practical application in flexible electronics. In addition, the film preparation requires a high temperature vacuum process, which is not compatible with plastic substrates. Consequently, it is necessary to develop an economical and easy method (e.g., a solution-processable method) to fabricate gate insulators with requisite dielectric properties and flexibility.

Organic dielectrics are an interesting alternative to inorganic dielectrics since the films can be easily spin cast, dip coated, or ink-jet printed on large-area substrates at low temperatures. Various organic dielectrics have been investigated including polyvinylphenol, polymethacrylate, polyimide, polyvinyl alcohol, benzocyclobutene, and parylene. However, solution-processable dielectrics based on siloxane bonds have received relatively little attention. In this letter, we report organosiloxane-based organic-inorganic hybrid dielectric materials synthesized by a sol-gel reaction. Since our materials are composed of a cross-linked network formed by hydrolysis and condensation reactions between alkoxides and alkyl (aryl)-substituted alkoxysilane, the organic character that imparts low temperature and solution processabilities could be easily incorporated into an inorganic siloxane matrix of good dielectric stability.

A precursor solution of organic-inorganic hybrid dielectric was prepared from a combination of methyltriethoxysilane and tetraethyorthosilicate. In order to initiate the hydrolysis and condensation reactions, de-ionized (DI) water and acid catalyst were added to the mixed precursor solution. After the synthesized precursor solution was diluted, it was coated on a heavily doped silicon substrate using a spin-coating technique. The obtained films were heat treated in order to evaporate the solvent and to complete the sol-gel reactions. The electrical properties of the hybrid dielectrics were investigated by capacitance-voltage (C-V) measurements at a frequency of 1 MHz and current-voltage (I-V) characteristics and ATR-FTIR spectra of the sol-gel hybrid dielectrics heat treated at 150, 170, and 190 °C. The film thickness of the hybrid dielectric is 260 nm and the dielectric constants of the hybrid dielectrics heat treated at 150, 170, and 190 °C are 4.5, 4.3, and 4.0, respectively.

FIG. 1. (Color online) (a) J-E characteristics and (b) ATR-FTIR spectra of the sol-gel hybrid dielectrics heat treated at 150, 170, and 190 °C. The film thickness of the hybrid dielectric is 260 nm and the dielectric constants of the hybrid dielectrics heat treated at 150, 170, and 190 °C are 4.5, 4.3, and 4.0, respectively.

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measurements using a Au/dielectric/heavily doped Si structure. To fabricate coplanar-type transistors, Au/Cr electrodes were patterned by a shadow mask on top of either the thermally grown SiO2 or the hybrid dielectric deposited on a heavily doped silicon substrate. The width and the length of current density–electric field

<table>
<thead>
<tr>
<th>Heat-treatment temperature (°C)</th>
<th>( \beta_s \times 10^{-5} )</th>
<th>( \beta_{PF} \times 10^{-5} )</th>
<th>( \beta_e \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>23.7</td>
<td>7.37</td>
<td>5.34</td>
</tr>
<tr>
<td>170</td>
<td>24.5</td>
<td>7.78</td>
<td>5.34</td>
</tr>
<tr>
<td>190</td>
<td>26.2</td>
<td>6.53</td>
<td>5.34</td>
</tr>
</tbody>
</table>

*All values need to be multiplied by \( 10^{-5} \) [unit: eV/(V/m)^{1/2}].

The silanol group (Si–OH) gradually diminishes and the intensity of the siloxane bond (Si–O–Si) increases as the heat-treatment temperature increases. This indicates that the condensation reaction is thermally induced to form the siloxane network, thereby consuming the hydroxyl groups. On the other hand, the intensity of the methyl group (CH3) is unaltered. Therefore, it is believed that the dielectric characteristics of the sol-gel hybrid films are determined by the presence of the hydroxyl group, not by the methyl group.

In order to attain an in-depth understanding of the \( J-E \) relations in conjunction with the structural evolution of the hybrid dielectrics as a function of the heat-treatment temperature, the conduction mechanism is analyzed. The parabolic behavior in the leakage current can be interpreted mainly by two mechanisms, field-enhanced Schottky emission \( (J_s) \) and Poole-Frenkel emission \( (J_{PF}) \) inside the dielectric. The Schottky emission mechanism is an electrode-limited conduction, occurring at low voltages at which the electrons on the surface of the injecting electrode transit above the potential barrier. The Poole-Frenkel emission mechanism is due to field-enhanced thermal excitation of trapped electrons into the insulator conduction band. Both Poole-Frenkel and Schottky emissions result from Coulomb lowering of the potential barrier under an applied electric field and are, respectively, expressed as follows:

\[
J_s = AT^{2} \exp \left[ \frac{qE}{4e_0\varepsilon kT} - \frac{q\Phi_s}{kT} \right]
\]

for Schottky emission,

\[
J_{PF} = BE \exp \left[ \frac{qE}{\pi e_0\varepsilon kT} - \frac{q\Phi_{PF}}{kT} \right]
\]

for Poole-Frenkel emission,

where \( A \) and \( B \) are constants, \( e \), \( e_0 \), \( q \), \( E \), \( k \), and \( T \) are high-frequency dielectric constant, permittivity in vacuum, electronic charge, electric field, Boltzmann constant, and temperature in kelvins, respectively. \( \Phi_s \) is the barrier height for the injecting electrons for the Schottky emission while \( \Phi_{PF} \) is the barrier for the trapped electrons for the Poole-Frenkel emission.

To distinguish the conduction mechanisms associated with the sol-gel hybrid dielectric, the \( J-E \) plots in Fig. 1(a) are converted to \( \ln(J) \) vs \( E^{1/2} \) for Schottky emission and \( \ln(J/E) \) vs \( E^{1/2} \) for Poole-Frenkel emission. The slopes \( (m) \) of the linear regions in the plots can be described as follows:

\[
m_s = \beta/2kT \quad \text{for Schottky emission},
\]

\[
m_{PF} = \beta kT \quad \text{for Poole-Frenkel emission},
\]

where \( \beta = \sqrt{q/4e_0\varepsilon} \). Using this equation, \( \beta \) can be theoretically calculated from the optical dielectric constant [the square of the measured refractive index \( (n) \)]. The \( \beta \) values for each mechanism are also evaluated based on the slopes of the linear region determined by performing a linear regres-

![Schematic diagram of the charge trapping mechanism in which the injected electrons are trapped.](image-url)
The hybrid dielectric was heat treated at 190 °C and the film thickness of 75°, respectively. Because of the resemblance of the intrinsic trap site in the siloxane-based dielectric, the film heat treated at 190 °C and the film thickness of the thermally grown SiO2 is 200 nm.

Based on the relative intensities in the ATR-FTIR spectra of Fig. 1(b), the hybrid film heat treated at 190 °C has the lowest concentration of silanol groups and exhibits the smallest leakage current with the least parabolic behavior, consistent with the proposed emission mechanism.

Figure 3 shows the transfer characteristics of the OTFTs fabricated using both the sol-gel hybrid film and the HMDS-treated thermally grown SiO2 as a dielectric layer. The electrical performance parameters are summarized in Table II. The contact angles for DI water on the hybrid dielectric displays similar mobility (∼5 × 10⁻³) and on current (∼5 × 10⁻⁷) to those of the OTFT fabricated with HMDS-treated thermally grown SiO2 without additional surface modification with the SAMs. However, slightly higher off current is observed, resulting from the increased leakage current associated with the hybrid dielectric.

In summary, we have demonstrated the synthesis of organosiloxane-based gate dielectric materials. A sol-gel reaction between methyliothiolsilane and tetraethylorthosilicate led to the formation of solution-processable dielectric materials. Using this dielectric material, high quality organic-inorganic hybrid films exhibiting a dielectric strength of 1.4–1.65 MV/cm were obtained at 190 °C. It is proposed that conduction in the hybrid dielectrics is governed by the Poole-Frenkel emission mechanism. We have also shown that the organic-inorganic hybrid dielectric can be applied to the fabrication of organic transistors with relatively enhanced electrical properties, compared with a transistor based on HMDS-treated thermally grown SiO2.

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<table>
<thead>
<tr>
<th>Dielectric type</th>
<th>(\mu_{on}) (cm² V⁻¹ s⁻¹)</th>
<th>(I_{on}) (A)</th>
<th>(I_{off}) (A)</th>
<th>(V_{th}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid Dielectric</td>
<td>(5 \times 10^{-3})</td>
<td>(5 \times 10^{-7})</td>
<td>(6 \times 10^{-10})</td>
<td>0.3</td>
</tr>
<tr>
<td>HMDS-treated thermally grown SiO₂</td>
<td>(4 \times 10^{-3})</td>
<td>(5 \times 10^{-7})</td>
<td>(4 \times 10^{-10})</td>
<td>0.3</td>
</tr>
</tbody>
</table>