Highly Dielectric and Photo-patternable Gate Insulators for Organic Field-effect Transistors

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A highly dielectric and photo-patternable polymer material has been developed as a gate insulating layer in organic field-effect transistors (OFETs). The partially cyanomethylated poly(vinyl phenol) (PVPCM) was synthesized as a highly dielectric polymer matrix. The photosensitive PVPCM (PS-PVPCM) consisting of PVPCM (72 wt%), 4,4’-methylenebis[2,6-bis(hydroxymethyl)phenol] (25 wt%) as a cross-linker, and Irgacure PAG-103 (3 wt%) as a photoacid generator showed a good patterning performance such as high resolution of 6 μm, high sensitivity of 15.5 mJ/cm², and good contrast of 3.3 when i-line lithography was employed. PVPCM and PS-PVPCM exhibited high dielectric constants (PVPCM = 4.51 and PS-PVPCM = 4.29). The OFET performance using poly(3-hexylthiophene) as a polymer semiconductor and PS-PVPCM as a gate insulator showed the excellent charge mobility of 0.102 cm²/Vs and on/off ratio of 1.1 × 10⁶.

Keywords: high dielectric constant, organic field-effect transistor, gate insulator, cross-linker, photoacid generator

1. Introduction

Organic field-effect transistors (OFETs) have attracted great interest due to their potential for lightweight, low cost fabrication, compatibility with a flexible substrate, and the device fabrication through solution processes [1]. For these reasons, OFET is expected to be applied to future generation electronic devices such as flexible displays and low-end electronics such as radio frequency identification (RFID) cards [2,3].

During the past decade, much effort has been exerted for improving the OFET performance, and the carrier mobility of organic semiconductors has now approached or surpassed those of amorphous Si. However, gate insulators in OFET-based devices are mainly fabricated with inorganic insulating materials, such as SiO₂, Ta₂O₅, and HfO₂ [4-6]. While such inorganic insulators have attractive characteristics, such as a high dielectric constant, high heat and chemical resistance, and long-term stability, polymeric gate insulators are the most likely candidates for flexible device applications due to their high flexibility and solution processability.

The drain-source current (I_sd) of OFETs in the saturation regime is expressed by equation 1;

\[ I_{sd} = \frac{W \mu C_i}{2L} (V_g - V_T)^2 \]  

where μ is the mobility of the semiconductors, C_i is the capacitance per unit area of the gate insulator, V_g is the gate applied voltage, V_T is the threshold voltage, and W and L are the channel width and length, respectively. Since C_i can directly affect the OFET properties as represented by Equation 1, a high C_i is required for gate insulators. There are two ways of increasing C_i; one is to make ultrathin gate insulators, while the other is to use high-dielectric-constant (high-k) materials [7-9]. However, thinner insulators might cause serious current leakage and the generation of pinholes. Thus high-k gate insulators are highly required.

In order to apply to low-cost and large-area device fabrications, polymer gate insulators should be patternable with a high pattern resolution to allow the creation of the electrical connection between the different electrode layers. Previously, the photo-patternable polymeric gate insulators based on poly(vinyl phenol) (PVP), poly(methyl
methacrylate) (PMMA), and polyimide (PI) have been reported [10-13]. However, these gate polymers have relatively low dielectric constants. To the best of our knowledge, photo-patternable and high-k gate insulators have never been reported.

In this study, we developed novel photosensitive polymeric gate insulators with an improved dielectric constant. The photosensitive polymer, consisting of partially cyanomethylated PVP (PVPCM) as a high-k polymer, 4,4’-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) as a cross-linker, and Irgacure PAG-103 as a photoacid generator (PAG), shows a higher dielectric constant compared with PVP, a widely used polymer as a gate insulator, due to the incorporation of the polar cyano group. We have demonstrated photolithographic properties of PVPCM with i-line UV exposure in detail. Photosensitive PVPCM (PS-PVPCM) showed the high resolution of 6 μm with a good sensitivity of 15.5 mJ/cm² and contrast of 3.3. Furthermore, the OFET device using the regioregular poly(3-hexythiophene) (rr-P3HT) as a polymeric semiconductor and PS-PVPCM as a gate insulator exhibited excellent transistor properties such as the high mobility of 0.102 cm²/Vs and on/off ratio of 1.1 × 10⁶.

2. Experimental
2-1. Materials

N,N-Dimethylformamide (DMF) was purified by vacuum distillation. Irgacure 103 kindly donated by BASF Japan Ltd. was used without further purification. Poly(4-vinylphenol) (Mw = 20,000) was purchased from Sigma-Aldrich Co. The 2.38 wt % aqueous tetramethylammonium hydroxide solution (TMAHaq) was used as a standard developer. MBHP was prepared according to the previous report [14]. Other reagents and solvents were used as received.

2-2. Synthesis of PVPCM

To a solution of poly(4-vinylphenol) (1.24 g, 10.4 mmol) in DMF (10 mL) was added 0.46 equivalent of potassium carbonate (0.66 g, 4.77 mmol). After stirring for 10 min under nitrogen, bromoacetonitrile (3.45 ml, 51.9 mmol) was added, and the reaction mixture was stirred for 6 h at room temperature. After the reaction, PVPCM was precipitated from the DMF solution into water for two times and dried overnight at 80 °C under reduced pressure. The light brown solid was obtained (1.21 g, yield 86 %). The degree of cyanomethylation was determined by 1H NMR to be 43 %. 1H NMR (300 MHz, CDCl₃, ppm): δ = 8.85 (s, 1H), 6.05-7.00 (m, 4H), 4.99 (s, 2H), 0.40-2.25 (m, 3H).

2-3. Dissolution rate

PVPCYM was dissolved in cyclopentanone, followed by addition of MBHP and PAG (the total solid content was 20 wt%). The resist films with 1.5-μm thickness were obtained by spin-casting from the solutions on silicon wafers. These films were pre-baked at 80 °C for 1 min, and then exposed to a filtered super-high pressure mercury lamp at 365 nm (i-line), followed by post-exposure baking (PEB) at temperature (100-140 °C) for 1 min. The dissolution rate (Å/sec) of the film was determined from changes in the film thickness before and after the development with the mixture of 2.38 wt% TMAHaq and iso-propanol (IPA) (2.38 wt% TMAHaq / IPA = 85 / 15 wt%) (TMAHaq/IPA) followed by rinsing with water.

2-4. Photosensitivity

The photosensitive polymer film with 1.5-μm thickness on a silicon wafer was prepared by dissolving PVPCM, MBHP, and PAG in cyclopentanone, followed by spin-casting on the silicon wafer and pre-baking at 80 °C for 1 min, and exposed to irradiation at the wavelength of 365 nm with changing an exposure dose, post-exposure baked at 130 °C for 1 min, and then developed with TMAHaq/IPA for 5 sec at room temperature. A characteristic photosensitive curve was obtained by plotting a normalized film thickness against exposure dose (unit: mJ/cm²). Image-wise exposure through a mask was carried out in a contact-printing mode.

2-5. Device fabrication for dielectric constant measurement

The cyclopentanone solution consisting of PVPCM (72 wt%), MBHP (25 wt%), and a PAG (3 wt%), was spin-coated on the ITO patterned glass substrate to form the film with 1.40 μm thickness, followed by pre-baking at 80°C for 1 min, irradiation at 150 mJ/cm², PEB at 130 °C for
1 min, and then developed with TMAHaq/IPA. These films were then cured at 250 °C for 30 min. Al electrodes were deposited on the patterned polymer film to complete the device fabrication.

2-6. Device fabrication for OFET measurement

For the fabrication of the bottom-contant OFET devices, first PS-PVPCM with 500 nm thickness was photo-patterned on Au gate electrodes deposited on a glass substrate in the similar way as the preparation for the dielectric constants measurement. Then Au source and drain electrodes (channel width (W) = 500 μm and channel length (L) = 100 μm) were photolithographically patterned onto the PS-PVPCM film, followed by spin-casting the rr-P3HT solution on top of the PS-PVPCM layer and the electrodes.

2-7. Measurements

$^1$H NMR spectrum (300 MHz) was recorded with a Bruker DPX300S spectrometer. The film was spin-coated on a silicon wafer from a polymer solution in cyclopentanone, and the film thickness was measured with Veeco Instrument Dektak$^3$ surface profiler. Scanning electron micrograph (SEM) images were taken with a Technex Lab Tiny-SEM 1540 with 15kV acceleration voltage for imaging. Pt/Pd was sputtered on film in advance of the SEM measurement.

3. Results and Discussion

3-1. Synthesis of PVPCM

One of the most suitable photo-patternable dielectrics is PVP, in which a phenol unit acts as an alkaline developable and cross-linkable functional group during the photo-pattern formation step. On the other hand, the introduction of cyanooalkyl groups is a well-established method to increase the k values of polymers due to their high polarity and simple aprotic structures. For instance, the high-k gate polymers, such as cyanoethylated pullulan (CYEPL) [9] and cyanoethylated poly(vinyl alchol) (PVA) [15], have been reported. Based on these considerations, the matrix polymer, PVPCM, was designed and prepared by a polymer reaction between PVP and bromoacetonitrile (Scheme 1). The degree of cyanomethyl substitution was calculated to be 43% based on the integral ratio of the 6.05-7.00 and 4.99 ppm peaks assignable to the aromatic protons and the methylene protons next to the nitrile group in the $^1$H NMR spectrum (Figure 1). Further incorporation of the cyanomethyl group caused a lowering of the solubility in TMAHaq, a developer used in the photo-patterning process. Since the low solubility of the polymer matrix makes it difficult to employ the polymer in photo-patterning processes, we selected the 43% substituted PVP as a matrix polymer for the following photolithographic and electronic measurements.

3-2. Photolithographic evaluations

To initially evaluate the photo-patterning properties, the photosensitive PVPCM was formulated using a cross-linker MBHP and a PAG. The patterning process is shown in Scheme 2. It is assumed that sulfonic acids generated in the exposed area catalyze the formation of benzyl carbocation species, which undergo electrophilic substitution on the aromatic rings and hydroxyl group to produce C- and O-alkylated polymers [16,17]. These reactions convert the alkaline soluble PVPCM into cross-linked PVPCM as shown in Scheme 2. The patterned films should be insoluble in the solvents used in the following electrodes and semiconductors deposition processes. In order to obtain a sufficient cross-
linking density, the resist with 25 wt% MBHP and 3 wt% PAG was used for the following evaluation. The PEB temperature is crucial in the chemically amplified resist system because diffusion of the generated acids from PAG after i-line exposure in the film is an important factor. Thus, the effect of the PEB temperature on the dissolution rate in TMAHaq/IPA was investigated.

The dissolution rates in the unexposed area slightly decrease with the increasing PEB temperature, while the PS-PVPCM films in the exposed area become insoluble after PEB in the temperature range from 100 to 140 ºC for 1 min (Figure 2). This indicated that the cross-linking reaction in the exposed area was successfully catalyzed by the photo-generated acids under these conditions, resulting in a large dissolution contrast between the exposed and unexposed areas.

Then, the sensitivity of PS-PVPCM was studied. The photosensitivity curve of the resist film with a 1.5 μm thickness shown in Figure 3 indicates a high sensitivity (D0.5) of 15.5 mJ/cm² and good contrast (γ0.5) of 3.3, after PEB treatment at 130 ºC for 1 min, followed by development with TMAHaq/IPA.

Figure 4 represents the SEM image of a contact-printed pattern. A clear negative pattern with a 6-μm feature is observed when a 1.5-μm thick film was used.

3-3. OFET characteristics

In order to investigate the potential of the photo-patterned gate insulators, the dielectric constants of the pristine PVPCM and PS-PVPCM were characterized using metal-insulator-metal (MIM) devices. PVPCM and PS-PVPCM consisting of PVPCM (72 wt%), MBHP (25 wt%) and PAG (3 wt%) were spin-coated on the ITO patterned glass substrate, followed by the photolithographic
Table 1. Dielectric constants of PVP, PVPCM, and PS-PVPCM

<table>
<thead>
<tr>
<th>Gate insulator</th>
<th>Dielectric constant (1MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>3.97</td>
</tr>
<tr>
<td>PVPCM</td>
<td>4.51</td>
</tr>
<tr>
<td>PS-PVPCM</td>
<td>4.30</td>
</tr>
</tbody>
</table>

Figure 5. Schematic image of bottom-contact OFET process. After patterning, the films were heated at 250 °C for 30 min to obtain a sufficient cross-linking density. At the end, an Al layer was deposited by evaporation on the patterned polymer films as an electrode. The results of the dielectric constant measurements are summarized in Table 1. The dielectric constant of PVPCM is higher than that of PVP due to the highly polar nitrile group. Although the patterned films of PS-PVPCM showed decreased dielectric constants, the dielectric constant of PS-PVPCM surpassed that of PVP, a widely used polymeric gate insulator.

The polymer OFETs were fabricated with PS-PVPCM as the gate insulator and rr-P3HT as the polymeric semiconductor (Figure 5). The transfer current-voltage plots are shown in Figure 6. The mobility was calculated using Equation (1) described in the introduction. The charge carrier mobilities can be extracted from the slopes of the linear plots of the square root of the drain current versus gate voltage. Table 2 summarizes the mobilities, threshold voltages, and on/off current ratios of these devices. The OFETs exhibited an excellent charge mobility in the saturation region of 0.102 cm²/Vs and on/off ratio of $1.1 \times 10^6$, while the threshold voltage was 4.18 V. The positive shift in the threshold voltage was probably caused by the residues of the additives such as cross-linkers and PAGs in the PS-PVPCM film surface. These OFETs with PS-PVPCM have properties superior to the previously reported polymer OFETs, in which rr-P3HT, PVP, and poly(melamine-co-formaldehyde) methylated (PMF) (PVP:PMF = 73:27, by wt.) were employed as the polymeric semiconductor, a gate insulator, and a cross-linker, respectively [18].

Figure 6. Plots of $I_{ds}$ and $I_{ds}^{1/2}$ versus $V_{gs}$ using the OFET device with PS-PVPCM ($L = 100 \mu m$, $W = 500 \mu m$, $V_{ds} = 40 V$) and cross-linked PVP ($L = 50 \mu m$, $W = 1000 \mu m$).

Table 2. Mobility, threshold voltage, and on/off ratio of the OFET devices with PS-PVPCM ($L = 100 \mu m$, $W = 500 \mu m$, $V_{ds} = 40 V$) and cross-linked PVP ($L = 50 \mu m$, $W = 1000 \mu m$).

<table>
<thead>
<tr>
<th>Gate insulator</th>
<th>Mobility $\mu$ (cm²/Vs)</th>
<th>Threshold voltage $V_{th}$ (V)</th>
<th>on/off ratio $I_{on}/I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PVPCM</td>
<td>0.102</td>
<td>4.18</td>
<td>$1.1 \times 10^6$</td>
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<tr>
<td>Cross-linked PVP</td>
<td>0.073</td>
<td>-5.1</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

4. Conclusions

A highly dielectric and photo-patternable polymer material has been developed as a gate insulating layer for use in OFETs. The PS-PVPCM film consisting of PVPCM (72 wt%), MBHP (25 wt%), and PAG (3 wt%) showed a good patterning performance, such as the high resolution of 6 μm, high sensitivity of 15.5 mJ/cm², and good contrast of 3.3 when i-line lithography was employed. Furthermore, PVPCM and PS-PVPCM showed higher dielectric constants (PVPCM = 4.51 and PS-PVPCM = 4.29) compared to PVP, a widely used polymeric gate insulator. This PS-PVPCM was used in OFET devices with a polymer semiconductor, rr-P3HT. The OFET exhibited an excellent charge mobility (0.102 cm²/Vs) and
on/off ratio \((1.1 \times 10^6)\) compared to the reported OFET consisting of rr-P3HT and the photo-patternable PVP.

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References