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Jaemin Lee^a, Hong-Ku Shim^a, Jeong-Ik Lee^b,
Yong Suk Yang^b, Seong Hyn Kim^b, Hye Yong Chu^b,
Lee-Mi Do^b & Taehyoung Zyung^b

^a Center for Advanced Functional Polymers,
Department of Chemistry and School of Molecular
Science (BK21), Korea Advanced Institute of Science
and Technology

^b Basic Research Lab., Electronics and
Telecommunications Research Institute

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CHEMICAL MODIFICATION OF GATE DIELECTRIC SURFACES IN ORGANIC THIN FILM TRANSISTOR (OTFT) THROUGH MOLECULAR SELF-ASSEMBLY

*Jaemin Lee and Hong-Ku Shim**

Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology

Jeong-Ik Lee, Yong Suk Yang, Seong Hyn Kim, Hye Yong Chu, Lee-Mi Do, and Taehyoung Zyung*
Basic Research Lab., Electronics and Telecommunications Research Institute

To modify SiO₂ dielectric surface of bottom-contact OTFT device, octadecyltriethoxysilane (OTES) was used to find optimum condition of surface modification for triethoxysilane derivatives. Either spin-coating method or solution dipping method was applied to modify the dielectric surface with OTES. Optimization process was performed with varying solution concentration, reaction time and so on. Through surface modification of OTFT, 0.01–0.04 cm²/V/s of hole mobilities were observed depending on modification conditions.

INTRODUCTION

Over the last decade, much attention has been focused on the interface of organic semiconductor devices where electrical contact occurs and charges, either holes or electrons, pass through. Of the known applications of organic semiconductors, organic thin-film transistors (OTFTs) are very promising due to their potentiality of low-cost, large-area, flexible electronic applications. In these OTFTs, the compatibility between inorganic

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*Address correspondence to Professor Hong-Ku Shim, Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong Yuseong-gu, Daejeon 305-701, Republic of Korea. E-mail: hkshim@mail.kaist.ac.kr, Dr. Jeong-Ik Lee, Basic Lab., ETRI, 161 Kajong-dong, Yuseong-gu, Daejeon 305-350, Republic of Korea. e-mail: jiklee@etri.re.kr

layers, such as metallic electrodes or dielectric layers, and organic layers is closely related to device performance. This is not necessarily confined to OTFTs but general in other semiconductor devices such as organic light-emitting diodes (OLEDs) [1]. As a suitable tool for surface modification, self-assembled monolayers (SAMs) are very popular because of their ease of formation and their wide applicability [2]. Modification of gold electrode with thiol derivatives was reported to improve device performance of OTFT by the enhancement of contact between metallic gold and organics [3,4]. Jackson *et al.* reported improved OTFT characteristics after treatment of SiO₂ dielectric surfaces with octadecylchlorosilane (OTS), a well-known self-organizing material [5]. Moreover, Bao *et al.* reported effects of dielectric surface treatment with various silane reagents on OTFT device characteristics [6].

In general, alkoxysilanes are more stable in air than chlorosilanes, and moreover, it is easier to synthesize and purify compared with chlorosilanes. Therefore, when we need a novel functional SAM on oxide surface, alkoxy silane has some advantages against chlorosilane. In this paper, we report the modification of SiO₂ dielectric surface with octadecyltriethoxysilane (OTES), which might also be applied to new functional alkoxy silanes, and related device characteristics. To find optimized condition of surface modification with OTES, both spin-coating and solution dipping was investigated.

EXPERIMENTAL

TFT substrates cleaned as follows unless otherwise stated. TFT substrates were first cleaned by dipping Chromerge[®] cleaning solution for 5 minutes. They were then washed thoroughly with deionized water and dried by N₂ gas blowing. Finally the cleaning process was finished with O₂ plasma cleaning for 3 minutes, and the cleaned substrates were used immediately upon preparation.

To fabricate OTFT device, 2 weight% of poly(3-hexylthiophene) in chloroform was prepared and filtered through 0.2 μ m PP syringe filter. They were spin-coated on the substrates at 1500 rpm for 40 seconds and then thermally annealed at 100°C for 1 h in a glove box. Our OTFT is a bottom-contact device, comprised of a polythiophene channel, a 300 nm thick SiO₂ gate insulator layer, a hard doped n-type Si wafer as the gate, and Au source and drain electrodes. Channel width is 100 μ m, and channel length is 10 μ m. The I-V characteristics of the TFT device were obtained using HP4145B semiconductor parameter analyzer in an air environment. Hole-mobility of the device was calculated in the saturation region at -100 V of source-drain voltage, by the equation described in the reference [7].

RESULTS AND DISCUSSION

Spin-Coating of OTES

As stated earlier in the introduction section, interface between inorganic dielectric layer and organic semiconducting layer is important in the aspect of OTFT device performance. Actually some dielectric surface modification methods are already known, and of the known methods, hexamethyldisilazane (HMDS) treatment is widespread. In this HMDS treatment, HMDS is usually spin-coated on the TFT substrates, so we applied this spin-coating process to the case of octadecyltriethoxysilane (OTES). Like silazane moiety in HMDS, ethoxysilane groups in OTES can react with hydroxyl (-OH) groups of oxide surface to form a covalent bond. OTES was dissolved in anhydrous ethanol followed by filtration with 0.2 μm PP syringe filter. Then they were spin-coated on as-cleaned substrates for 40 seconds and followed by thermal curing at 100°C for 30 minutes in a glove box. To find the optimal condition of OTES spin-coating, hole-mobility of the device was measured with varying the concentration of OTES. Measured values are plotted in Figure 1. As is shown, there is an optimal concentration for spin-coating, in this case, 20 mM. The maximum mobility was 0.040 $\text{cm}^2/\text{V/s}$ at 20 mM. But the surface after OTES spin-coating looks opaque, and Figure 2 shows the microscope image of substrates after 20 mM OTES solution spin-coating. Large particles which is thought to be polymerized OTES is easily

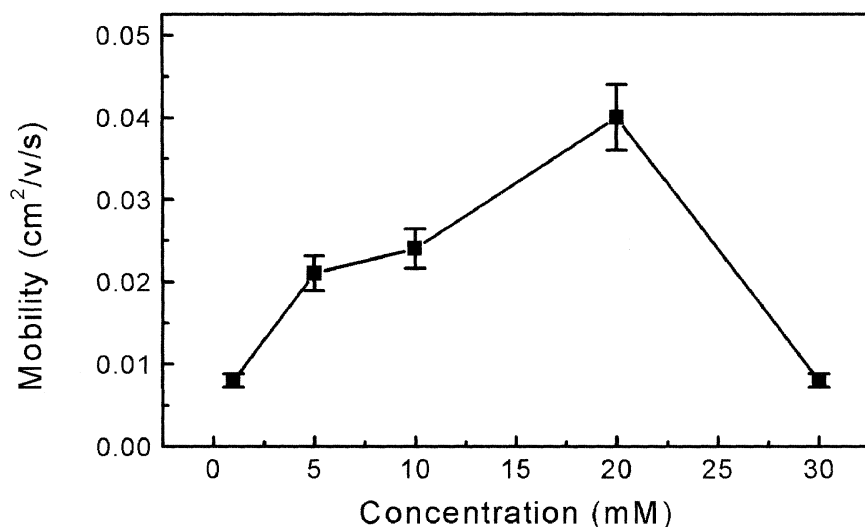


FIGURE 1 Mobility of spin-coated device as a function of solution concentration.

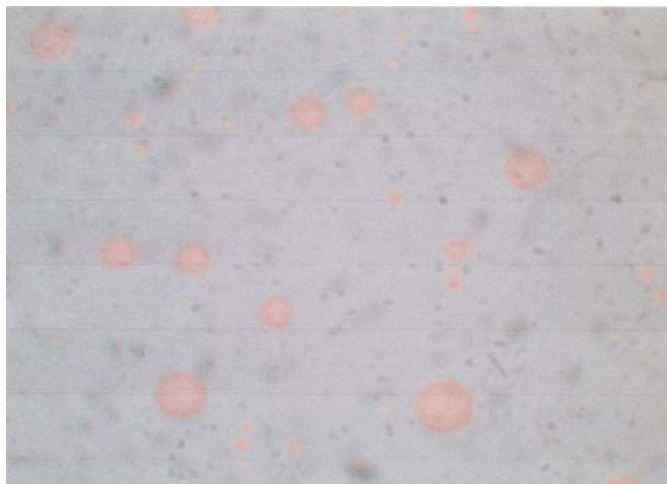


FIGURE 2 Optical micrograph image of substrate after OTES spin-coating. (See COLOR PLATE I)

seen. Although the device performance was improved, this kind of rough surface is not suitable for the electronic devices.

Dipping of OTES

Because of rough surface formation after OTES spin-coating, another surface modification method, dipping in silane solution, was tried. Similar to spin-coating, OTES solution of ethanol was prepared, and they were filtered through 0.2 μm PP syringe filter. For the optimization of this process, we first changed the concentration of OTES solutions, 0.1, 1, 5, and 20 mM, respectively. The substrates were dipped into these solutions for 5 minutes followed by cleaning in ethanol, acetone, methanol and DI water. After N_2 blowing, the modified substrates were thermally cured at 100°C for 30 minutes in a glove box. Figure 3 shows mobility of the device with respect to the concentration of OTES solution. In this experiment, dipping in 1 mM OTES solution resulted in the highest mobility, 0.040 $\text{cm}^2/\text{V/s}$, and the mobility was nearly maintained as the concentration exceeds 1 mM. But in the case of 0.1 mM dipping, the mobility was very small, 0.008 $\text{cm}^2/\text{V/s}$. Figure 4 shows the I-V characteristics of both devices, 0.1 mM (a) and 1 mM (b). From this result, in this OTES dipping SAM method, we can know that minimum concentration to guarantee the device performance is 1 mM and the higher concentration is also acceptable.

After the concentration optimization, we then focused on the dipping time of SAM formation. Here, 20 mM OTES solution of sufficiently high

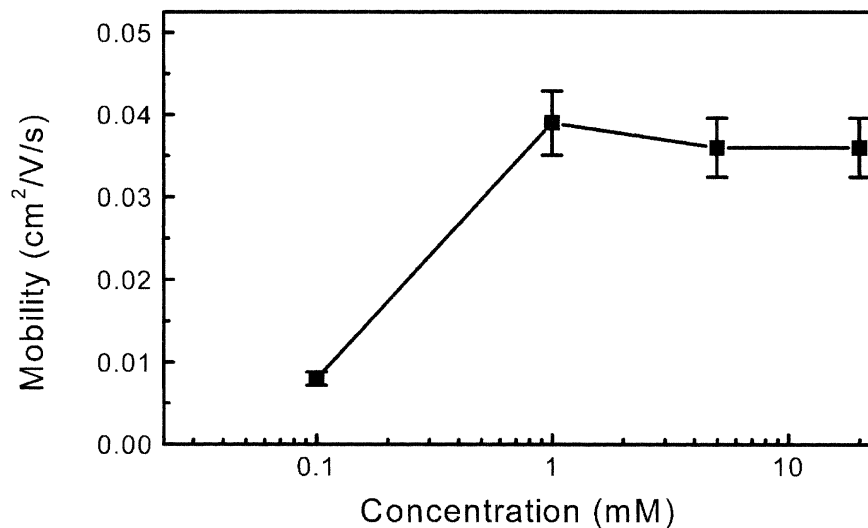


FIGURE 3 Mobility of dipping SAM device as a function of solution concentration.

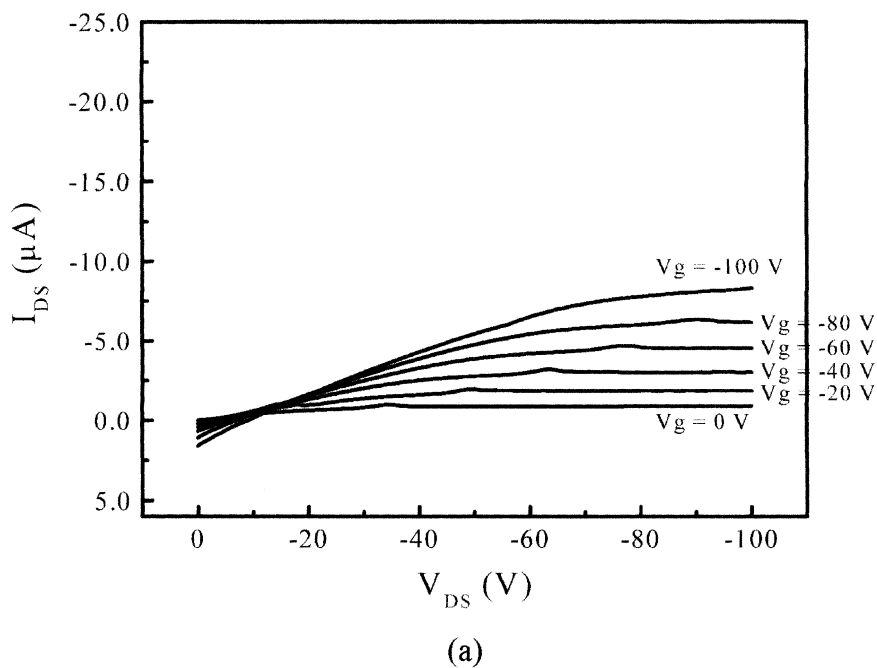
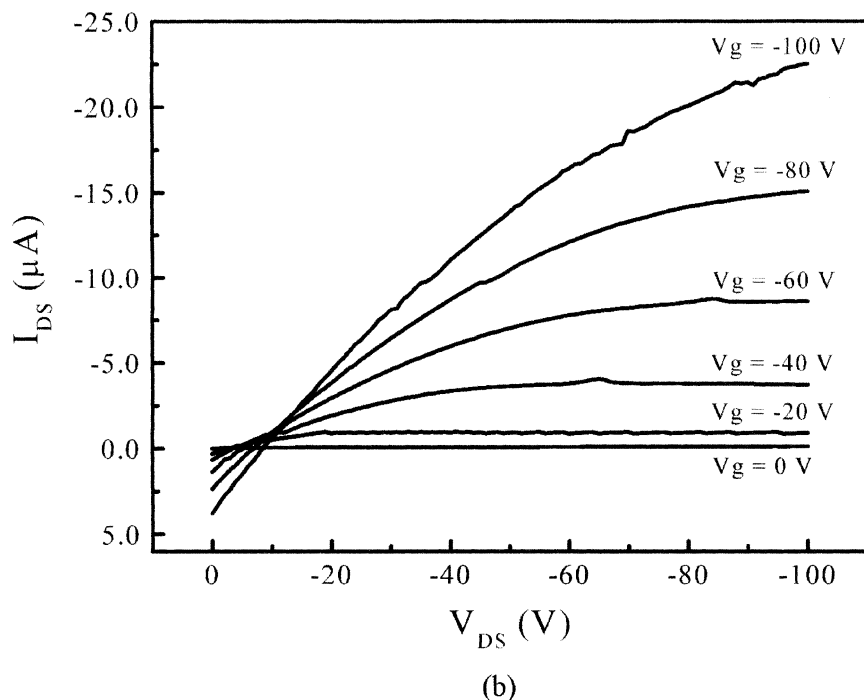


FIGURE 4 I-V characteristics of dipping SAM device. (a) 0.1 mM, (b) 1 mM.

**FIGURE 4** (Continued.)

concentration was equally used. Contrary to the earlier experiment in concentration optimization, the substrates were dipped into the solution for various times, 5, 30, 60 minutes, respectively. Figure 5 shows plot of device mobility with respect to the dipping time. Although the difference of mobility is not very wide as is in the earlier experiment, the mobility does not seem to depend on dipping time. From the above results, we can conclude that full coverage of OTES SAM might be obtained if the dipping time and the concentration exceed certain time and concentration, which are, here, 5 min and 1 mM.

The effect of cleaning method on modified device characteristics was also investigated. Instead of Chromerge[®] and O₂ plasma cleaning, another substrates cleaned by piranha solution (H₂SO₄:H₂O₂ = 7:3) was prepared. Piranha cleaning is a well-known method for SiO₂ and gold electrode cleaning [8]. As is shown in Figure 5, the mobility of both devices, O₂ plasma cleaning and Piranha cleaning, was nearly the same, which means both methods are acceptable as the cleaning process.

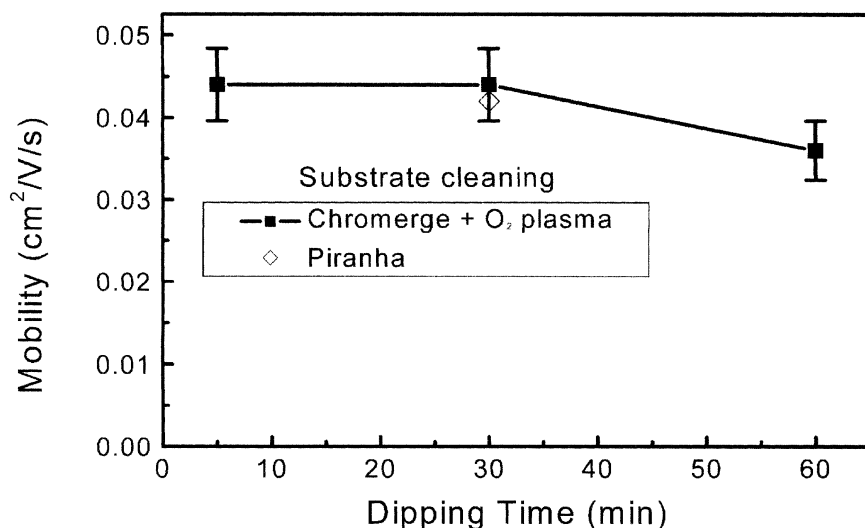


FIGURE 5 Mobility of dipping SAM device as a function of dipping time.

CONCLUSION

To investigate the effect of surface modification in OTFT devices, commercially available compound, octadecyltriethoxysilane (OTES), was used for the modification of SiO_2 dielectric surface. Although spin-coating of OTES solution resulted in comparatively high mobility value, the surface was very rough and was not suitable to these devices. So we adopted solution dipping method, and the optimization was performed. With varying solution concentration, we observed that about 1 mM of concentration is sufficient to enhance device characteristics. It is also known from variation of solution dipping time, that 5 min is the optimized time of dipping for surface modification. In addition to SAM optimization, effect of substrate cleaning was also investigated. Both O_2 plasma cleaning and Piranha cleaning was acceptable as the cleaning process. The surface characterization with changing the SAM fabrication conditions, will further explain the obtained results. The variation of the terminal group of the SAM and possible further optimization of the SAM-modified OTFT is under investigation.

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