Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 640-641

P-10-6

Fabrication and characterization of poly(3-hexylthiophene)-based field-effect transistors with silsesquioxane gate insulators

Kenji Tomatsu[1], Takashi Hamada[1,4], Takashi Nagase[1,4], Takashi Kobayashi[1,4], Shuichi Murakami[2,4], Kimihiro Matsukawa[3,4] and Hiroyoshi Naito[1,4]
[1] Department of Physics and Electronics, Osaka Prefecture University
1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan
Phone: +81-72-252-9269 E-mail: tomatsu@pe.osakafu-u.ac.jp
[2]Technology Research Institute of Osaka Prefecture
[3]Osaka Municipal Technical Research Institute
[4] Innovation Plaza Osaka, Japan Science and Technology Agency

1. Introduction

Organic field-effect transistors (OFETs) are gaining attention in recent years as potential alternatives to amorphous silicon-based technologies for large-area and low-cost devices for flat-panel displays, electronic papers, smart cards, and radio-frequency identification tags. Solution processable polymer semiconductors and gate dielectrics have attracted growing interest as key materials for low-end and flexible OFETs. The performances of OFETs have been progressed tremendously over the past few years and the field-effect mobility as high as 0.1 cm^2/Vs has been reported in regioregular poly(3-hexylthiophene) (P3HT) [1]. It is well known that the performance of OFETs is strongly affected by the semiconductor/dielectric interface. The improvements of OFET characteristics have been achieved by modifying the surface of silicon dioxide (SiO_2) dielectrics with self-assembled monolayers (SAMs) [1,2] and polymer dielectrics [3] prior to the deposition of organic semiconductors. The development of polymer gate dielectrics is therefore important not only for the fabrication of low-cost and flexible devices but also for controlling the interfacial properties of OFETs.

A class of silsesquioxanes has extensively been studied because of their excellent thermal, mechanical, and electrical insulating properties and particularly, polymethysilsesquioxane (PMSQ) is recognized as one of promising materials for intermetal insulators in ultra-large scale integrated circuit technology. Thus, silsesquioxanes would be a good candidate for gate insulating materials in OFETs. However, the silsesquioxanes contain many silanol groups, which cause the decrease of electrical insulating properties.

In this study, we synthesize systematically PMSQs with low silanol concentration by using a sol-gel method and investigate the performances of the P3HT FETs fabricated on the PMSQ-modified gate dielectrics.

2. Experiments

PMSQs were prepared from methyltriethoxysilane in a mixed solvent of toluene and propyrene glycol monomethyl ether acetate (PGMEA) by a sol-gel method (Fig. 1). Methyltriethoxysilane and toluene were added to a round-bottom flask of 100 mL and deionized water with formic acid was added dropwise. The reaction mixture was stirred for 30 min at room temperature, followed by stirring at 50 ºC. Then, PGMEA was added to the mixture, which was stirred at 50 ºC for 2 h under reduced pressure.

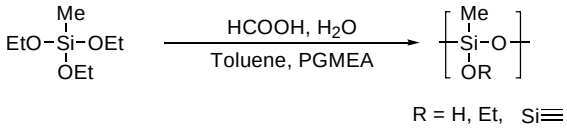

Fig. 1. Synthesis scheme of PMSQ.

For our studies, top-contact FET devices were fabricated using a heavily doped silicon wafer with a thermally grown 300-nm thick SiO_2 layer on the surface as the substrate. The substrates were cleaned with acetone and isopropanol in an ultrasonic bath. Then, PMSQ (8 wt% in PGMEA) was spin coated on the substrate surfaces and was cured at 150 ºC for 1 hour in vacuum. Regioregular P3HT (1 wt% in chloroform) was deposited by spin coating on the PMSQ surface, followed by annealing at 70 ºC for 30 min in vacuum. Finally, 50-nm thick interdigitated Au source and drain electrodes were evaporated on the top of the polymer layer through a shadow mask. The channel length and total channel width were 100 μm and 5.92 cm, respectively. For comparison, the P3HT FETs formed on the non- and SAM-modified SiO_2 surfaces were also fabricated. For the SAMs, hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS) were used. HMDS was spin coated onto the SiO_2 surface and OTS (0.45 wt% in toluene) was dip coated at 60 ºC.

The devices were characterized by using Keithley 2400 source meters. Most of device fabrications and electrical measurements were performed in oxygen-free environments, a glove box filled with N_2 and vacuum. The surface properties of dielectric layers were characterized by water contact angle measurement. The electrical properties of PMSQ films were measured by impedance spectroscopy using the sandwiched samples of Al/PMSQ/Al.

3. Results and Discussion

Electrical properties of PMSQ films

The electrical properties of PMSQ films were found to be changed remarkably depending on the solvent and water content used in the synthesis, and PMSQ films prepared in

the toluene solvent showed high resistivity over 10^{14} Ωcm. The relative permittivity ε' remained constant in the frequency range from 10 mHz to 100 kHz and in the temperature range from 293 to 413 K. These results indicate the low concentration of ionic impurities, silanol groups, in the PMSQ film. The obtained relative permittivity of the PMSQ film was 3.9. We found that the molar ratio of H_2O to methyltriethoxysilane was important factor to determine the resistivity of PMSQ films. These results will be reported in a further study.

Electrical properties of P3HT FETs with different dielectric surfaces

Figures 2(a) and 2(b) show the output curves of P3HT FETs fabricated on the PMSQ-modified and non-modified SiO_2 substrates, respectively. Both devices show *p*-type characteristics with clear transitions for linear to saturation behavior and follow well the standard MOSFET gradual channel model. The increases of drain current I_D were observed in the device with the PMSQ-modified substrate as compared with that with the SiO_2 substrate, indicating the improvement in field-effect mobility.

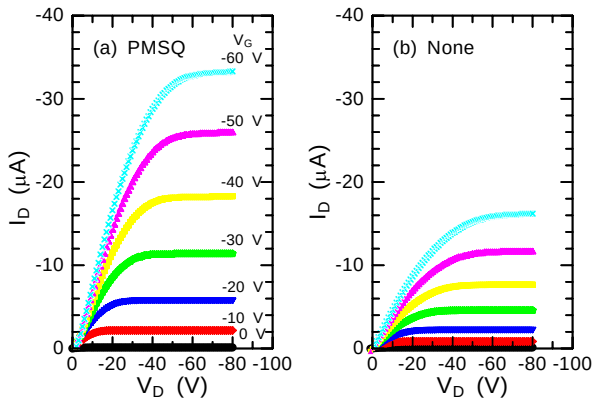

Fig. 2. Output characteristics of P3HT FETs fabricated on the PMSQ-modified SiO_2 substrate (a) and non-modified SiO_2 substrate (b) at V_G = 0, -10, -20, -30, -40, -50, -60 V.

Figure 3 shows the transfer curves of the P3HT FETs formed on various dielectric surfaces. The devices with SAM-modified dielectrics also exhibited similar increases in the I_D. The performance parameters of P3HT FETs with the different dielectric surfaces were extracted from the transfer curves of Fig. 3 and summarized in Table 1. The mobility μ and threshold voltage V_T were determined by using the standard equation in the saturation regime. The mobility for the P3HT FET with the non-modified SiO_2 surface is calculated to be 1.4×10^{-3} cm^2/Vs, which is in agreement with the previous result [2]. It can be seen that the devices with the SAM- and PMSQ-modified SiO_2 substrates show higher mobility than the device with the non-modified SiO_2 substrate and a larger water contact angle, *i.e.*, a more hydrophobic surface gives higher mobility. The enhancements of the mobility in P3HT FETs with SAM-modified substrates have been reported by many authors and our observations are consistent with the previous results. The mobility enhancement may result from the improvement of structural ordering of P3HT molecules on the hydrophobic surfaces [2], but is still controversial issues. We note that the correlation between the water contact angle and the mobility is also valid in the devices with the PMSQ-modified substrate. This result may be attributed to the very smooth surface of PMSQ films, whose average surface roughness is 0.23 nm; if the PMSQ film has a large surface roughness, the mobility enhancement similar to the devices with the SAM-modified SiO_2 substrates would not be observed. The PMSQ gate dielectrics are useful for improving the surface roughness as well as surface energy of dielectrics.

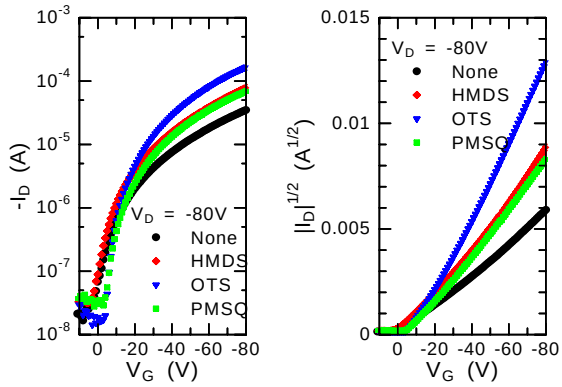

Fig. 3. Transfer characteristics of P3HT FETs with different dielectric surfaces.

Table 1. Water contact angle and device performance of the OFETs with different dielectric surfaces.

modification agent	contact angle	μ (cm^2/Vs)	on/off ratio	V_T (V)
PMSQ	96°	5.1×10^{-3}	2.4×10^{3}	-5.8
HMDS	84°	3.5×10^{-3}	2.5×10^{3}	-1.5
OTS	100°	1.1×10^{-2}	9.8×10^{3}	-12
None	21°	1.4×10^{-3}	1.9×10^{3}	1.4

4. Conclusions

We have synthesized the PMSQs by a sol-gel method and fabricated the P3HT FETs with the PMSQ gate dielectrics. The PMSQs with low silanol concentration were successfully fabricated and the PMSQ films prepared in toluene solvent exhibited high electrical resistivity over 10^{14} Ωcm. The P3HT FET fabricated on the PMSQ-modified SiO_2 surface showed the high mobility of 5.1×10^{-3} cm^2/Vs and the mobility enhancement as compared with the device with the SiO_2 surface was observed. We believe that the PMSQs are useful for the printable gate dielectrics of OFETs.

References

[1] H. Sirringhaus *et al.*, Nature **401**, 685 (1999).
[2] S. Grecu, *et al.*, Organic Electronics **7**, 276 (2006).
[3] Y. Wu *et al.*, Appl. Phys. Lett. **89**, 013505 (2006).