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Effect of length of alkyl chain consisting of fluorine and carbon in self-assembled monolayers

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We investigated the interfacial properties of fluorocarbon self-assembled monolayers (FC-SAMs) with different alkyl chain lengths. It was found that the substrate characteristics were changed rapidly with the fabrication time and temperature of the SAM. FC-3SAM, which has the shortest alkyl chain in this study, showed a contact angle of 54.1 º when it was fabricated in an electric oven at 60 ºC for the first minute. The FC-3SAM showed a contact angle of up to 76.9 º when it was fabricated in an electric oven at the same temperature condition for 180 minutes. FC-10SAM, which has the longest alkyl chain in this study, showed a contact angle of 64.7 º when it was fabricated at a temperature condition of 60 ºC for 1 minute, and a contact angle of 98.7 º at a temperature condition of 60 ºC for 180 minutes. It was found that the FC-10SAM shows an increased contact angle and hydrophobic properties due to a well-aligned molecular structure resulting from a strong van der Waals force. In contrast, the FC-3SAM shows a small contact angle due to the intermolecular disorder resulting from a weak van der Waals force. The average roughness of FC-SAMs was investigated using AFM. The surface roughness of FC-SAMs, which verifies the results of contact angle, was confirmed. At a fabrication time of 120 minutes, the FC-10SAM showed an improvement in average roughness by 62% compared to that of FC-3SAM due to its good alignment.

Key words: Self-assembled monolayer, Alkyl chain, Fluorocarbon.

Introduction

Solid surface technology has been widely used in industrial and scientific fields such as displays and biosensors, which are nanoelectronics applications [1-5].

A typical material which can easily control solid surface properties is a self-assembled monolayer (SAM). The self-assembled monolayer can improve the electrical conductivity of an organic thin-film transistor (OTFT) by controlling the solid surface with an easy and stable method [6]. Tokito et al. found that the electron mobility of an OTFT increases depending on the alkyl chain of the SAM. A SAM with an alkyl chain achieved a very high electron mobility of 1.2 cm^2/Vs [6]. It was considered that the SAM with an alkyl chain achieved high electron mobility due to the inhibition of electron trapping on the SiO_2 gate insulator by the SAM with an alkyl chain [6].

In addition, self-assembled monolayers have also been used in organic light-emitting diode (OLED) applications [7]. Ju et al. fabricated a SAM pattern on a substrate using Micro Contact Printing (μ-CP) so that an OLED structure can be self-aligned on a portion other than the pattern, which demonstrated that OLED patterning can be performed without using a pillar process, a shadow mask process, a lithography pillar process, and etc. [7]. Ju et al. also fabricated a double layer of a patterned conductive polymer and a carbon nanotube using μ-CP and SAM [7]. A self-assembled monolayer provided functionalized electrode surfaces by organic molecules containing free anchor groups such as amines and disulphides [8]. The monolayer produced by self-assembly allows tremendous flexibility with respect to several applications depending upon their terminal functionality [8]. The SAM with chain alkane thiol creates a very packed and ordered interface, which can produce a microenvironment such as a membrane, useful in immobilization of molecules [8]. The high choice of molecules combined with an electrochemical, piezoelectric transduction method of recognition presents great trust for their utilization as accurate biosensors [8]. Many examples have demonstrated that monolayer design is a key in controlling the performance of these SAM-based biosensors, regardless of the sensing mechanism [8].

A study was conducted on the characteristics evaluation of a liquid crystal (LC) biosensor on a self-assembled monolayer [9]. Biradar et al. studied a self-assembled monolayer based on liquid crystal biosensor for free cholesterol detection [9]. An enzyme (ChOx) was immobilized on a self-assembled monolayer for 12

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hours for biosensing purposes [9]. The study was conducted on the structure of SAM/ChOx/LC (5CB) cells for cholesterol concentrations ranging from 10 mg/dl to 250 mg/dl [9]. The sensing mechanism was verified using polarizing optical microscopy [9]. Also, many scientists have conducted studies using a self-assembled monolayer [10, 11].

In this study, we aim to identify the optimized fluorocarbon self-assembled monolayer and thereby to serve the needs of related applications, by investigating the detailed interfacial properties of self-assembled monolayers with an alkyl chain consisting of fluorine and carbon with varying the alkyl chain length based on fabrication time and temperature.

Experimental Procedure

The indium tin oxide (ITO) used as the positive electrode was a product of Samsung Corning Co., Ltd. The ITO was deposited on the entire glass to a thickness of 180 nm, and the sheet resistance was 10 Ω/sq. The aluminum used as the negative electrode was a product with 99.99% purity from Sigma-Aldrich. To clean the ITO substrate, the ITO was put in a carrier and then sequentially ultrasonically cleaned in SC-1, acetone, ethyl alcohol and distilled water at 50 °C for 20 minutes each. SC-1 refers to an aqueous solution prepared with hydrogen peroxide solution, ammonia water and distilled water at a volumetric ratio of 1:1:5. Following the ultrasonic cleaning, nitrogen gas was blown to remove the remaining moisture. Finally, for sufficient drying, the substrate was dried by baking on a hot plate at 90 °C for 20 minutes. The self-assembled monolayer with a fluorocarbon structure used was a product from Gelest. The N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and (tris(8-hydroxyquinolinato) aluminum) (Alq_3) were products with D2448 and T1527 from Tokyo Chemical Industry Co.

Results and Discussion

A self-assembled monolayer consists of three parts: a head part which comes into contact with a substrate, an alkyl chain part which constitutes the body part, and a terminal part which constitutes the upper part. Usually, carbon atoms and hydrogen atoms form the alkyl chain of the SAM. In this study, we used a self-assembled monolayer with an alkyl chain using fluorine instead of hydrogen. In other words, we used a fluorocarbon self-assembled monolayer (FC-SAM) in this study. The FC-SAM was easily fabricated in an electric oven due to the SAM's characteristics that is self-aligned by a gas phase method.

We used three types of alkyl chains of different lengths for self-assembled monolayers: FC-3SAM, FC-8SAM, and FC-10SAM. In order to investigate the deposition rate of the SAMs, we observed the SAMs

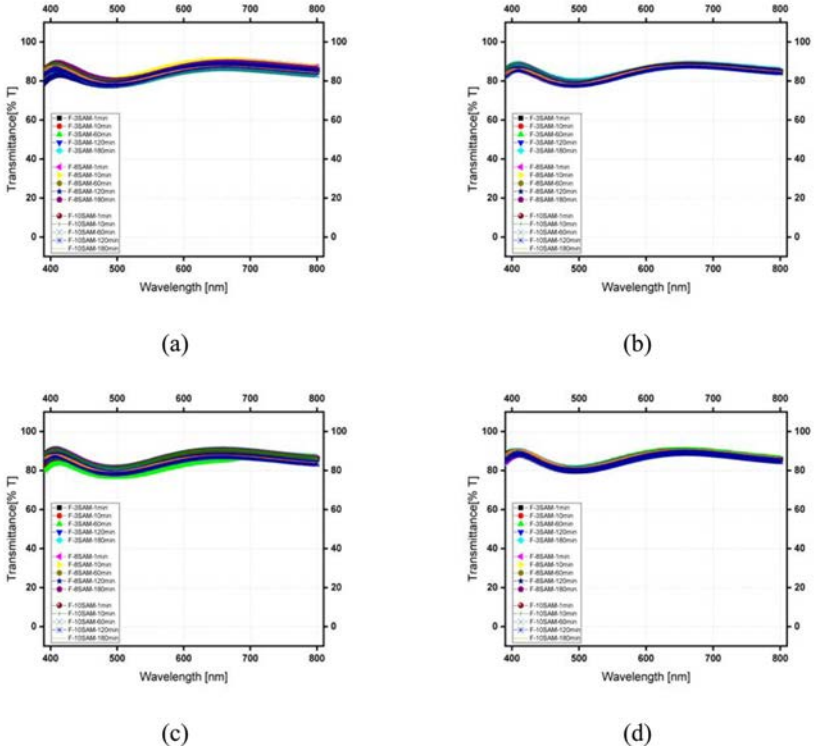


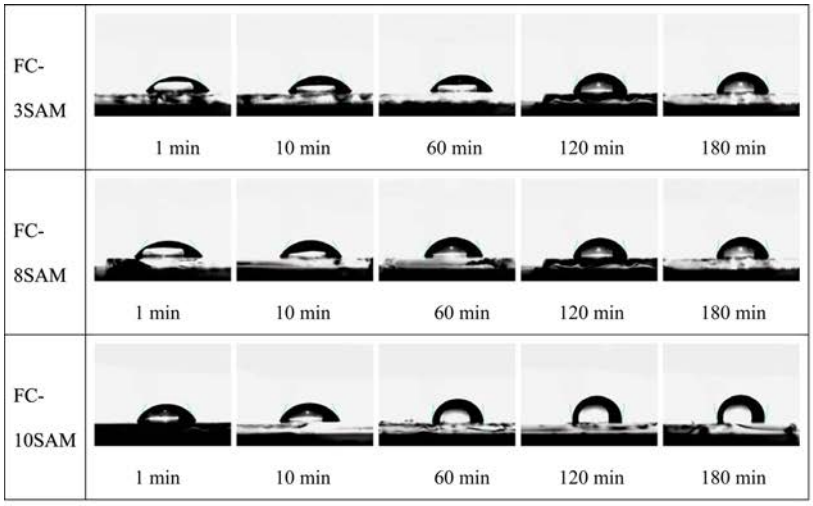
Fig. 1. Transmittance-wavelength characteristics of FC-SAMs of different alkyl chain lengths in the visible region at (a) 60 °C, (b) 90 °C, (c) 120 °C, and (d) 150 °C.

formed on an ITO substrate by changing the fabrication time and the deposition temperature.

Fig. 1 shows transmittance-wavelength characteristics of FC-SAMs of different alkyl chain lengths in the visible region with varying fabrication times and temperatures. The fabrication time of the FC-SAMs was set to 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes. The fabrication temperature of the FC-SAMs was set to 60 ºC, 90 ºC, 120 ºC, and 150 ºC. Fig. 1(a) shows the transmittance-wavelength characteristics of FC-3SAM, FC-8SAM, and FC-10SAM at a fabrication temperature of 60°C with varying fabrication times. At a fabrication temperature of 60 ºC, the FC-3SAM, FC-8SAM, and FC-10SAM showed almost the same transmittance of approximately 90% in the visible light region, regardless of the fabrication time. Fig. 1(b) shows the transmittance-wavelength characteristics of FC-3SAM, FC-8SAM, and FC-10SAM at a fabrication temperature of 90 ºC with varying fabrication times. At a fabrication temperature of 90 ºC, the FC-3SAM, FC-8SAM, and FC-10SAM showed almost the same transmittance of approximately 90% in the visible light region regardless of the fabrication time. Fig. 1(c) shows the transmittance-wavelength characteristics of FC-3SAM, FC-8SAM, and FC-10SAM at a fabrication temperature of 120 ºC with varying fabrication times. At a fabrication temperature of 120 ºC, the FC-3SAM, FC-8SAM, and FC-10SAM showed almost the same transmittance of approximately 90% in the visible light region regardless of the fabrication time. Fig. 1(d) shows the transmittance-wavelength characteristics of FC-3SAM, FC-8SAM and FC-10SAM at a fabrication temperature of 150 ºC with varying fabrication times. At a fabrication temperature of 150 ºC, the FC-3SAM, FC-8SAM, and FC-10SAM showed almost the same transmittance of approximately 90% in the visible light region regardless of the fabrication time.

As a result, like the FC-3SAM and FC-8SAM, the FC-10SAM showed almost the same transmittance of 90% in the visible light region, regardless of the fabrication temperature and fabrication time. The very high transmittance of the FC-SAMs was attributed to their very thin thickness and the absence of absorption. Therefore, FC-SAM is capable of passing light efficiently.

Fig. 2 shows changes in contact angles of FC-SAMs of different alkyl chain lengths with varying fabrication times and temperatures. The fabrication time of the FC-SAMs was set to 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes. The fabrication temperature of the FC-SAMs was set to 60 ºC, 90 ºC, 120 ºC, and 150 ºC. Fig. 2(a) shows changes in contact angles of the FC-3SAM, FC-8SAM, and FC-10SAM at a fabrication temperature of 60 ºC with varying fabrication times. At a fabrication temperature of 60 ºC of FC-3SAM, the contact angles of FC-3SAM are 54.1 º, 56.5 º, 69.0 º, 75.5 º, and 76.9 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minute, respectively; the contact angles of FC-8SAM are 55.1 º, 60.7 º, 69.3 º, 78.1 º, and 79.2 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; and the contact angles of FC-10SAM are 64.7 º, 66.0 º, 87.2 º, 97.4 º, and 98.7 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively. It was found that the contact angle of the FC-SAMs gradually saturates approximately from 120 minutes. Fig. 2(b) shows changes in contact angle of FC-3SAM, FC-8SAM and FC-10SAM at a fabrication temperature of 90 ºC with varying fabrication times. At a fabrication temperature of 90 ºC of FC-3SAM, the contact angles of FC-3SAM are 57.6 º, 59.9 º, 68.3 º, 83.6 º, and 84.6 º at fabrication times of 1 minute, 10minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; the contact angles of FC-8SAM are 49.7°, 69.3 º, 88.9 º, 96.7 º, and 97.8 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; and the contact angles of FC-10SAM are 74.9 º, 81.1 º, 95.6 º, 104.1 º, and 105.3 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively. It is considered that the low contact angle of FC-8SAM at a fabrication time of 1 minute is due to the measurement performed on a part where deposition was not made properly while the deposition was in progress. Fig. 2(c) shows changes in contact angles of FC-3SAM, FC-8SAM and FC-10SAM at a fabrication temperature of 120 ºC with varying fabrication times. At a fabrication temperature of 120 ºC of FC-3SAM, the contact angles of FC-3SAM are 62.9 º, 68.5 º, 82.8 º, 84.5 º, and 85.6 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; the contact angles of FC-8SAM are 57.5 º, 68.6 º, 96.1 º, 104.7 º, and 105.8 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; and the contact angles of FC-10SAM are 75.5 º, 79.2 º, 102.6 º, 107.9 º, and 108.7 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively. It is considered that the reason why the contact angles of the FC-8SAM at fabrication times of 1 and 10 minutes are ~~is~~ lower than those of the FC-3SAM is due to the instability of initial deposition, resulting in a slight decrease in contact angles. Fig. 2(d) shows changes in contact angles of FC-3SAM, FC-8SAM, and FC-10SAM at a fabrication temperature of 150 ºC with varying fabrication times. At a fabrication temperature of 150 ºC of FC-3SAM, the contact angles of FC-3SAM are 64.6 º, 73.6 º, 89.0 º, 93.3 º, and 94.5 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; the contact angles of FC-8SAM are 58.3 º, 62.9 º, 90.0 º, 98.2 º, and 99.9 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively; and the


FC-
3SAM
1 min
10 min
60 min
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FC-
8SAM
1 min
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10SAM
1 min
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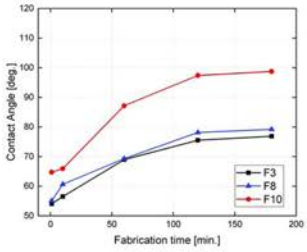
180 min


Contact Angle [deg.]
Fabrication time [min.]
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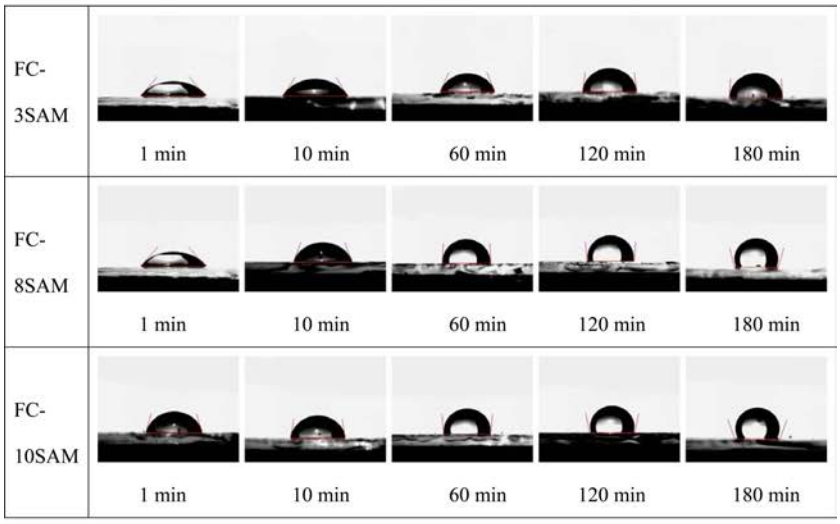
(a)


FC-
3SAM
1 min
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8SAM
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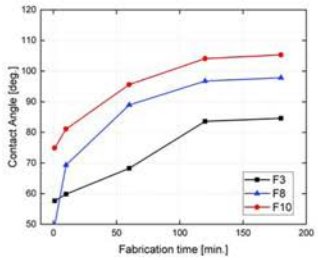
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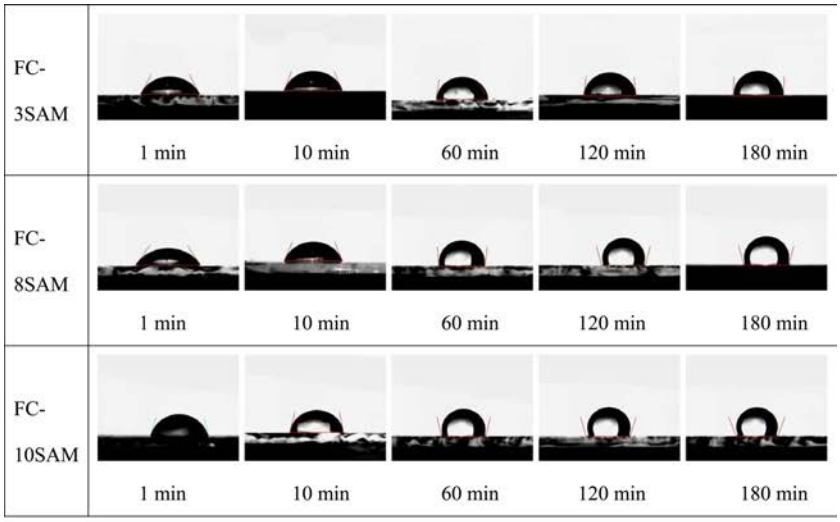
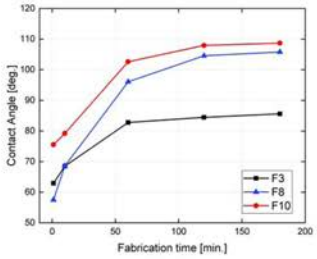
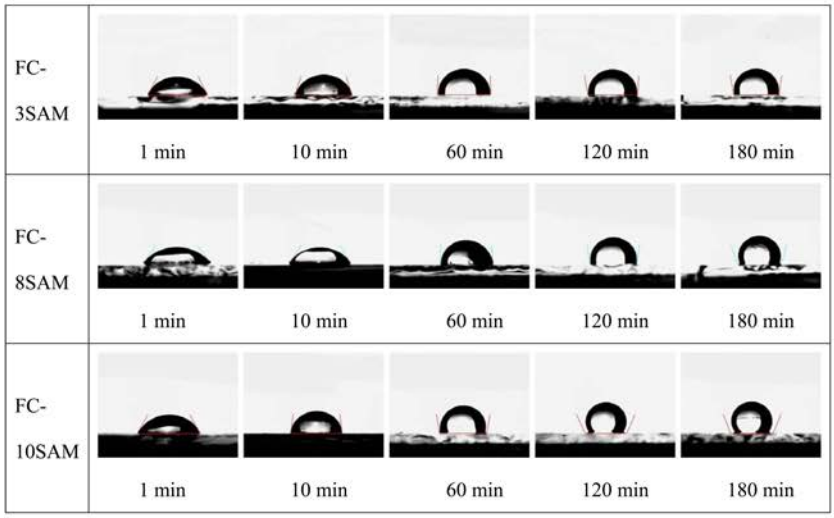
Fabrication time [min.]
F3
F8
F10

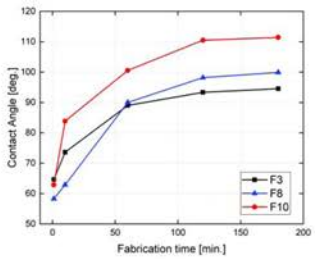
(b)





(c)





(d)

Fig. 2. Changes in contact angles and contact angle–fabrication time characteristics of FC-3SAM, FC-8SAM, and FC-10SAM by with varying fabrication times from 1 minute to 180 minutes at several fabrication temperatures; (a) 60 °C, (b) 90 °C, (c) 120 °C, and (d) 150 °C.

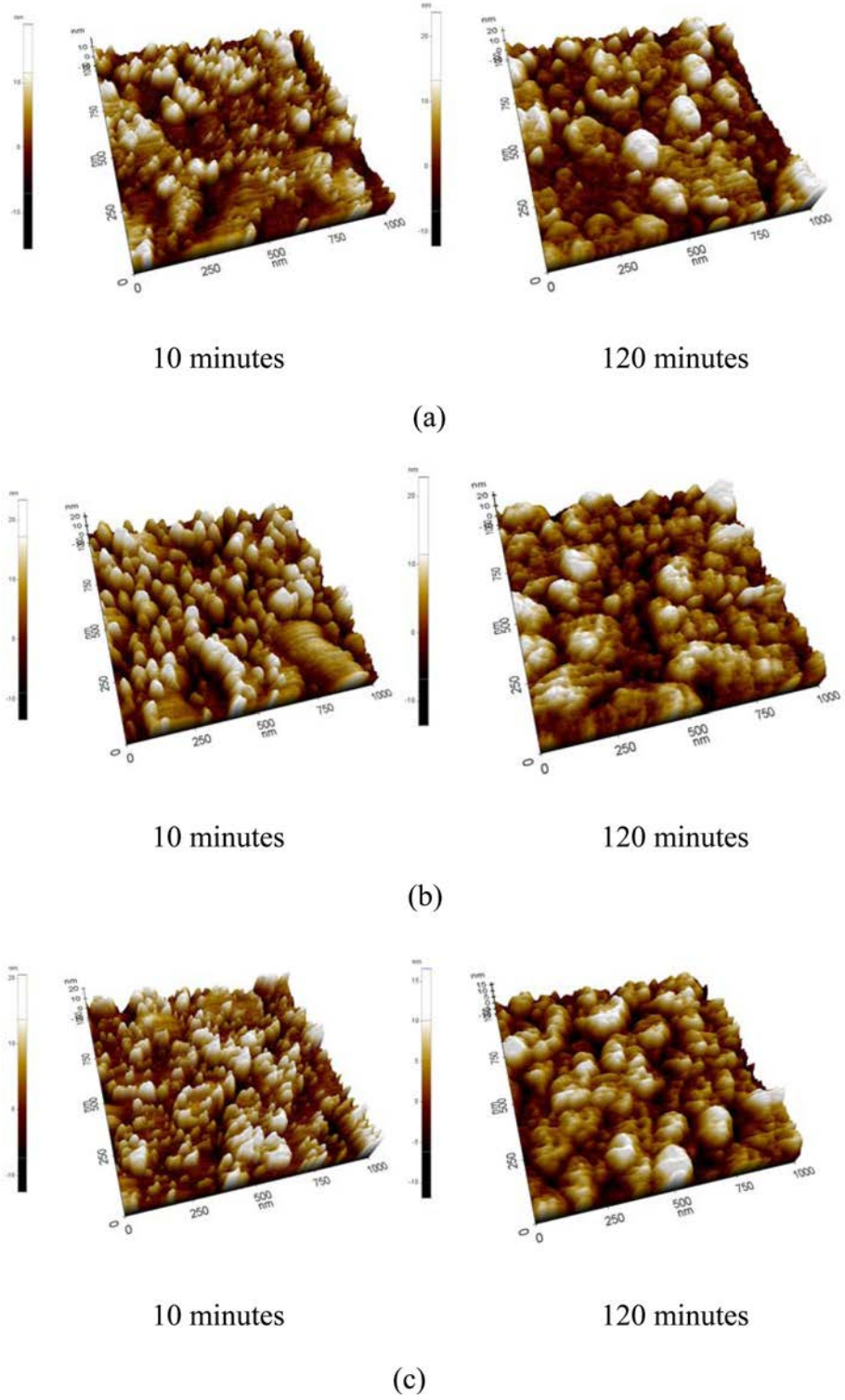


Fig. 3. AFM surface morphologies of (a) FC-3SAM, (b) FC-8SAM, and (c) FC-10SAM at fabrication times of 10 minutes and 120 minutes and at a fabrication temperature of 120 ºC.

contact angles of FC-10SAM are 62.98 º, 83.9 º, 100.6 º, 110.5 º, and 111.4 º at fabrication times of 1 minute, 10 minutes, 60 minutes, 120 minutes, and 180 minutes, respectively. It is considered that the reason why the contact angle of FC-8SAM at a fabrication time of 10 minutes and fabrication temperature of 150°C is lower than that of FC-8SAM at 1 minute is due to a disorder of the SAM during the initial film formation, where the SAM alignment was in progress. The results of changes in contact angle of the FC-

SAMs with different alkyl chain lengths with varying fabrication times and temperatures showed that the FC-3SAM, which has a short alkyl chain, had a low contact angle due to an unstable alignment resulting from a weak van der Waals force. In contrast, the FC-10SAM, which has a long alkyl chain, was found to have a high contact angle due to a well-aligned molecular structure resulting from a strong van der Waals force. The FC-10SAMwas found to have hydrophobic properties. The coverage ratio can be calculated by Cassie's law [12]. The equation based on Cassie's law can be expressed as follows:

$$\cos\theta = (1\text{-}C_1)\cos\theta_1 + C_1\cos\theta_2 \quad (1)$$

In the above equation, C_1 has a value between 0 and 1, and θ is the contact angle of a modified FC-SAM on an ITO substrate. θ_1 is the contact angle of the reference ITO, and θ_2 is the highest contact angle of a FC-SAM based on the assumption of 100 percent. We did not calculate the coverage ratio because various fabrication temperatures, fabrication times, and ITO were not considered in this study. From the fabrication time of FC-SAMs, it was found that the film was formed rapidly at an early stage. From the tendency that the contact angle saturates above a fabrication time of about 120 minutes, it was understood that about 120 minutes is sufficient for film formation of FC-SAM.

Fig. 3 shows the average surface roughness of FC-SAMs with different alkyl chain lengths at a fabrication temperature of 120 ºC, at which a film was formed sufficiently, and the initial fabrication times of 10 minutes and 120 minutes, measured with atomic force microscopy (AFM). At a fabrication time of 10 minutes, the average roughness is 3.82 nm, 4.93 nm, and 5.37 nm for the FC-3SAM, FC-8SAM, and FC-10SAM, respectively. At a fabrication time of 10 minutes, while the FC-10SAM showed a high average roughness due to the growth of a long self-assembled monolayer, the FC-3SAM showed a low average roughness due to the growth of a short self-assembled monolayer.

At a fabrication time of 120 minutes, the average roughness is 4.65 nm, 3.65 nm, and 2.90 nm for the FC-3SAM, FC-8SAM, and FC-10SAM, respectively. The average roughness of the SAMs decreases as the alkyl chain becomes longer. These results support that in case where the alkyl chain is long and the fabrication time is sufficient, the self-assembled monolayer is well-aligned due to the strong van der Waals force, as explained above for the contact angle. In contrast, the average roughness of the SAMs increases as the alkyl chain becomes shorter. From these results, it can be seen that when the alkyl chain becomes shorter, the degree of disorder increases due to the weak van der Waals force of the self-assembled monolayer, resulting in a high average roughness. If FC-SAMs, which can transmit light well and can be produced in large quantities with an easy method, are used as the hole-injection layer of OLEDs, it will greatly serve the needs of the display material industry.

Conclusions

In this study, we investigated the interfacial properties of self-assembled monolayers with fluorocarbons of different chain lengths. Fluorocarbon self-assembled monolayers were fabricated by varying fabrication times and temperatures. They showed an almost constant transmittance of about 90% in the visible region. This might be attributed to the thin film characteristics of FC-SAMs. We confirmed the optimal fabrication temperature and fabrication time of fluorocarbon self-assembled monolayers by conducting experiments with changing the fabrication time and temperature. The contact angle of fluorocarbon self-assembled monolayers was found to be almost constant at a fabrication time of about 120 minutes and at a fabrication temperature of 120 ºC. FC-10SAM, which has a long alkyl chain, showed a high contact angle due to a good alignment resulting from a strong van der Waals force between molecules. In addition, the FC-10SAM showed a high contact angle due to its low wettability to a substrate. FC-3SAM showed a low contact angle due to the high degree of disorder resulting from its short alkyl chain. We investigated the surface roughness of FC-SAMs using AFM at the optimal fabrication temperature of 120°C and the optimal fabrication time of 120 minutes for FC-10SAM, which showed superior performance among the fluorocarbon self-assembled monolayers with different chain lengths. The AFM results were found to support the results of the contact angle. These results show that the FC-10SAM has a lower average roughness than FC-3SAM. That is, the FC-10SAM shows improved surface roughness due to its sufficient film formation.

A self-assembled monolayer has high transmittance and can be mass-produced using an easy method. Thus, if it is used as an interface material for OLED displays, it could become the next-generation display materials.

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