

Application of Technology for Long-term Retention of Plasma Treatment : Hydrophobic Treatment

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Abstract: Static and dynamic surface properties can be controlled by applying dry Self-Assembled Monolayer (SAM) formation techniques. By introducing fluorinated SAM raw materials, the static contact angle showed high hydrophobicity. Dynamic hydrophobicity could also be controlled by introducing alkyl-based SAM raw materials. Furthermore, it was found that surface modification for various applications was possible by changing the introduced SAM raw materials.

Keywords: plasma, SAMs, hydrophobic, out of liquid

1. Introduction and purpose

As plasma irradiation, dry methods such as vacuum ultraviolet (VUV) and corona discharge have traditionally been used as surface modification techniques. And also surface modification by wet coating of polymers is used. However, the surface properties of plasma and other hydrophilic treatments cannot be retained over time. Hydrophilic treatment by dry methods is carried out in pretreatment prior to the formation of adhesive layers, polymers and other coating films. This treatment has resulted in improved wettability and adhesion. However, the time available for retention to the coating process is short and permanent hydrophilic treatments have not been developed. In the case of polymer coated films, the interaction between the material and the substrate is weak and therefore less stable.

Recently, polymer brush bonding technology to substrates has been investigated as a surface modification technique that can retain hydrophilic surface properties [1]. In this technology, this is achieved by grafting surface molecules using a living radical polymerisation method [3]. This polymerisation method uses a solvent and a catalyst. Another known technology is the formation of self-assembled monolayers (SAMs) [4]. However, it is known that these technologies are also mainly formed by wet methods such as sol-gel methods and use solvents and catalysts [4]. In addition, long reaction times are required to form SAMs by conventional vapour phase methods [5].

Therefore, the wet process has the problem that it cannot be adopted for applications where contamination of residual substances is avoided because of the need for a solvent and a catalyst. The conventional vapour phase method also has a long tact time, which makes it difficult to use in production processes.

In surface modification for water repellency, both static and dynamic surface properties are in demand. In this paper, the application of plasma technology to new SAM formation processes and the control of static and dynamic surface properties were investigated. The results confirm that it is possible to introduce and surface modify SAMs according to the target liquid and the application. Besides, the static and dynamic contact angles of the sample surface

to water were measured for this surface modification process and their control was discussed.

2. Experimental methods

Polyethylene (PE) plates were prepared as sample substrates.

As fluorinated SAM raw material, trimethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane (CAS RN: 51851-37-7 Tokyo Kasei Kogyo) was used. Three materials were used as SAM raw materials with alkyl groups: trimethoxy-n-octylsilane (CAS RN: 3069-40-7 Tokyo Chemical Industry), hexadecyltrimethoxysilane (CAS RN: 16415-12-6 Tokyo Chemical Industry) and dodecyltrimethoxysilane (CAS RN: 3069-21-4 Tokyo Chemical Industry). We used a capacitively coupled (CCP) vacuum plasma system SAMy-400A (Sakigake Semiconductor Co., Ltd.) with a configuration that allows the supply of vapour of the SAM raw material in the chamber for the formation of SAMs. Water vapour was injected into the chamber as a plasma gas for the activation process of the sample substrate.

An overview of the SAM formation process using vacuum plasma equipment is shown in Fig. 1~3.

(i) Substrate surface activation (Fig. 1)

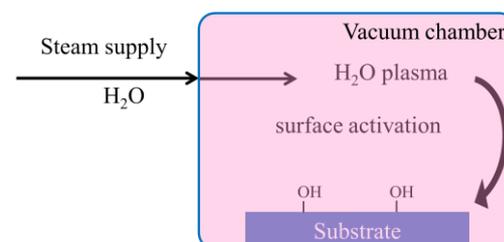


Fig. 1 Surface activation with vacuum plasma

The sample substrate surface was activated by steam plasma to introduce OH groups.

(ii) SAM feedstock supply and formation (Fig. 2).

The vapour of the SAM raw material was fed into the chamber of the vacuum plasma system to form hydrogen

bonds between the SAM intermediates and the OH groups on the sample surface.

(iii) Fixation of SAM formation (Fig. 3).

The SAM was fixed by dehydration-condensation reactions.

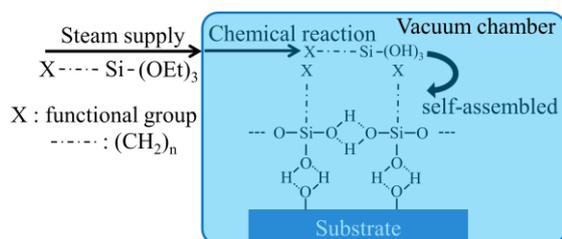


Fig. 2 SAM formation

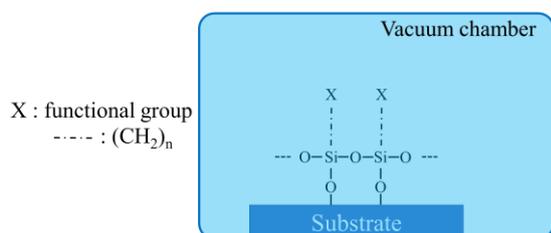


Fig. 3 Fixation of SAM in the vacuum chamber

The contact angle to water was measured for the sample substrates using a contact angle meter LSE-ME5 (Nick Co., Ltd.).

The SAM raw materials are those in Table. and the structure is shown in Fig. 2.

- Fluorinated X-perfluoro group, dotted $(\text{CH}_2)_2$
- Alkyl groups: C_8 , C_{12} and C_{16} reagents

of the following were used. After treatment, the contact angle was measured using purified water and the functional groups immediately after treatment, over time and on the surface were measured using FT-IR:Fourier Transform Infrared Spectroscopy (IRAffinity-1S, Shimadzu corporation).

3. Result and considerations

The results of the static contact angle measurements are shown in Table. Samples with fluorinated SAM raw materials showed higher hydrophobic than those with alkyl materials. However, the hysteresis of the dynamic contact angle by visual inspection (henceforth CA_H) showed a higher hysteresis in the fluorinated system.

CA_H are A-B shown in Fig. 4. Different results for CA_H , which is important for out of liquid, were obtained for the

fluorinated and alkyl systems. This means that dynamic and static surface properties were controlled.

When fluorinated SAM raw materials were used, the static contact angle increased from 103° before treatment to 118° as shown in Table. The polar nature of the fluorinated SAM raw materials suggests that they were more likely to hydrogen bond with H_2O used during the contact angle measurement. Therefore, the static contact angle confirmed pretty high hydrophobic and the dynamic contact angle measurement showed a high CA_H , as the water droplets stayed and were pulled even when the plate was tilted with water droplets.

On the other hand, when alkyl-based SAM raw materials were used, the static contact angles were 105° , 74° and 82° , as shown in Table. This suggests that the chain length of the same alkyl-based SAM raw material has an effect on the static contact angle. SAM raw materials with alkyl groups are non-polar and do not form hydrogen bonds with H_2O . In addition, the alkyl chains have a fixed length and can move. Therefore, when the dynamic contact angle is measured, the droplets are likely to roll off.

The opposite properties of CA_H were obtained for fluorine and alkyl systems with respect to water. The results suggest that it is possible to introduce SAM and surface modification according to the target liquid and application. The relationship between changes in physical properties, composition and structure of the water-repellent sample surface and the conditions for hydrophobic will be discussed in detail in the presentation.

Table. Contact angle

Reagent	Contact angle($^\circ$)	
	Before treatment	After treatment
(1H,1H,2H,2H-Tridecafluorooctyl) trimethoxysilane	103	118
Trimethoxy-n-octylsilane		105
Trimethoxy (hexadecyl)silane		74
Dodecyl trimethoxysilane		82

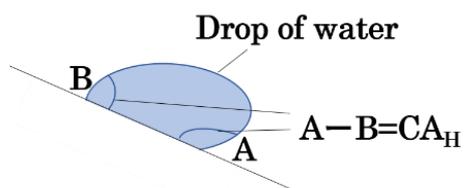


Fig.4 Dynamic contact angle

4. Conclusions

We have found that static and dynamic hydrophobic can be controlled by applying plasma technology. Static contact angle control is possible with fluorinated SAM raw material and dynamic contact angle control is possible with alkyl SAM raw material for water.

5. References

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