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# Preparation of transparent water-repellent films by radio-frequency plasma-enhanced chemical vapour deposition

A. HOZUMI, H. SEKOGUCHI, N. KAKINOKI, O. TAKAI
*Department of Materials Processing Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan*

Preparation of transparent water-repellent films was carried out using three kinds of fluoroalkyl silanes (FASs) by radio-frequency plasma-enhanced chemical vapour deposition. The effects of the reaction conditions on the structures and properties of the films were studied. The films prepared showed high water repellency like poly(tetrafluoroethylene). The contact angles for water drops were about 107°. The obtained contact angles depended on the length of perfluoroalkyl groups ($C_nF_{2n+1}$–) in FASs. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to investigate the film properties. The existence of the fluorine-containing groups such as –$CF_3$, –$CF_2$– and >CF– was confirmed at the film surfaces. The contact angle decreased when oxygen was added to the plasma because of the decrease in the fluorine concentration in the deposited films by the decomposition of C–F bonds. The transmittance of the polycarbonate substrates coated using FASs was improved. The films also acted as an antireflective coating.

## 1. Introduction

Plasma-enhanced chemical vapour deposition (PECVD) is a suitable technique for preparing various kinds of films by initiating chemical reactions in a gas with an electric discharge [1, 2]. PECVD using low-temperature plasma has found important applications in microelectronics, optics, solar cells, mechanical industries and plastic industries.

Recently, water repellency has been required in various fields. The most common method, well known as a water-repellent treatment for glass, is to spread a fluoropolymer or a fluoroalkyl silane (FAS) on a substrate and to prepare a water-repellent film. This method using fluoropolymer has a burning process carried out at about 350 °C and cannot be applied to low-heat resistance substrates such as resins. Moreover, this has such problems as inferiority in transparency and weakness in adhesion between the films and the substrates. The spread coating using a FAS is hard to obtain because of the strong chemical bonding between an alkoxy group and a hydroxy group on the surface of glass, and the prepared film comes off gradually [3].

Surface modification of materials is often performed using plasma, but there have been very few trials to modify the surface to keep high water repellency and high transparency. In a previous study, we reported the preparation of highly water-repellent and highly transparent films at low substrate temperatures by radio-frequency (r.f.) PECVD using FAS ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$) as a raw material [4] and proposed the solution to these problems by using this technique.

In this study, we have used two more kinds of FAS, which have the different lengths of perfluoroalkyl groups ($C_nF_{2n+1}$–) and investigated the effects of their length on the water repellency of the deposited films. The evaluation of water repellency was done by measuring the contact angles for water drops. The chemical bonding states of the deposited films were studied by using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The optical properties were measured with a double-beam spectrometer and an ellipsometer.

## 2. Experimental procedure

### 2.1. Preparation of transparent water-repellent films

The apparatus for a r.f. PECVD system is shown in Fig. 1. It was made up of a discharge tube, a vacuum system and a gas supply system. The discharge tube consisted of a high-purity quartz glass cylinder of length 1000 mm and inside diameter 35 mm. Stainless steel holders supported this tube at both ends. The gas pressure was measured with a Pirani gauge.

A 13.56 MHz generator supplied the r.f. power which was transferred to the reactant gas with an impedance-matching network terminating in a 5.5 turn, inductively coupled coil of copper tubing 6 mm in diameter.

The preparation conditions and raw materials are shown in Tables I and II, respectively. The reactants used were three kinds of FAS ($CF_3(CF_2)_nCH_2CH_2Si(OCH_3)_3$, $n = 0$, 5 and 7). We hereafter call these three

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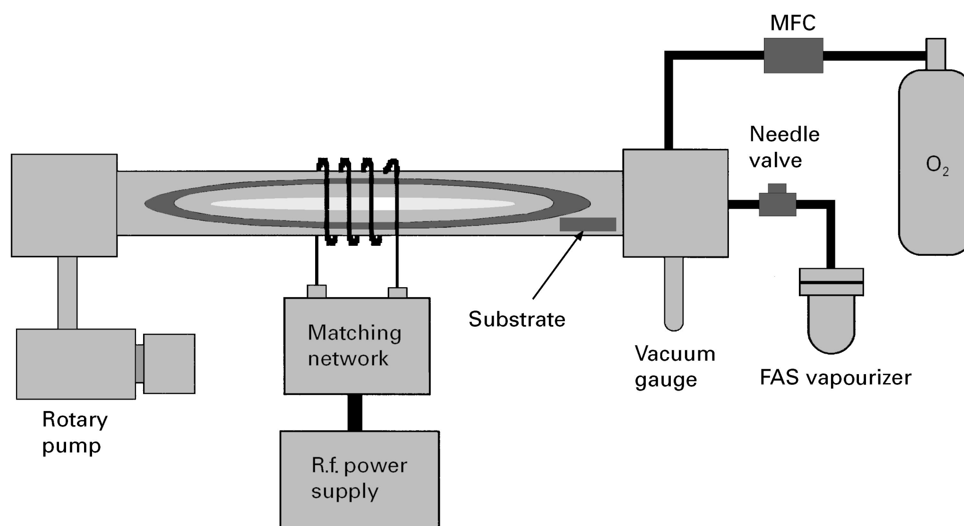



*Figure 1* Schematic diagram of the r.f. PECVD system: MFC (Mass Flow Controller).

TABLE I Preparation conditions of the water-repellent films

| | |
|---|---|
| Total pressure (Pa) | 5–25 |
| Partial pressure of FAS (Pa) | 5–20 |
| Partial pressure of oxygen (Pa) | 0–5 |
| r.f. power (W) | 100–300 |
| Deposition time (min) | 300–500 |
| Substrate position (mm) (from the centre of the plasma) | 15–30 |

FASs–as FAS-3, FAS-13 and FAS-17 in that order. The FAS was contained in a stainless steel vaporizer which was kept constant at around 50 °C during deposition. We used the vapour of the FAS. The substrates used were glass, polished Si wafers and polycarbonate (PC). They were used after degreasing and located at positions between 300 and 500 mm away from the centre of the plasma to avoid direct thermal damage by the plasma, especially for resin substrates. The substrate temperature was measured with a chromel–alumel thermocouple. The typical substrate temperature during deposition was from room temperature to 50 °C. The pre-treatment with an oxygen plasma was carried out to remove impurities on the substrate and to modify the resin substrates to obtain strong adhesion between the substrates and the deposited films. The films thickness was measured by a stylus method.

## 2.2. Measurement of contact angles

Water repellency was examined by measuring the contact angle. The contact angles for water drops (about 2 mm diameter) were measured with a contact-angle meter (model D-013-D2, ERMA Co., Ltd) by a drop method at 25 °C in air [5]. Water was used as an example of a hydrophile material. The contact angles were measured at five points and the average value was calculated after eliminating their minimum and maximum values. The contact angle was measured when the constant time (1 min in this study) passed after dropping of water.

## 2.3. Analyses of the chemical bonding states

The chemical bonding states in the deposited films were investigated using an XPS system (model ESCA 3200, Shimadzu Co., Ltd) with Mg Kα radiation at 10 kV and 30 mA and a FTIR system (model JIR-5300, JEOL Co., Ltd).

## 2.4. Measurement of transmission spectra and refractive indexes

The water-repellent films were deposited on the PC substrates and their optical transmission spectra were measured with a double-beam spectrometer (model UV3101PC, Shimadzu Co., Ltd). The refractive indexes of the films prepared onto silicon wafers were determined with an ellipsometer (model SP2300, PLAS MOS) at a wavelength of 633 nm.

# 3. Results and discussion

## 3.1. Preparation of water-repellent films

First, films were prepared on glass substrates using FASs without oxygen. The deposition rates depended on the preparation conditions such as the kind of

TABLE II FASs used

| | Material | Molecular weight | Boiling point (°C) (pressure (Pa)) | $n_D^{25}$ |
|---|---|---|---|---|
| FAS-3 | $CF_3CH_2CH_2Si(OCH_3)_3$ | 218.1 | 143–145 ($1.0 \times 10^5$) | 1.355 |
| FAS-13 | $CF_3(CF_2)_5CH_2CH_2Si(OCH_3)_3$ | 468.1 | 50–52 (133) | 1.334 |
| FAS-17 | $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$ | 568.1 | 85–87 (133) | 1.332 |

FAS, the r.f. power, the FAS pressure and the substrate position. The deposition rate increased with increasing FAS pressure and decreased as the substrate position became close to the centre of the plasma. The relationships between the r.f. power and the deposition rates are shown in Fig. 2. At the FAS pressure of 15 Pa, the deposition rate passed a maximum at about 200 W and then decreased as the r.f. power increased. A similar tendency was observed at other FAS pressures. The maximum deposition rate, about 100 nm $min^{-1}$, was achieved with FAS-3 at a r.f. power of 200 W and a substrate position 500 mm away from the centre of plasma.

The relationships between the r.f. power and the contact angles for films deposited onto glass substrates at the FAS pressure of 15 Pa are shown in Fig. 3.

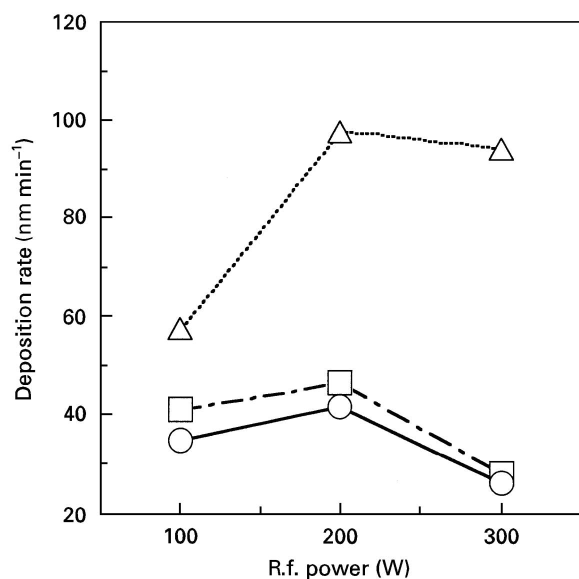



*Figure 2* Relationships between the r.f. power and the deposition rates at a FAS pressure of 15 Pa. (△), FAS-3; (□), FAS-13; (○), FAS-17.

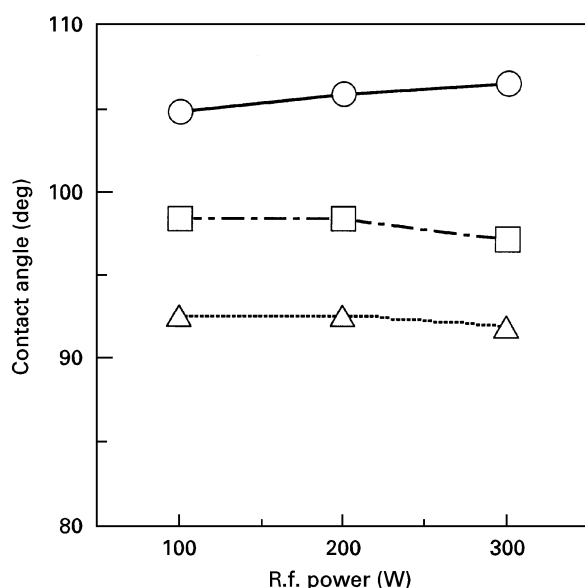



*Figure 3* Relationships between the r.f. power and the contact angles for the films deposited onto glass at a FAS pressure of 15 Pa. (△), FAS-3; (□), FAS-13; (○), FAS-17.

The contact angles increased with increase in the length of perfluoroalkyl groups and FAS-17 gave the highest contact angle. Generally the film which has a contact angle more than 80° shows high water repellency. Therefore all the deposited films showed high water repellency. The maximum contact angle was about 107° which was comparable with the contact angle for poly(tetrafluoroethylene) (PTFE) (108°) [6]. Since the contact angle for the glass substrate was about 27°, the water repellency was improved largely by the present treatment using r.f. PECVD.

Fig. 4b shows the photograph of the glass coated with FAS-17. The glass substrate was wettable as shown in Fig. 4a. The water drops on the coating shown in Fig. 4b were globular and the water repellency was proved to be improved markedly. For PC substrates, the maximum contact angle for water drops was about 105°. The contact angle for the original PC substrate was about 70°. The water repellency was also improved for the other PC substrates.

Fig. 5 indicates the effects of the FAS-17 pressure on the contact angles. A higher pressure gave a higher contact angle. The r.f. power had little effect on the contact angle when the FAS-17 pressure was 15 Pa. However, the contact angle decreased with increase in the r.f. power when the FAS-17 pressure were 5 and 10 Pa.

Here we consider two reactions in the plasma process using fluorocarbon [7, 8]. One is the polymerization reaction by the activated radicals and the other is the decomposition reaction of the polymerized film

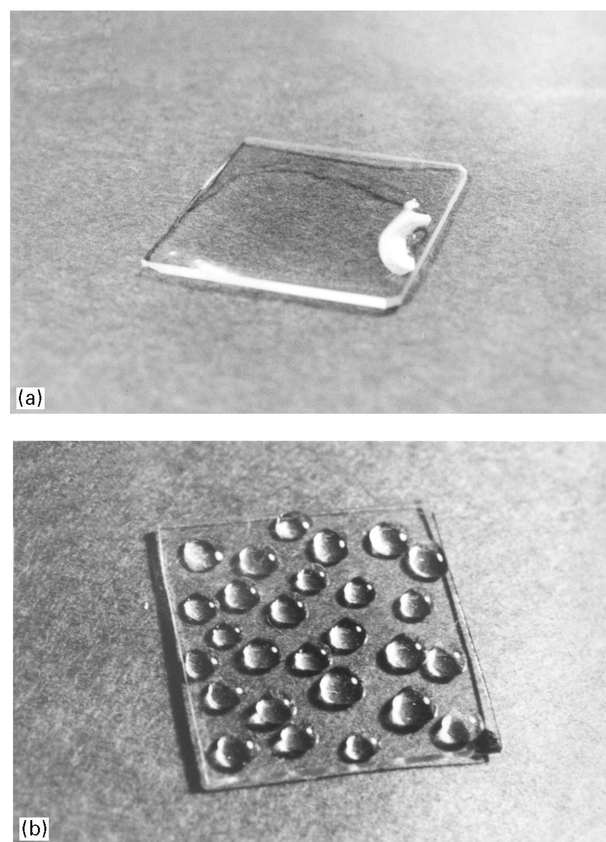



*Figure 4* Water repellency of the film deposited onto glass with FAS-17 (FAS pressure, 15 Pa; r.f. power, 200 W): (a) original glass; (b) glass coated with FAS-17.

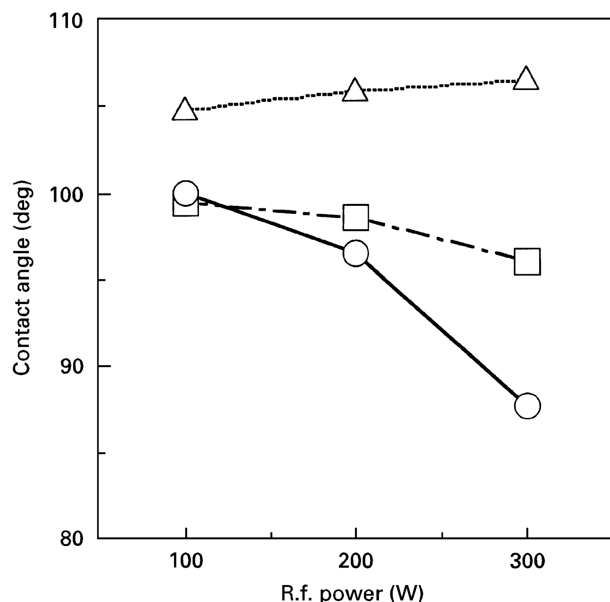



*Figure 5* Relationships between the r.f. power and the contact angles for the films deposited onto glass using FAS-17. (△), 5 Pa; (□), 10 Pa; (○), 15 Pa.

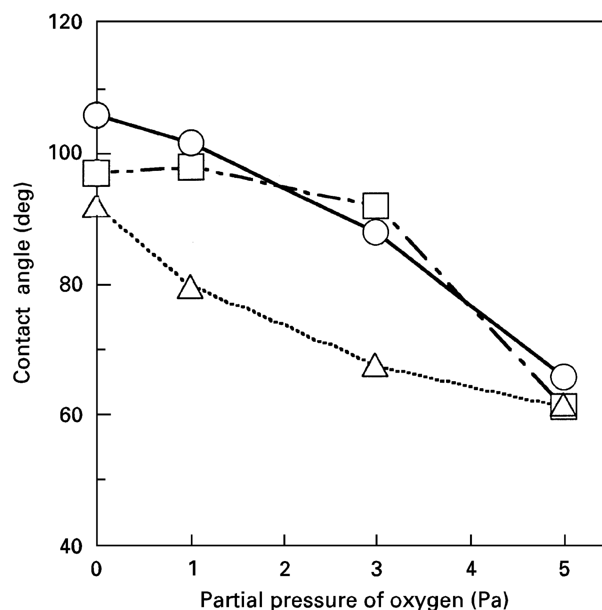



*Figure 6* Relationships between the partial pressures of oxygen and the contact angles (total pressure, 15 Pa; r.f. power, 300 W. (△), FAS-3; (□), FAS-13; (○), FAS-17.

by the highly reactive atomic fluorine which is formed from the decomposition of the fluorocarbon. The introduction of a higher energy into the plasma enhanced the decomposition of C–F bonds in the FAS molecules when the concentration of FAS-17 was low in the gas phase. The decomposition reaction of C–F bonds proceeded at 300 W and highly reactive atomic fluorine was formed. It acted on the decomposition of the deposited film and no formation of the uniform film occurred. The same tendency was observed when other FASs were used.

## 3.2. Effects of oxygen addition on the film properties

Secondly, oxygen was added to the plasma to enhance the oxidation of the films and to investigate its effects on the contact angle.

Fig. 6 shows the relationships between the partial pressures of oxygen and the contact angles. The r.f. power was kept at 300 W and the total pressure was 15 Pa. The contact angle decreased with increasing partial pressure of oxygen. The deposition rate also decreased. For FAS-13 and FAS-17, the film thickness could not be measured with the stylus method when the oxygen pressure was 5 Pa, but the contact angles were larger than that of a non-treated glass substrate (27 °). This result shows that the film formation by FASs takes place, although the film thickness is below the minimum limit of measurement in the stylus apparatus used.

Two reasons for the decrease in the deposition rate are considered in the oxygen-containing plasma process. One is due to the decrease in the FAS concentration as the total pressure is fixed. The other is due to the decomposition reaction of the prepared films by activated species of oxygen and fluorine which were formed from the decomposition of C–F bonds in the oxygen-containing plasma. The FTIR and XPS measurements were carried out to explain the effect of the oxygen addition on the contact angles.

## 3.3. Fourier transform infrared measurement

The FTIR measurement was carried out to investigate the changes in the chemical bonding states of the films with increase in the partial pressure of oxygen. Fig. 7 shows the infrared spectra of the deposited films onto Si wafers prepared with FAS-3. In Fig. 7, the absorption bands due to the asymmetric Si–O–Si stretching vibration and the Si–OH stretching vibration were detected at 1080 $cm^{-1}$ and 906 $cm^{-1}$, respectively. The three absorption bands due to the C–F stretching vibration of the $CF_3$– groups were detected at 1132, 1215 and 1243 $cm^{-1}$ [9] when the FAS-3 pressure was 15 Pa and the oxygen pressure was 0 Pa. The peak intensity of the C–F bondings at 1132, 1215 and 1243 $cm^{-1}$ and the Si–OH bonding at 906 $cm^{-1}$ decreased with increasing partial pressure of oxygen. On the other hand, the peak due to the Si–O–Si stretching vibration at 1080 $cm^{-1}$ shifted to lower frequencies with increasing partial pressure of oxygen. The peak position reached 1072 $cm^{-1}$ finally. The absorption band due to the Si–O–Si stretching vibration appears at 1070 $cm^{-1}$ for fully oxidized silicon [10]. This result indicates that the oxidation of the films is enhanced on increase in the partial pressure of oxygen. In Section 3.2, we described the decline in the water repellency of the obtained films on addition of oxygen to the plasma. The contact angles decreased from 92 to 61 ° on addition of oxygen. The FTIR measurement agreed well with this result. The addition of oxygen enhanced the oxidation of the deposited films but nevertheless enhanced the decomposition of C–F bonds. Similar tendencies were observed when FAS-13 and FAS-17 were used.

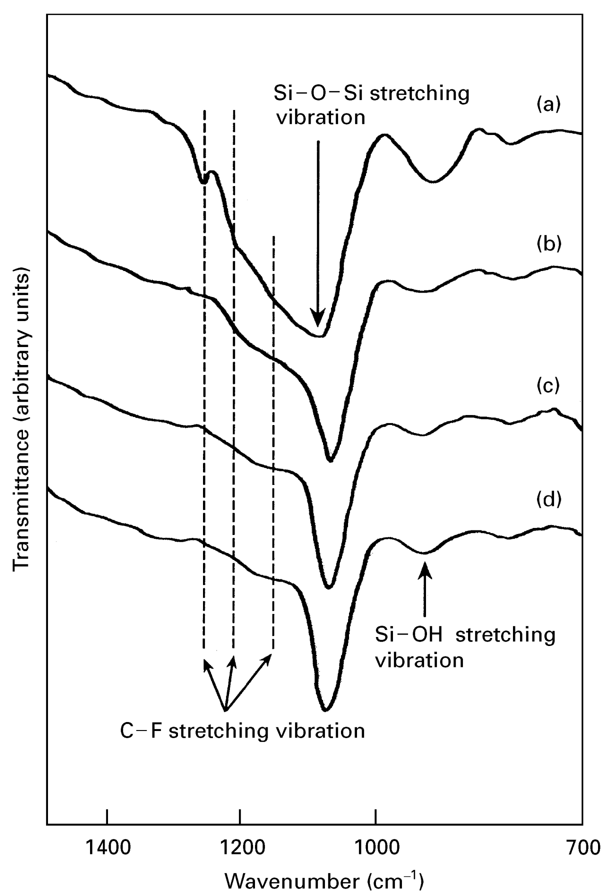



*Figure 7* FTIR spectra of the deposited films with FAS-3 at the following partial pressures of oxygen (total pressure, 15 Pa; r.f. power, 300 W: (a) 0 Pa; (b) 1 Pa; (c) 3 Pa; (d) 5 Pa.

## 3.4. X-ray photoelectron spectroscopy measurement

The changes in the chemical bonding states of the films on addition of oxygen were also studied using XPS. The peaks due to C 1s, F 1s, O 1s and Si 2p were detected in the X-ray photoelectron spectra. The C 1s spectra for the surfaces of the films deposited onto Si wafers with FAS-3 and FAS-17 at 15 Pa and 300 W without oxygen are shown in Fig. 8a and b, respectively. These spectra could be divided into five or six components. The components are denoted $C_1$, $C_2$, $C_3$, $C_4$, $C_5$ and $C_6$ from lowest binding energy upwards and are identified according to the chemical shifts given in Table III [11]. The surfaces of the prepared films were covered with the chemical components such as $-CF_3$ ($C_6$), $-CF_2-$ ($C_4$ and $C_5$) and $>CF-$ ($C_3$). The surface which is covered with these fluorine-containing groups shows the hydrophobic property because of the decrease in surface energy [12]. Comparing Fig. 8b with Fig. 8a, the peak areas of the fluorine-containing groups were large for FAS-17. The fluorine concentration at the surfaces of the films prepared with FAS-3 and FAS-17 was 16.4 at% and 41.9 at%, respectively. The film prepared with FAS-17, therefore, showed a better hydrophobic property.

Fig. 9a and b shows the C 1s spectra for the surfaces of the films deposited onto Si wafers using FAS-3 and FAS-17, respectively, at a FAS partial pressure of 10 Pa, an oxygen partial pressure of 5 Pa, and a r.f. power of 300 W. The peak intensity of C 1s spectra became weaker with increasing partial pressure of oxygen. The area ratios of the chemical components in the C 1s spectra changed markedly. The chemical components of the fluorine-containing groups such as $C_5$ and $C_6$ decreased especially compared with the C 1s spectra shown in Fig. 8a and b.

Fig. 10 shows the relationships between the partial pressures of oxygen and the atomic concentration of each element in the films prepared with FAS-3. The concentrations of fluorine and carbon decreased with

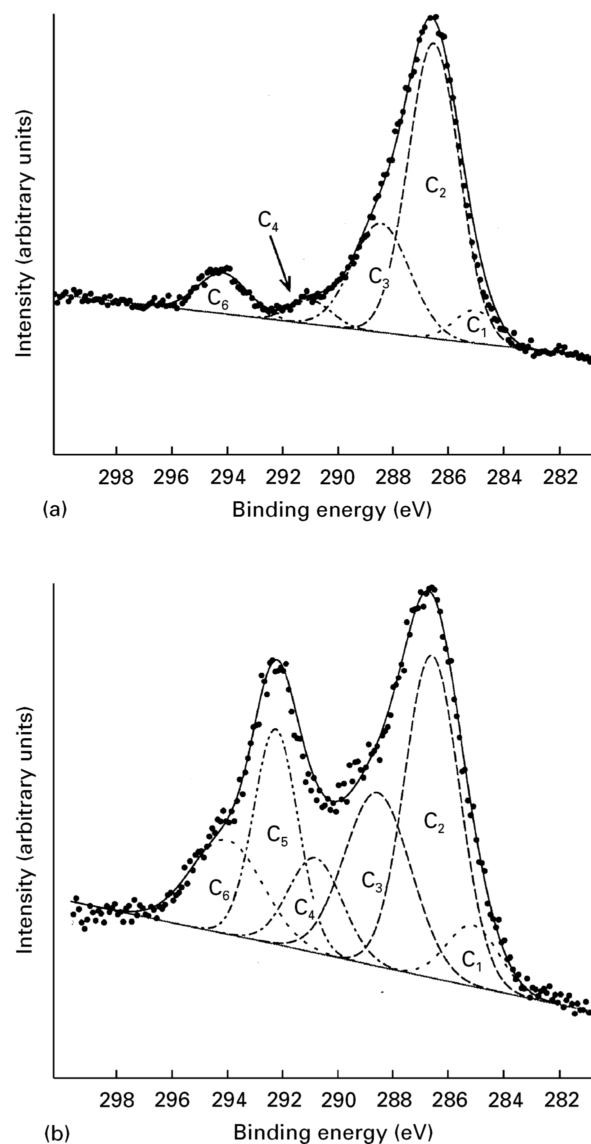
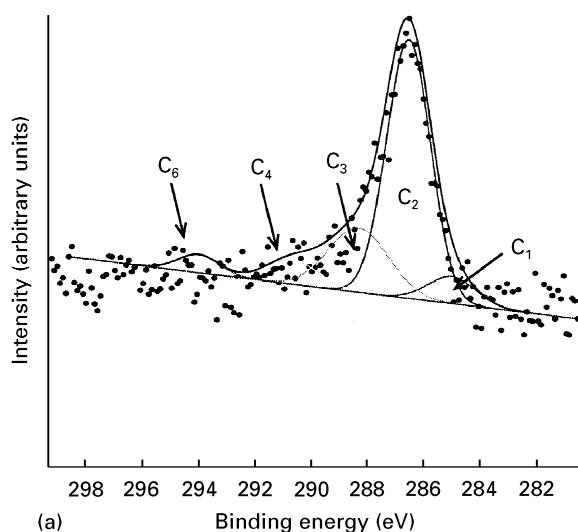



*Figure 8* X-ray photoelectron C 1s spectra of the films prepared with FASs (FAS pressure, 15 Pa; r.f. power, 300 W): (a) FAS-3; (b) FAS-17.

TABLE III Chemical components identified in the X-ray photoelectron C 1s spectra for the surfaces of the deposited films

| Component | Binding energy (eV) | Functional group |
|---|---|---|
| $C_1$ | 285.0 | $CH_2$–$CH_2$ |
| $C_2$ | 286.5 | $CF_2$–$\underline{C}H_2$, C–O |
| $C_3$ | 288.4 | CHF–CHF |
| $C_4$ | 290.8 | $\underline{C}F_2$–$CH_2$ |
| $C_5$ | 292.2 | $CF_2$–$CF_2$ |
| $C_6$ | 294.0 | $\underline{C}F_3$–$CF_2$ |



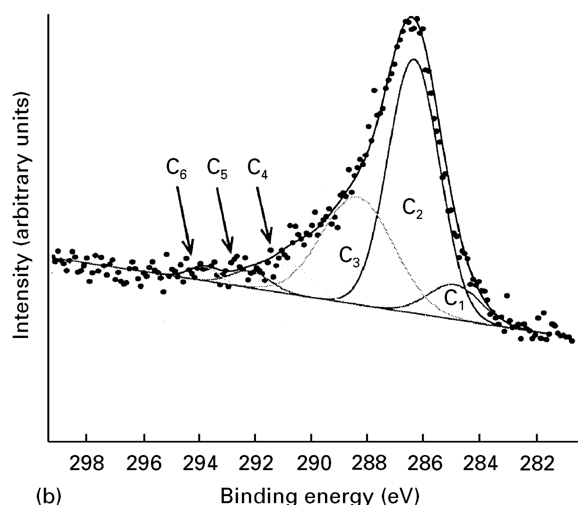




*Figure 9* X-ray photoelectron C 1s spectra of the films prepared with FASs and oxygen (FAS partial pressure, 10 Pa; oxygen partial pressure, 5 Pa; r.f. power, 300 W): (a) FAS-3; (b) FAS-17.

increasing partial pressure of oxygen. On the other hand, the concentrations of silicon and oxygen increased. The oxygen concentration contained the concentration due to the absorbed oxygen species at the surface in this study. The properties of the obtained films changed from "organic" to more "inorganic" with increasing partial pressure of oxygen. In particular, a marked change in the C 1s spectra was observed. The area ratios of the fluorine-containing groups which showed a hydrophobic property decreased in the C 1s spectra. This shows decomposition of the C–F bonds. From the results of FTIR and XPS measurements, the decrease in the contact angle was due to the decrease in the fluorine concentration in the deposited films because of decomposition of the C–F bonds, which agreed well with the results obtained from Figs. 6 and 7.

## 3.5. Optical properties of the deposited films

Fig. 11 shows the optical transmission spectra of the PC substrate before and after coating with the water-repellent film. The film was prepared with FAS-13 at a pressure of 15 Pa and a r.f. power of 200 W. The film thickness was 1.2 μm. Air was adopted as the reference. The transmittance of the PC substrate after coating was improved in the visible range. An increase of about 1.5% in the transmittance was obtained by coating the film.

The refractive indices of the films prepared on Si wafers with three kinds of FAS are plotted against the partial pressure of oxygen in Fig. 12. They were measured with an ellipsometer at a wavelength of 633 nm. The lowest refractive index was 1.39 when FAS-17 was used and the partial pressure of oxygen was 0 Pa. This value was comparable with that of the film prepared by the plasma polymerization using $CF_3CF=CFCF_3$

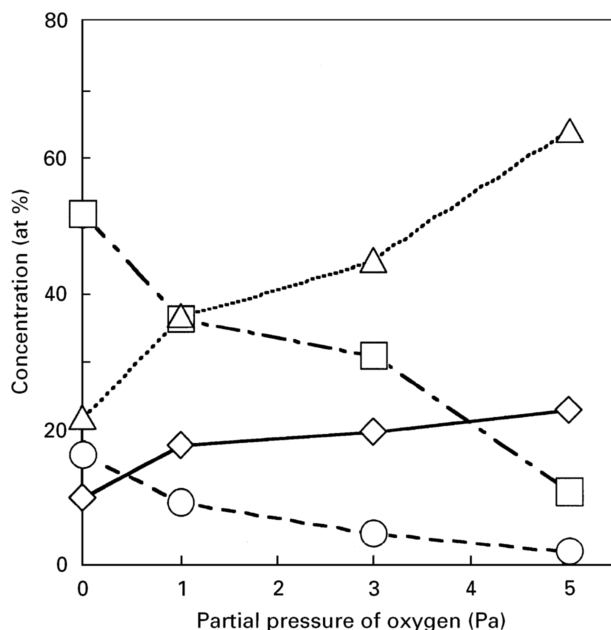



*Figure 10* Relationships between the partial pressures of oxygen and the atomic concentration of each element (total pressure, 15 Pa; r.f. power, 300 W). (△), O; (□), C; (◇), Si; (○), F.

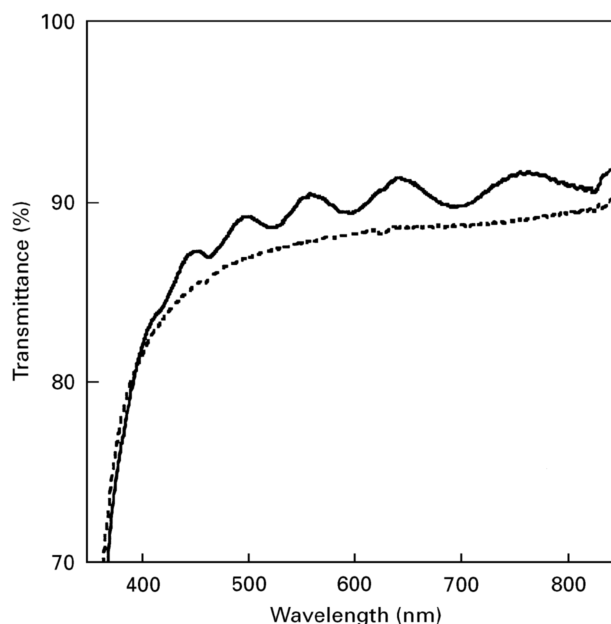



*Figure 11* Optical transmission spectra for a PC substrate before coating (-----) and after coating (——) of the film prepared with FAS-13 (FAS pressure, 15 Pa; r.f. power, 200 W; film thickness, 1.2 μm).

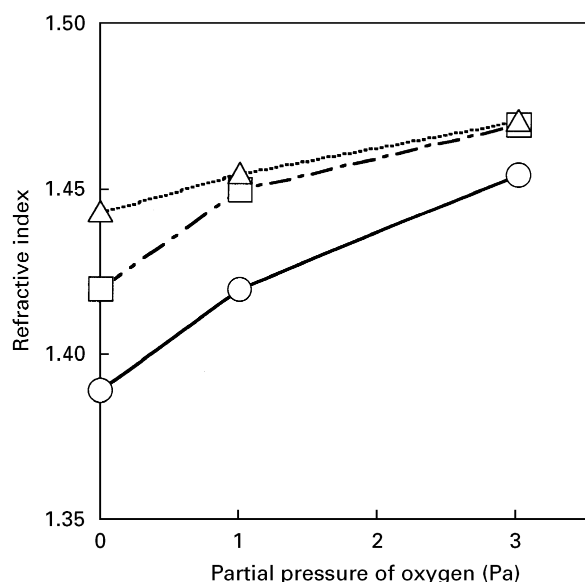



*Figure 12* Relationships between the partial pressures of oxygen and the refractive indices (total pressure, 15 Pa; r.f. power, 300 W). (△), FAS-3; (□), FAS-13; (○) FAS-17.

as a monomer gas (1.37–1.38) [13]. Generally the films containing fluorine have low refractive indices. The values obtained were lower than the indices of the glass substrate (1.52) and the PC substrate (1.57); the reflection decreased and the transmission increased on coating the water-repellent films as shown in Fig. 11. The deposited films also acted as an antireflective coating.

The refractive indices increased with increasing partial pressure of oxygen for all films. This was due to the decrease in the fluorine concentration in the films by decomposition of C–F bonds owing to the oxygen addition as obtained in Figs 7 and 10.

## 4. Conclusion

Transparent water-repellent films were prepared on various kinds of substrate using three kinds of FAS by r.f. PECVD at low substrate temperatures. The water repellency was improved greatly and depended on the length of the perfluoroalkyl groups in the FASs. The maximum contact angle for water drops was about 107°. This value was comparable with the contact angle for PTFE (108°). Fluorine-containing groups such as $-CF_3$, $-CF_2-$ and $>CF-$ covered the surfaces of the films. The addition of oxygen enhanced the oxidation of the films and decreased the deposition rate and the contact angle. The decrease in the deposition rate was due to the decomposition of the deposited films by the activated species oxygen and fluorine which were formed from the decomposition of the C–F bonds in FAS molecules. The decrease in the contact angle was due to the decrease in the fluorine concentration in the deposited film. The transmittance of the PC substrates coated with FASs was improved in the visible range. Use of the r.f. PECVD technique enabled a water-repellent treatment of various materials to be carried out at low substrate temperatures. This technique is suitable for the low-heat-resistance materials such as resins.

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