

# Effects of substrate temperature on structure and mechanical properties of sputter deposited fluorocarbon thin films

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## Abstract

Fluorocarbon thin films were formed by radio-frequency magnetron sputtering using a polytetrafluoroethylene target with different substrate temperatures in the range  $-5$ – $200^{\circ}\text{C}$ . Using X-ray diffraction and Fourier transform infrared spectroscopy, it was confirmed that the films were amorphous and contained C-F bonds. X-ray photoelectron spectroscopy measurements indicated that the amount of cross-linking in the films increased with increasing substrate temperature. Corresponding to the change in the molecular structure, the adhesion strength of the films to the Si substrate, estimated by micro-scratch testing, improved with increasing substrate temperature.

Keywords: rf sputtering, thin film, PTFE, fluorocarbon, adhesion strength

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## 1. Introduction

Polytetrafluoroethylene (PTFE) has many superior properties, such as chemical inertness, thermal stability, hydrophobicity, low dielectric constant, and low coefficient of friction. These properties are very important for applications such as low friction films [1], interlayer dielectrics in integrated circuits [2], and biomedical devices [3]. However, the adhesion strength of PTFE films to other materials is rather poor for applications [4, 5], and it is difficult to form PTFE thin films by wet processes, such as spin coating. Fluorocarbon films have been prepared by RF sputtering using a PTFE target [6–10]. Yamada *et al.* [6,7] reported that fluorocarbon films have a complex molecular structure involving double-bonding, cross-linking and branching. Oya *et al.* [8] reported that PTFE thin films become carbon rich with increasing substrate temperature. Tang *et al.* [9] found that the degree of cross-linking was influenced by the RF power and gas pressure used, and higher hardness and elastic modulus values were obtained for films with low fluorine content and a high degree of cross-linking. However, the relationship between molecular structure and adhesion strength for fluorocarbon films is not fully understood.

Lahmar *et al.* [11] investigated the relationship between deposition temperature and adhesion strength of sputter deposited copper films on a steel substrate and reported that the critical load increased rapidly with increasing deposition temperature or heat treatment after deposition. In contrast, Uemura *et al.* [12] investigated the adhesion of sputtered polyimide films deposited on a copper substrate at RT and 250°C and reported that the adhesion strength of the films was reduced by heating. In this work, we prepared fluorocarbon thin films by RF sputtering of a PTFE target in a pure argon atmosphere, and investigated the effects of substrate temperature on the structure and mechanical properties in order to improve the adhesion strength of the films to Si substrates.

## 2. Experimental details

Fluorocarbon films were deposited using an RF (13.56 MHz) magnetron sputtering system with a base pressure of  $1.0 \times 10^{-4}$  Pa in this work. A PTFE disk 50 mm in diameter and 5 mm thick was used

as the sputtering target. Fluorocarbon films were deposited on silicon wafers and quartz glass substrates. Ar was used as the sputtering gas and the gas flow rate was controlled to 1 cm<sup>3</sup>/min with a mass flow controller. RF power and sputtering gas pressure were maintained at 50 W and 0.67 Pa, respectively. The substrate temperature was changed from -5 to 200°C.

The thickness of the films was measured with an ellipsometer at a laser wavelength of 633 nm. The structure of the films was evaluated by X-ray diffraction (XRD) with Cu K $\alpha$  radiation. The chemical bonding state of the films was characterized by Fourier transform infrared spectroscopy (FTIR) in N<sub>2</sub> atmosphere and X-ray photoelectron spectroscopy (XPS) with an Al K $\alpha$  radiation source. Carbon 1s XPS peaks were deconvoluted using a peak synthesis procedure which employed a Gaussian lineshape, and Shirley's method [13] was used for background subtraction. Optical properties were examined by UV-VIS spectrophotometry using the transmission method for films deposited on quartz glass substrates. Mechanical properties were examined using micro-scratch testing, with a diamond stylus with a 25  $\mu$ m radius under a loading rate of 0.83 mN/s. The thicknesses of the films were in the range of 80–180 nm for the XPS and optical measurements, and 340-390 nm for the FTIR and mechanical measurements.

### 3. Results and discussion

Fig. 1 shows the deposition rate of the films as a function of substrate temperature. The deposition rate clearly decreased with increasing substrate temperature. It is thought that the sticking coefficient of sputtered atoms on the substrates decreased with increasing substrate temperature. Because of the very low deposition rate at a substrate temperature of 200°C, samples deposited at and below 150°C were used in the following experiments.

XRD data indicated that all the deposited fluorocarbon films were amorphous. To understand the effect of substrate temperature on the chemical bonding state of the films, FTIR and XPS were employed. Fig. 2 shows FTIR spectra of the films deposited at different substrate temperatures. The large absorption peaks around 1200 cm<sup>-1</sup> are due to CF<sub>2</sub> asymmetric stretching (1208–1220 cm<sup>-1</sup>) and symmetric stretching (1152–1160 cm<sup>-1</sup>) bands [10, 14, 16], and the small absorption peaks

at  $740\text{ cm}^{-1}$  are due to the  $\text{CF}_3$  deformation band [10, 15]. The sharp peaks observed in the region from  $1400\text{ cm}^{-1}$  to  $1900\text{ cm}^{-1}$  are due to bending vibration of residual  $\text{H}_2\text{O}$  molecules in the  $\text{N}_2$  atmosphere during the FTIR measurement. No major change in the FTIR spectra was found.

The C 1s XPS spectra of bulk PTFE and the films deposited at various substrate temperatures are shown in Fig. 3. Five different chemical components are observed from the spectra. The deconvoluted peaks were assigned as follows:  $\text{CF}_3$  at 293.0 eV,  $\text{CF}_2$  at 290.9 eV, CF at 288.7 eV, C-CF at 286.5 eV and  $\text{CH}_x$  at 284.1 eV [6-8, 10, 15, 17]. The expressions  $\text{CF}_3$ ,  $\text{CF}_2$ , and CF mean carbon atoms linked to three, two, and one fluorine atoms, respectively, and C-CF and  $\text{CH}_x$  mean carbon atoms which bond with other carbon atoms that linked to fluorine atoms and carbon atoms of hydrocarbon contaminants, respectively. The fluorine to carbon (F/C) molar ratio of the films was estimated to be 1.2–1.3 from the C 1s XPS spectra [6]. In contrast, the C 1s XPS spectrum of the bulk PTFE practically consists of only  $\text{CF}_2$ , and the relative peak area of  $\text{CF}_2$  was approximately 99%. These results mean that the deposited films were carbon-rich in composition and had a network structure and grafted chains to the substrate [3,18], which are different from the simple linear chain molecular structure of conventional PTFE molecules. Fig. 4 shows the relative peak areas of the five peaks in the C 1s XPS spectra shown in Fig. 3 as a function of substrate temperature. It is found that the amount of C-CF species, which indicate the formation of network structure [7, 19], increased at high substrate temperatures. The highly cross-linked molecular structure of the sputtered films is considered to be formed because most of sputtered species from the polymer target are atoms and low molecular weight fragments [18, 20], and these species bond together and form polymer films at the substrate surface.

Fig. 5 shows the absorption spectra of the films deposited at various substrate temperatures. The absorption coefficient of the film in the short wavelength region of 200–500 nm increased with increasing substrate temperature. This suggests strongly that conjugated C=C double bonds, which cause absorption due to  $\pi$ - $\pi$  transitions [16,21], were formed for the film deposited at the higher substrate temperature, although FTIR peaks due to C=C double bond ( $1600$ – $1700\text{ cm}^{-1}$  [1,16]) could not be confirmed in Fig. 2.

Micro-scratch testing was carried out to estimate the adhesion strength of the fluorocarbon films to

the Si substrate. The critical load increased with increasing substrate temperature and the maximum value of the critical load was obtained for the film deposited at a substrate temperature of 150°C, as shown in Fig. 6. Fig. 7 shows micrographs, after micro-scratch testing, of specimens deposited at different substrate temperatures. For the films deposited at -5–100°C, the critical loads are low and the critical load points, where adhesive failure occurs, are clearly seen. However, for the film deposited at 150°C, the critical load is high and the critical load point is blurred. The differences in these observations suggest a change in the failure mechanism. The amount of polymer chains grafted to the substrate surface may increase with increasing substrate temperature. In addition, the amount of the cross-linking and C=C double bonds, which are expected to make the films harder, increased with increasing substrate temperature. Due to the change in the interface structure and molecular structure, the film deposited at higher substrate temperature has good mechanical properties.

#### **4. Conclusions**

Amorphous fluorocarbon films were prepared by RF magnetron sputtering using a PTFE target. From C 1s XPS spectra, it was found that the amount of cross-linking in the films increased with increasing substrate temperature. Corresponding to the change in the molecular structure, the critical load increased with increasing substrate temperature. The adhesion strength of the fluorocarbon films was clearly shown to be improved at higher substrate temperatures.

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## **Figure captions**

Fig. 1. Deposition rate of films as a function of substrate temperature.

Fig. 2. FTIR spectra of films deposited at different substrate temperatures.

Fig. 3. C 1s XPS spectra of (a) bulk PTFE and films deposited at various substrate temperatures: (b)  $-5^{\circ}\text{C}$ , (c)  $20^{\circ}\text{C}$ , (d)  $100^{\circ}\text{C}$ , and (e)  $150^{\circ}\text{C}$ .

Fig. 4. Relative peak area of the C 1s XPS peaks shown in Fig. 3 as a function of substrate temperature.

Fig. 5. Absorption spectra of films deposited at various substrate temperatures.

Fig. 6. Critical load of films as a function of substrate temperature.

Fig. 7. Optical micrographs of films deposited at different substrate temperatures of (a)  $-5^{\circ}\text{C}$ , (b)  $20^{\circ}\text{C}$ , (c)  $100^{\circ}\text{C}$ , and (d)  $150^{\circ}\text{C}$  after micro-scratch testing.

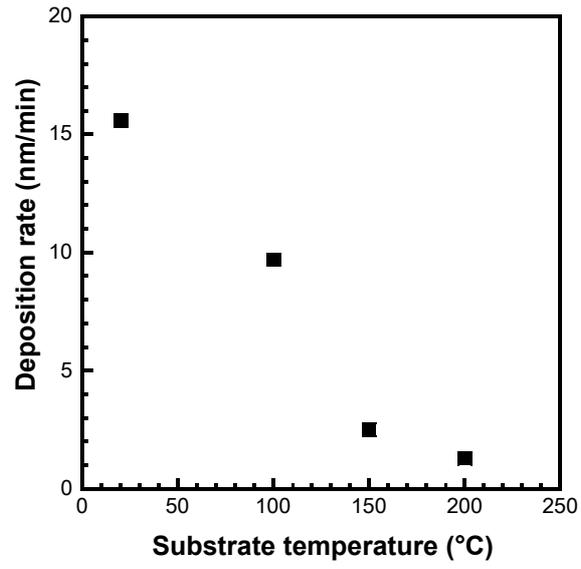


Fig. 1

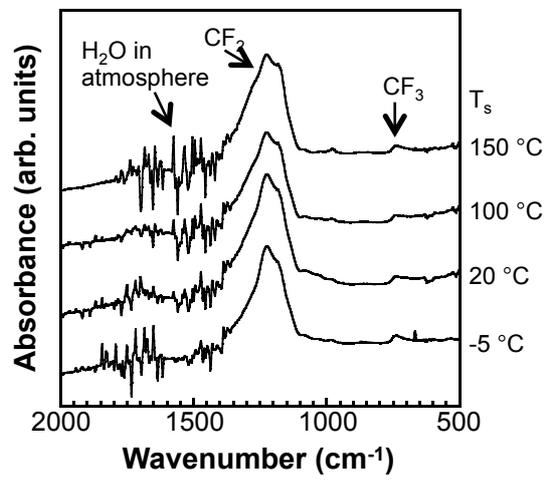


Fig. 2

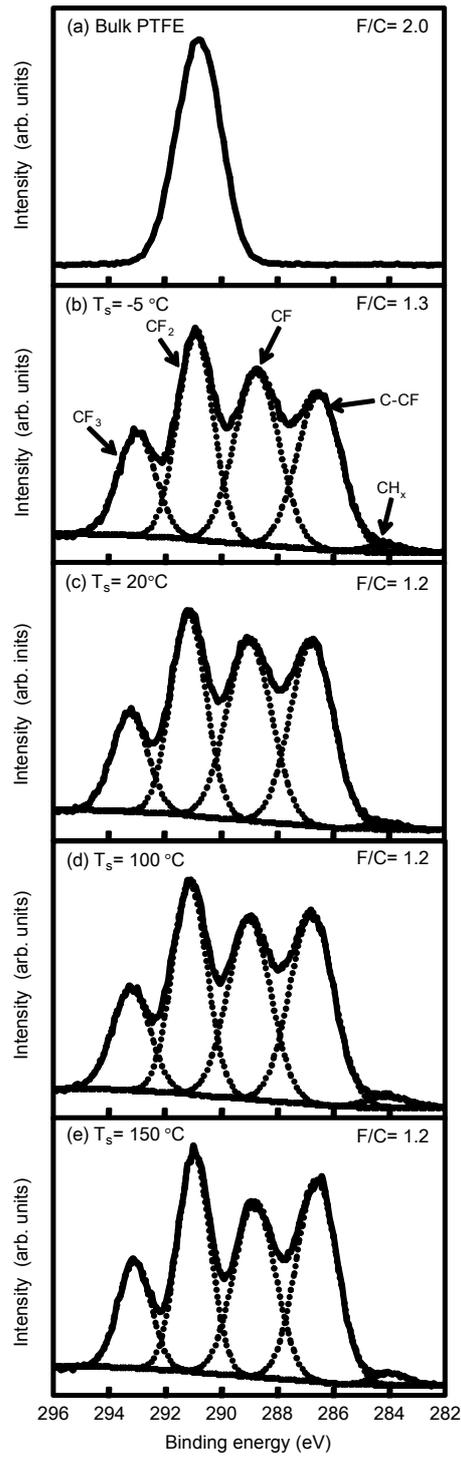


Fig. 3

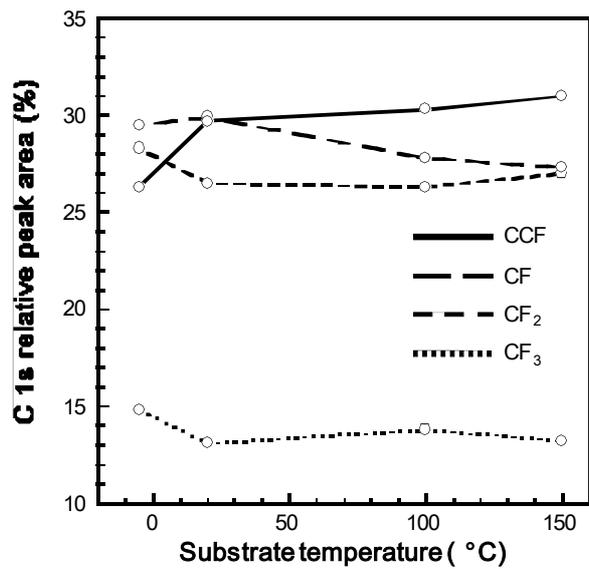


Fig. 4

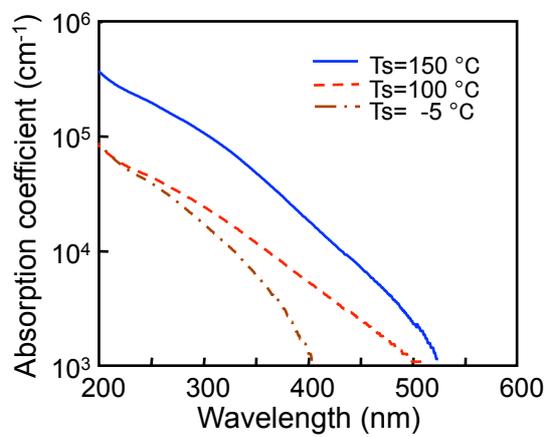


Fig. 5

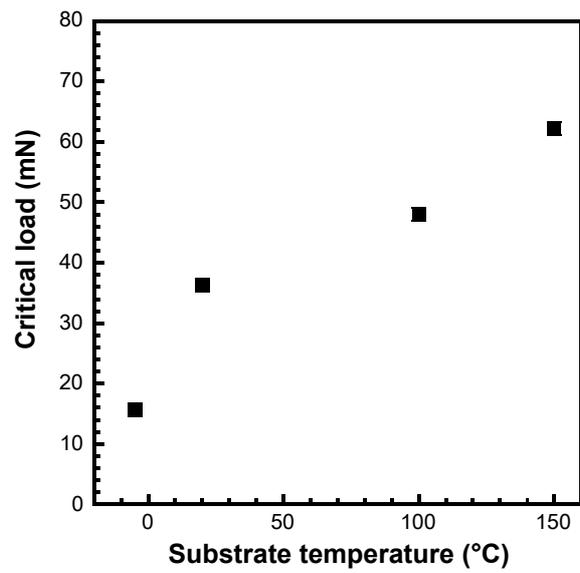


Fig. 6

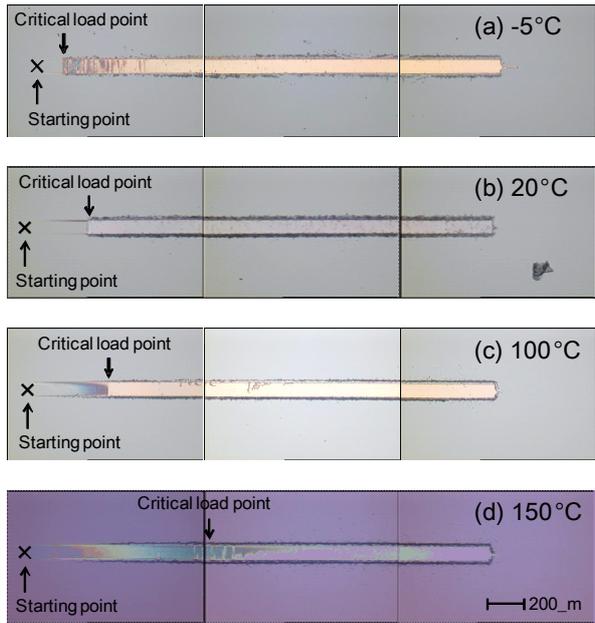


Fig. 7