



Adsorption properties of fluorocarbon thin films prepared by physical vapor deposition methods

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ABSTRACT

To investigate their potential as gas sensors, fluorocarbon thin films were deposited onto the gold electrode of a quartz crystal microbalance by vacuum evaporation (VE), plasma assisted vacuum evaporation (PE-VE) and RF sputtering (RF-SP). The adsorption properties of these thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were then evaluated and compared to their surface morphologies. These fluorocarbon thin films have low sensitivities to non-polar solvents which contain methyl and aromatic groups, and high sensitivities to polar solvents which contain carbonyl and hydroxyl groups. The adsorbed mass of all gases besides water was found to increase with increasing film surface free energy. The adsorbed mass of water was largest for the film prepared by PE-VE, which is thought to be the result of the larger polar component of its surface free energy. In addition, the film prepared by RF-SP was shown to have a high sensitivity for polar solvents such as ethanol, acetone and acetaldehyde.

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1. Introduction

Highly sensitive detection methods for volatile organic compounds (VOCs) are needed in working environment handling the VOCs. The use of a quartz crystal microbalance (QCM) is one such method, and many studies have been carried out on the deposition of metallic, inorganic and organic thin films onto QCM surfaces for use as sensors. For example, Noda et al. reported measurements of the adsorbed mass of trichloroethylene on the copper electrode of a QCM [1]. Zeolite and indium–tin oxide (ITO) thin films were coated on QCM electrodes, and evaluated as chemical sensors [2,3]. Similarly, polystyrene dissolved in chloroform was tested as a biosensor [4]. However, there are few reports on fluorocarbon thin films deposited onto a QCM by physical vapor deposition (PVD). We have already reported on the gas adsorption properties of plasma polymer-like thin films deposited by RF sputtering using a polyimide target [5]. In this paper, we characterize the gas adsorption properties of fluorocarbon thin films deposited onto a QCM by different PVD methods.

Poly(tetrafluoroethylene) (PTFE) has been widely used in the mechanical, electrical and medical industries because it has excellent properties such as thermal stability, lubricating ability, and chemical stability, and development of PTFE coating techniques is important in these industries. There have been many reports on fluorocarbon

thin films prepared by PVD methods using PTFE, such as vacuum evaporation and RF sputtering [6–9]. PTFE polymer chains break into fragments when the material is heated to its sublimation temperature, and low molecular weight fluorocarbon films are formed when these fragments condense on a substrate. The primary decomposition products are tetrafluoroethylene and difluorocarbon diradicals (CF₂) [10]. In addition, Choukourou et al. reported that a thin film could be deposited by thermal degradation of polyimide by a glow discharge excited using an RF planar magnetron, which was described as a “polyimide-like thin film” [11]. In this study, fluorocarbon thin films prepared by vacuum evaporation (VE), plasma assisted vacuum evaporation (PE-VE) and RF sputtering (RF-SP) are referred to as thermal decomposition thin films, plasma thermal decomposition thin films and plasma polymer-like thin films, respectively.

In this paper, the surface morphologies, chemical structure and gas adsorption properties of these fluorocarbon thin films are discussed.

2. Experimental

Fluorocarbon thin films were deposited from PTFE starting material onto glass slides (76 mm × 26 mm, 2 mm thick) and the gold electrode of a QCM by VE, PE-VE and RF-SP. The films on the glass slides were used for analysis of surface morphology and chemical structure, and the gas adsorption properties were evaluated for the films on the QCM. An AT-cut device was used in this experiment, whose fundamental oscillation frequency was 9 MHz [1]. The arithmetic average surface roughness (Ra) of the glass substrate and gold electrode was 1.8 and 125 nm, respectively.

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Teflon® (DuPont., USA) pellets ($3 \times 3 \times 3$ mm) were used as the starting material for the VE and PE-VE processes. They were heated in a tungsten basket coated with alumina, and the temperature of the pellets in the basket was monitored with a Pt–Rh thermocouple [8]. The RF power in the coil was 0 and 200 W, respectively, for VE and PE-VE depositions, and the substrate bias voltage was 0 V in both cases. After the chamber was evacuated to a pressure of 2.0×10^{-2} Pa, the pressure was increased to 8 Pa by adjusting the main valve. In the case of PE-VE, a pure argon flow was introduced into the vacuum chamber at $1.0 \text{ cm}^3/\text{min}$. For VE deposition, we have previously reported that the deposition rate decreased with increasing pressure [8]. Furthermore, the films deposited at high pressure easily peeled off the glass substrate. However, in the present study, it was found that the thin film prepared at 8 Pa showed moderately good adhesion to the substrate.

Plasma polymer-like thin films were prepared with an RF sputtering apparatus (SBR-1104E, ULVAC Inc., Japan). A Teflon® (DuPont., USA) target (100 mm in diameter, 5 mm thick) was used as the sputtering target for the deposition. After the sputtering chamber was evacuated to a pressure of 1.3×10^{-2} Pa, the pressure in the chamber was increased to 1.3 Pa by adjusting the main valve. The films were sputtered at 100 W [8,9]. We have already reported that the deposition rate of such films by RF sputtering decreased with increasing pressure, and that high deposition rates could be achieved at pressures between 0.5 and 4 Pa [12]. Thus, in the current study, we chose a pressure of 1.3 Pa.

The mass of the fluorocarbon films coated on the gold electrode of the QCM was determined by the QCM system, and was found to be in the range 0.8–1.3 μg . The adsorption properties of these thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were evaluated using the QCM system. 100 μL of each liquid was dropped into a gas washing bottle and a dry nitrogen flow was introduced at 100 mL/min. Changes to the QCM oscillating mass due to gas adsorption on the gold electrode were indicated as frequency shifts. The QCM system was maintained at $20 \pm 1^\circ\text{C}$ [5].

Surface morphologies, elemental compositions and chemical bonding states of the fluorocarbon thin films on the glass slide substrate were determined by scanning probe microscopy (SPM-9600, Shimadzu Co. Ltd., Japan) and X-ray photoelectron spectroscopy (XPS) (XSAM800cpi, Shimadzu Co. Ltd., Japan). It has been reported that the C(1s) XPS spectra from fluorocarbon thin films can be resolved into five different components corresponding to C–CH, C–CF_x, CF, CF₂ and CF₃ [13]. This was found to be also the case in this study. The full width at half maximum (FWHM) of each peak was 2.00 eV. Chemical bonding states were also analyzed using Fourier transform-infrared (FT-IR) spectroscopy (Model FT-720; Horiba Co. Ltd., Japan). For these measurements, the fluorocarbon thin films were peeled off the glass slides using a spatula, and mixed with KBr. Absorption in the range $2000\text{--}400 \text{ cm}^{-1}$ was measured.

The contact angles of water and methylene iodide droplets were determined by taking photographs of these droplets on the fluorocarbon thin films. The volume of each droplet was 10 μL . These measurements were performed in atmosphere, and at least three separate measurements were used to determine the average contact angle.

3. Results and discussion

3.1. Surface morphologies and chemical structures of fluorocarbon thin films

Fig. 1(A), (B) and (C) shows surface morphologies of fluorocarbon thin films deposited by VE, PE-VE and RF-SP, respectively. Large planar particles, with diameters and heights of about 100 nm, can be observed on the surface of the film produced by VE. In the case of the PE-VE film, large rounded particles with diameters of 50–100 nm and heights of about 100 nm can be seen. On the other hand, the surface of

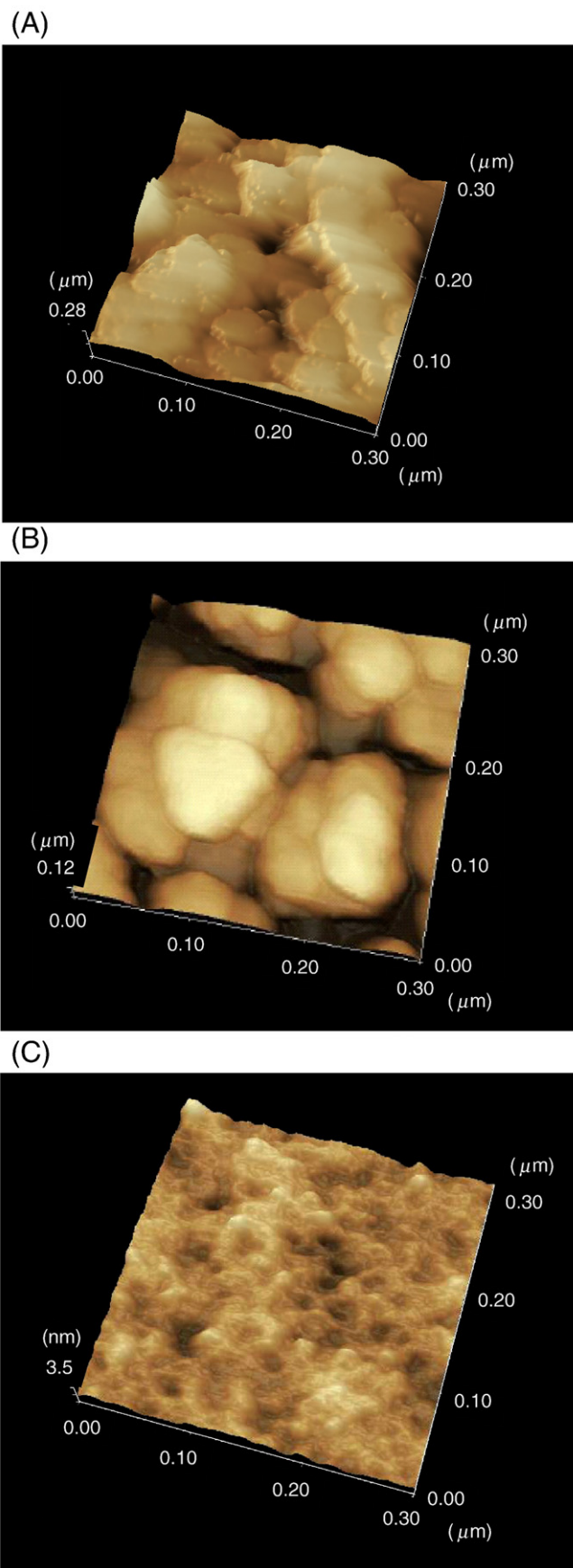


Fig. 1. Surface morphologies of the fluorocarbon thin films deposited onto glass slides by VE (A), PE-VE (B) and RF-SP (C).

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