Vacuum 87 (2013) 218–221

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

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

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A R T I C L E I N F O

Article history:
Received 30 June 2011
Received in revised form
26 April 2012
Accepted 22 May 2012

Keywords:
Rf sputtering
Thin film
PTFE
Fluorocarbon
Adhesion strength

A B S T R A C T

Fluorocarbon thin films were formed by radio-frequency magnetron sputtering using a polytetrafluoroethylene target with different substrate temperatures in the range −5 to 200 °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.

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 1.0×10^{-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^3/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 Kα radiation. The chemical bonding state of the films was characterized by Fourier transform infrared spectroscopy (FTIR) in N_2 atmosphere and X-ray photoelectron spectroscopy (XPS) with an Al Kα radiation source. Carbon 1s XPS peaks were deconvoluted using a peak synthesis procedure which employed a Gaussian lineshape, and Shirley's

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0042-207X/$ – see front matter
http://dx.doi.org/10.1016/j.vacuum.2012.05.029

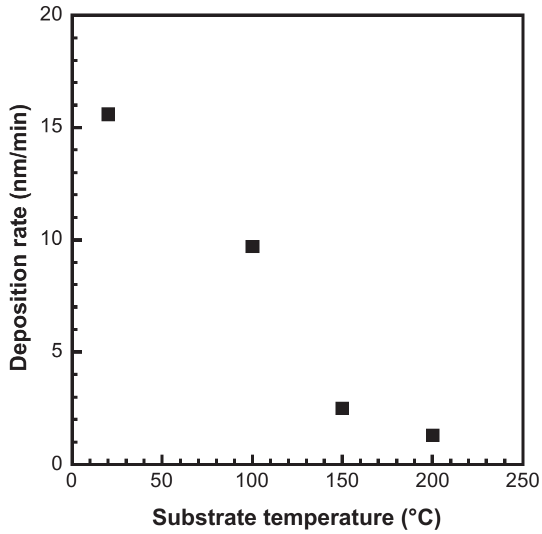

Fig. 1. Deposition rate of films as a function of substrate temperature.

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 μm 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^{-1} are due to CF_2 asymmetric stretching (1208–1220 cm^{-1}) and symmetric stretching (1152–1160 cm^{-1}) bands [10,14,16], and the small absorption peaks at 740 cm^{-1} are due to the CF_3 deformation band [10,15]. The sharp peaks observed in the region from 1400 cm^{-1} to 1900 cm^{-1} are due to bending vibration of residual H_2O molecules in the N_2 atmosphere during the FTIR measurement. No major change in the FTIR spectra was found.

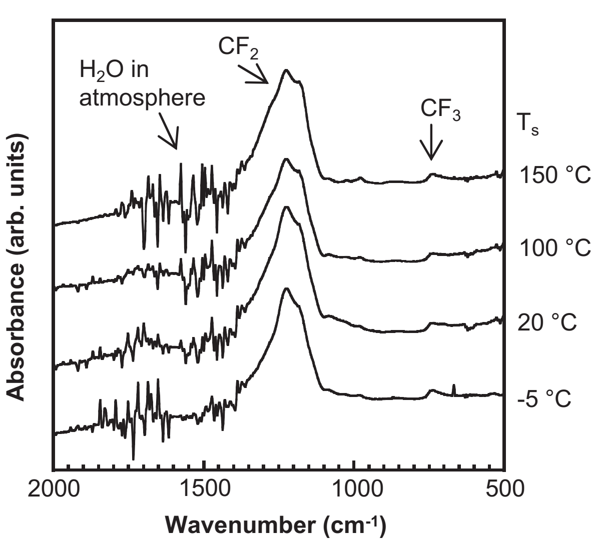

Fig. 2. FTIR spectra of films deposited at different substrate temperatures.

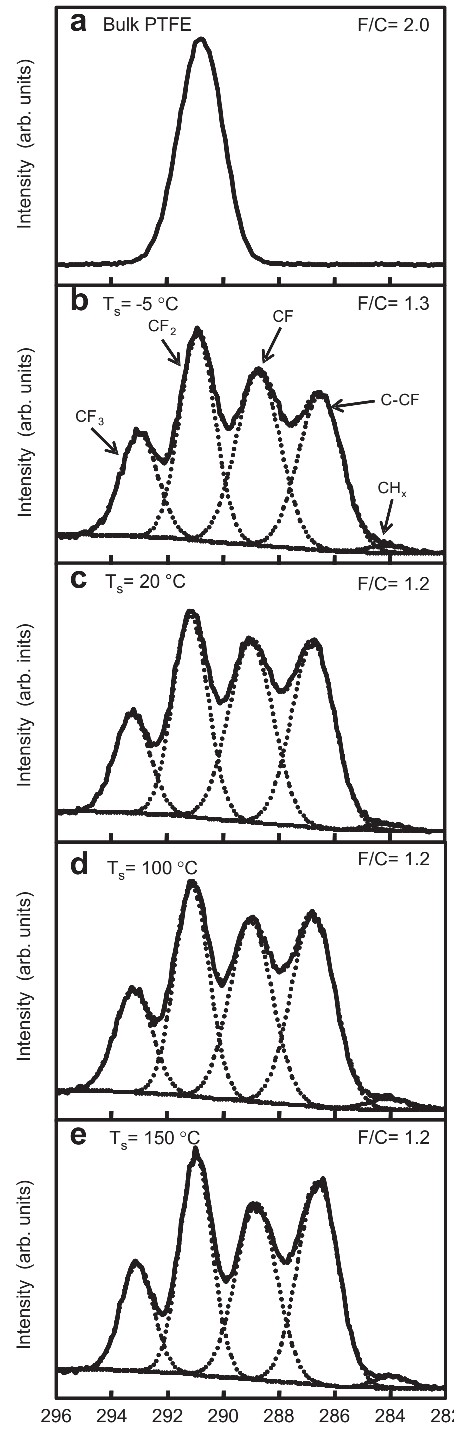

Fig. 3. C 1s XPS spectra of (a) bulk PTFE and films deposited at various substrate temperatures: (b) −5 °C, (c) 20 °C, (d) 100 °C, and (e) 150 °C.