Effect of annealing on hydrophobic stability of plasma deposited fluoropolymer coatings

Arun Kumar Gnanappa [a,*], Cian O'Murchu [a], Orla Slattery [a], Frank Peters [a], Balázs Aszalós-Kiss [b], Syed A.M. Tofail [b]

[a] Tyndall National Institute, Lee Maltings, Prospect Row, Cork, Ireland
[b] Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

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ABSTRACT

Fluorinated amorphous carbon (a-C:F) films e.g. plasma polymerised perfluorocyclobutane have long attracted much consideration due to their low surface energy, hydrophobicity, low refractive index, good electrical and thermal insulation and good thermal stability. Although a-C:F films have many advantages, hydrophobic stability over time in air and water remains a major concern. In this study, the effects of weathering conditions on the hydrophobicity of fluorocarbon films prepared from perfluorocyclobutane precursors were examined using water contact angle measurements. It was found that the high initial hydrophobicity of as-deposited films degrades rapidly in humid conditions. The stability of hydrophobicity can be significantly improved when a suitable treatment such as annealing is employed. The mechanism of weathering was explained with the help of a number of morphological and chemical characterisation techniques such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS). In particular, XPS results demonstrated that a reduction in the overall amount of –CF$_3$ radical, oxygenation of surface fluorides and the formation of an overlayer all influence the degradation of fluorocarbon in aquatic environment.

1. Introduction

Plasma polymerization of fluorocarbon thin films [1–3] has been the subject of active research because the deposited films can display a variety of desirable properties not easily obtained with other materials. Specifically, fluorocarbon thin films are being investigated for their use as "low-k" dielectric materials in semiconductor device fabrication [4–6], as bio-passivation coatings [7–11], as hydrophobic, non-stick coatings [12], and as low-friction coatings [13,14]. Plasma deposited fluorocarbons (FCs) offer some distinct advantages such as low dielectric constant, chemical inertness, good gap filling ability, and pinhole-free films [15]. However, the hydrolytic degradation of FCs has not been well studied.

Conventionally, plasma polymerization is one of the most popular techniques for obtaining a-C:F film with several favourable advantages such as controlled thickness, dry process, high deposition rate and less production cost. The properties of a plasma polymer film are strongly affected by its chemical structure, which in turn, is strongly dependent on the input plasma characteristics.

Previously, we reported on the significance of various process input factors and their impact on hydrophobicity [16]. Very few studies have been performed that investigate the effect of immersion and humidity on the structure and properties of these films. It is important that these films retain their chemical structure and properties (hydrophobic, mechanical, and thermal) when immersed in water. This paper focuses on the study of the surface evolution and its correlation with chemical state to understand better the mechanism behind the hydrophobic loss.

For the fluorocarbon films to have high hydrolytic stability, they should be structured as chains as long as possible (low concentration of the CF$_3$ tail groups) and with just the right level of cross-linking. There have been a few studies on the annealing of the film which improves the hydrophobicity of the film [17], frees it from carbon rich impurities [18] and removes the dangling bonds on the surface which are highly reactive towards environmental oxygen and water [15].

In the experiments in this work, a 300 nm thick film was grown with the standard Bosch conditions and subsequently analysed to determine its wetting properties using contact angle measurements, to determine its composition using X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) and to investigate its morphology using Scanning Electron

Microscope (SEM) and Atomic Force Microscopy (AFM). Typically, the film thicknesses were measured by Nanospec and compared with SEM and AFM imaging.

Even though there are many reports [19–24] in the literature discussing the low reactivity of fluorocarbon films, the contact angle results show a drop in value for samples that were immersed in water for a period [23,25]. The effect of changes in surface roughness and morphology in addition to chemical changes have been analysed to attempt to account for the hydrophobic degradation of the C:F films.

In order to investigate the effect of annealing on the hydrophobic stability, the fresh as-deposited films were annealed at 100 °C in vacuum. The annealed sample exhibited improved stability in comparison to the unannealed film. With surface morphological study not giving satisfactory results the surface chemical analysis of the films was carried out. Surface chemical analysis has also been done on the samples that were annealed and immersed in water.

2. Experimental

2.1. Film preparation

A Surface Technology Systems (STS) Silicon Etch tool was used to deposit films. Typical process conditions for the Bosch process include coil power – 2000 W, platen power – 200 W, pressure – 12.5 Pa, flow rate C_4F_8 – 200 sccm, SF_6 – 300 sccm. The silicon wafers were treated in C_4F_8 for 3 min to obtain a thin film of 300 nm. The thickness of the film was later confirmed by Nanospec, SEM, and AFM. More detailed explanations and a schematic of the setup have been discussed in our previous paper [16]. The wafer was scribed into small pieces and stored in a high vacuum desiccator at a relative humidity (RH) of lower than 20% and a temperature of 20 °C to reduce the effect of ambient conditions on the aging.

2.2. Contact angle measurement

Static advancing contact angle measurements were performed on the monolayer coatings by the sessile drop method using deionised water. A Data Physics OCA20 (UK) contact angle instrument was used for the contact angle measurements [26]. Typically, five measurements were recorded (volume of drop, 5 mL) and an average angle was calculated in an effort to minimize hysteresis. It has been reported that surface roughness modifies the contact angles and the contact angle hysteresis of wetting. In general, it is claimed that the contact angles are greater on rough surfaces than on smooth surfaces and that the wetting hysteresis increases with the surface roughness [27]. For a microfluidic application the contact angle hysteresis should be as low as possible in order to have a low friction between the surface and the water drop.

2.3. Atomic Force Microscopy (AFM)

Surface roughness of the etched Si (100) samples was determined using an Atomic Force Microscope (AFM, Dimension 3100, Nanoscope IV). Surface imaging was carried out in tapping mode under ambient conditions (25 °C, 40% RH) using a silicon tip (tip radius of about 10 nm) at scan sizes of 5×5 and 25×25 mm with a resolution of 256 data points per scan. Film thicknesses were measured by just dragging the AFM tip across the polymer film that has been scratched. A Nanospec was also used to measure the thickness of the deposited polymer and compare it with the AFM thickness. The thickness was measured using the refractive index value of the plasma polymer which was earlier determined using the optical coupler as 1.37 ± 0.003.

2.4. Scanning Electron Microscopy (SEM)

The SEM was performed in the usual way with a JEOL JSM 840 instrument, on polymer specimens first sputtered-coated with a thin ~10 nm layer of gold.

2.5. Fourier Transform Infrared (FTIR) Spectroscopy

The chemical structure of the films deposited on Si wafers was determined by using FTIR. The infrared spectra were measured with a SensIR Microscope Fourier Transform Infrared Spectrometer under transmission mode with an ATR objective lens. The spectra were analysed for any trace –OH peaks that are present in the film after immersion in water and also for the changes during the annealing of films.

2.6. X-ray Photoelectron Spectroscopy (XPS)

The elemental composition and the nature of chemical bonding prevalent at the surface of the plasma polymerised films were determined by XPS in a Kratos Axis 165 spectrometer. The X-ray source was an Al Kα monochromated with a crystal-plate monochromator. The energy of the photoexcitation was 1486.6 eV. The source was operated at an excitation voltage of 10 kV and a beam current of 12 mA. The total pressure in the spectrometer analysis chamber was lower than 8×10^{-7} Pa.

The loss of photoelectrons from the surface of an insulating material such as fluorocarbons leaves positive surface charge that causes a nonlinear shift in photoelectron spectra. The neutralisation of such surface charge was accomplished by creating a low-energy electron cloud by passing a small current through a tungsten filament coaxially placed to the electron optics system. An electromagnet underneath the sample redirected secondary electrons so that the sample becomes immersed in this electron cloud. This ensured that surface charge could be efficiently neutralised irrespective of the high electrical energy barrier of fluorocarbon polymers or the roughness of their surface. The current and the charge on the tungsten filament were adjusted so that the spectra were overcompensated. A linear correction factor was then used by taking the position of the C 1s peak for C bonded to F as CF_3 as a reference line and appearing at a binding energy (BE) of 293.9 eV. The accuracy of the referencing was verified by the appearance of C 1s peak for C bonded to C or hydrogen in the vicinity of 284.8 eV. The use of the C 1s peak in CF_3 as a reference binding energy also ensured that the F 1s peak appears in the vicinity of 688.8 eV for F bonded to C in perfluorocarbons.

The emitted photoelectrons were collected at a normal take-off angle from the sample surface. Elemental analyses were obtained
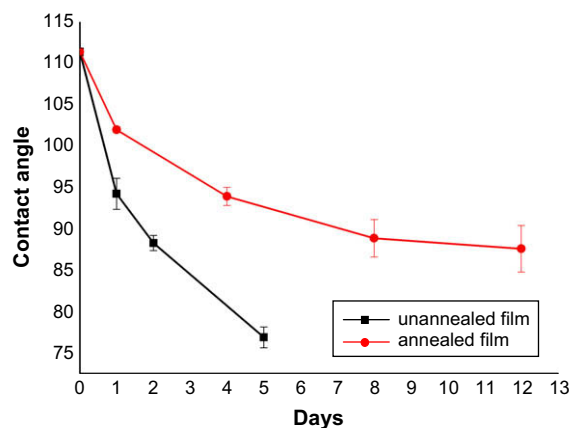

Fig. 1. Effect of annealing on degradation of plasma polymer film.