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Synthesis of superhydrophobic PTFE-like thin films by self-nanostructuration in a hybrid plasma process

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ABSTRACT

Superhydrophobic poly(tetrafluoro-ethylene) (PTFE) like thin films were grown on silicon wafers using a plasma-based hybrid process consisting on sputtering a carbon target in an Ar/CF_4 atmosphere. The influence of the bias voltage applied to the substrate (V_{Bias}) as well as of the gas mixture composition ($\%CF_4$) on the chemical composition, the wettability and the morphology of the deposited thin films were evaluated.
The chemical composition measured by X-ray Photoelectron Spectroscopy (XPS) has revealed that the F/C atomic ratio is always lower than for conventional PTFE (F/C = 2) and that it decreases when V_{Bias} increases (from F/C = 1 for $V_{Bias} = -100$ V to F/C = 0.75 for $V_{Bias} = -200$ V). This behavior is associated with the preferential sputtering of the fluorine atoms during the plasma-assisted growth of the films. Consecutively, a self-nanostructuration enhanced when increasing V_{Bias} is observed. As a consequence, the water contact angle (WCA) measurements range from 70° up to 150° depending on (i) the fluorine concentration and (ii) on the magnitude of the nanostructuration. In addition, for the films presenting the highest WCAs, a small hysteresis between the advancing and receding WCAs is observed (<10°) allowing these films to fulfill completely the requirements of superhydrophobicity. The nanostructuration is probably due to the chemical etching by fluorine atoms of the fluorinated group.
In order to get more understanding on the wettability mechanisms of these surfaces, the topography of the films has been evaluated by atomic force microscopy (AFM). The data have revealed, for all films, a dense and regular structure composed by conic objects (A_vH is their average height and A_vD is the average distance between them) for which the dimensions increase with V_{Bias}. A correlation between A_vH/A_vD, defined as the "morphological ratio", with the WCA was established. Theoretical evaluations of the WCA using the Wenzel and Cassie equations with, as inputs, the features of the deposited thin film surfaces measured by AFM suggest that the wetting regime is intermediate between these two ideal situations.

1. Introduction

PTFE-like thin films are very popular due to their interesting properties such as chemical inertness, low surface energy, low dielectric constant and low friction coefficient. These properties allow their use for numerous applications such as being anti-adhesive, biocompatible [1], and electrically insulating [2] coatings.

Magnetron sputtering [3], laser ablation [4], ion beam [5] and plasma enhanced chemical vapor deposition (PECVD) [6] are the most reported deposition techniques used to synthesize these coatings. Among them, magnetron sputtering offers several advantages such as a low deposition temperature, an often good adherence of the deposited films, a relatively high deposition rate, and a fine tuning of the chemical composition.

One of the most interesting properties of PTFE-like coatings is the so-called superhydrophobicity which often produces the well-known "lotus effect" [7]. The superhydrophobicity property of a surface is usually defined by a high water contact angle (WCA) of 150° and more, and a hysteresis of this WCA between advancing and receding angles remaining lower than 10° [8].

Such a situation can only be reached by combining a chemically hydrophobic surface with a specific (nano-)structuration. For example, for PTFE, the theoretical maximum WCA of a flat surface ranges between 102.5° [9] and 130° [10] depending on the reports but, in all cases, far from the 150° necessary to get a superhydrophobic situation [10]. On the other hand, for example, the WCA of a structured poly(ethylene

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glycol) surface only reaches 95°[12], this result illustrates that without an adapted surface chemistry, the structuration of polymer surfaces is not enough to reach superhydrophobicity.

In order to synthesize superhydrophobic PTFE-like surfaces, different strategies have already been evaluated, mainly related to the (post) nanostructuration of the PTFE coating. Reports were found on the deposition on a rough substrate [11] or the use of hot embossing [12], plasma etching [13], and electrospray [14]. If these approaches are efficient, their potential industrial transfer seems difficult because, most of the time, they involve more than one step.

It has been recently shown that by sputtering a PTFE target in argon [9], it is possible to synthesize superhydrophobic surfaces using a one step process. Nevertheless, due to the low thermal conductivity of the PTFE, the power applied to the target is limited and, as a consequence, the deposition rate remains low which is not acceptable in view of an industrial application. Another work reports on the possibility to grow superhydrophobic PTFE-like coating by PECVD using a pulsed RF process. The authors observed superhydrophobicity for narrow experimental windows (low duty cycle, short pulses) making again a potential industrial transfer difficult [15].

In this study, we report on the growth of superhydrophobic PTFE-like thin films using a one-step hybrid process which combines magnetron sputtering and PECVD processes. More precisely, an elemental carbon target is sputtered in Ar/CF_4 mixtures. Due to the low sputtering yield of carbon (~0.1 for 300 eV Ar^+ bombarding the target) [16], this technique can be considered as a PECVD process with a magnetron source generating the plasma. The role of sputtered carbon atoms on the deposition rate is negligible because of the low sputter yield of carbon compared to the deposition rate that could be achieved in PECVD. Nevertheless, the magnetron source likely enhances the plasma density and promotes a high reactivity of the reactive gas and, on the other side, allows for the bombardment by fast heavy particles generated at the target (i.e.; backscattered). As a drawback of the proposed approach, the poisoning of the target by the formation of an insulating PTFE target likely occurs and it was necessary to use a pulsed generator in order to avoid arcing.

2. Experimental setup

The experiments were performed in a commercial plasma chamber (TSD 400-CD HEF R&D). The target consists of 8 mm thick graphite rectangular plate (450×150 mm). The target to substrate (p-doped silicon wafer substrates) distance was fixed at 7 cm.

The vacuum system provides a base pressure of 5×10^{-5} Pa at a pumping speed of 1000 l/s. The gas purity was 99.999% for both Ar and CF_4. The gases were introduced via a gas pipe with holes drilled along the length and located along the target. The Ar and CF_4 flows are controlled by two independent mass flow meters. The working pressure in the chamber was not regulated; therefore, it ranges from 0.7 Pa to 1.2 Pa depending on the Ar/CF_4 ratio.

The Ar flow was kept constant (100 sccm) and the CF_4 one was varied between 0 and 66 sccm which corresponds to a flow ratio ranging between 0 and 40% in CF_4. The carbon target was sputtered by using a unipolar pulsed DC generator (Frequency: 250 kHz, pulse duration 1616 ns) and applying a constant sputtering power of 1 kW. The substrate holder was DC negatively polarized between −100 V and −200 V. The thickness of the deposited films ranges between 100 nm and 300 nm depending on the Ar/CF_4 ratio and V_{Bias}. These thicknesses correspond to deposition rates of 3.3 nm/min to 10 nm/min.

The stoichiometry of the deposited thin films was determined using a PHI versa probe 5000 X-ray Photon-electron Spectrometer (Al K_α radiation at 1486.6 eV, operating at 100 W). The analyzed area was 10×10 μm. A pass energy of 117.4 eV was used for the survey spectra and 23.50 eV for high resolution spectra, which corresponds to a full width at half maximum (FWHM) of the C1s peak (PTFE sample) of 1.4 eV. The atomic concentrations were determined by using Eq. (1):

$$N_A(\%) = \frac{\left(\frac{I_A}{S_A}\right)}{\left(\sum_n \frac{I_n}{S_n}\right)} \quad (1)$$

with N_A: the atomic concentration of the element A, I: the area of the XPS peak and S: the relative sensitivity factor. The C1s spectral envelope was fitted with the lowest number of physically meaningful components using a FWHM of 1.4 eV and a Gaussian–Lorentzian ratio of 70/30.

WCA measurements at room temperature using a Krüss DSA 100 machine were used to determine the wettability of the deposited film surface. For this purpose, water droplets were deposited with an automatic syringe on the sample surface. The WCA was automatically measured with the analysis software provided by Krüss and the Laplace–Young equation for the superhydrophobic samples or the tangent 1 method for the other samples was used to calculate the WCA value. The measurements were repeated 3 times at different areas of the sample and then averaged. Dynamic measurements were realized by increasing the volume of the drop from 2 μl to 15 μl at a rate of 30 $\mu l.min^{-1}$, giving the advancing angle. Then, the volume of the drop was decreased back to 2 μl at the same rate, giving the receding angle. WCA was measured every second during the advancing and receding processes.

All AFM images were recorded in ambient atmosphere at room temperature with a Nanoscope IIIa (Veeco, Santa Barbara, CA) microscope. The probes were commercially available silicon tips with spring constants of 24–52 $N.m^{-1}$, resonance frequencies varying in the 264–339 kHz range, and a typical radius of curvature in the 10–15 nm range. The images were recorded with the highest available sampling resolution (512×512 pixels). The AFM microscope was operated in tapping mode to minimize the sample damage due to mechanical interactions between the AFM tip and the surface of the samples.

3. Results and discussion

The effects of the composition of the gas mixture (%CF_4) and of V_{Bias} on the composition, the wettability and the morphology of the fluorinated thin films have been investigated.

Fig. 1 shows, as an example, typical XPS survey spectra of the deposited thin film (P_{DC} = 1 kW, V_{Bias} = −100 V, %CF_4 = 30%). As expected, not only the presence of carbon and fluorine was observed but also the presence of oxygen. The latter is attributed to the oxidation of the dangling bonds when the as-deposited films are exposed to the

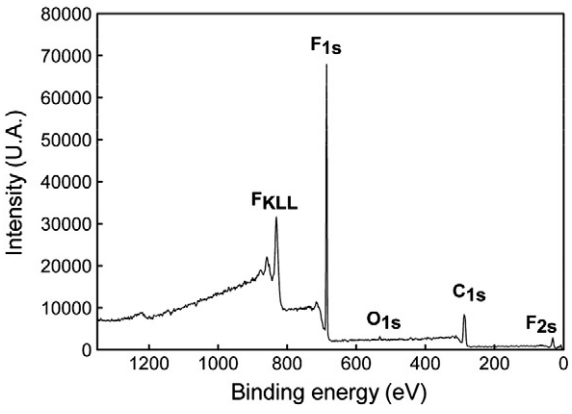

Fig. 1. Survey spectra of a PTFE like thin film (P_{DC} = 1 kW, V_{Bias} = −100 V, %CF_4 = 30%).