

Ultrathin carbon–fluorine film processing

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Available online 1 April 2005

Abstract

In conventional plasma polymerization processes, the bulk properties of the treated substrates are maintained whereas the surface properties are changed to the ones of the coating polymer. In contrast, materials with ultrathin non-closed layers and domains of plasma deposited compounds can show combined properties (from the surface of the bulk material and the non-closed layer) or even completely new behavior. This can be seen by analyzing e.g. the wettability (contact angle), the tribological properties, chemical functionalities or biological interactions.

Ultrathin closed and non-closed films (domains) of fluorocarbon polymer were produced by means of RF-CVD (radio frequency aided chemical vapor deposition, plasma polymerization) with CHF₃ as monomer gas; argon was added as additional process gas. Our work has been carried out in a symmetric capacitively coupled reactor at 13.56 MHz in the low-pressure, glow-discharge regime. The influence of pulsing the plasma by varying on- and off-times on the surface properties were investigated on silicon wafers as substrates. The obtained functionalized surfaces were characterized by means of advancing and receding contact angle measurements, X-ray photoelectron spectroscopy (XPS) as well as atomic force microscopy (AFM).

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PACS: 82.33.Xj; 82.35.Gh; 82.35.Lr; 33.60.Fy; 68.37.Ps; 68.03.Cd; 52.40.Hf

Keywords: Domains; Fluorocarbon; Thin film; Plasma polymerization

1. Introduction

The precise change of the surface elemental composition, the surface energy, and thus the wettability of surfaces are of great interest for biological, tribological, and other applications [1,2]. The tribological properties for example depend on the topography (roughness) of the surface, the elasticity, as well as on electrostatic surface interaction between the interacting parts. A promising approach for such surface modification is the plasma polymerization of fluorine containing monomers.

An ideally flat surface covered with regularly aligned and closely packed CF₃ groups shows an advancing water contact angle of about 120°. Such a covered surface has the

lowest polar surface energy among all the solid surfaces due to the small atomic radius and the large electronegativity of the fluorine [3–5]. Generally, the deposition of plasma polymer can be done in pulsed radio frequency discharges, resulting in different coatings which cannot be achieved by continuous wave deposition [6]. In the here presented process, CHF₃ was chosen as monomer and argon was added as carrier gas. The modifications achieved by this process varied from etched surfaces to films within the range of non-closed to closed coatings.

The characterization of these films was done by surface energy measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Surface energy and film properties were determined by measuring the advancing and receding contact angles on the substrates. From literature, it is known that chemical domains of 6 nm in lateral size already influence the contact angles [7]. The contribution of chemical inhomogeneities, e.g. domains, can be seen in the behavior of the

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hysteresis (difference in advancing and receding contact angle) for different liquids. A decrease in hysteresis is a sign for less chemical inhomogeneity [8].

XPS studies show the chemical composition of the plasma polymer. The layer thickness can be estimated by means of angle resolved XPS, but already the comparison of the silicon (or oxygen) and the carbon peaks in the spectra give information about the coverage.

AFM measurements allow the direct determination of the surface roughness and topography of the deposited polymer films.

2. Experiment

The substrates were coated in a symmetrical, capacitively coupled plasma reactor at 13.56 MHz radio frequency generated by a Dressler Cesar 1312 RF device. The generator was triggered externally by a pulse generator in a range from 5 to 200 ms on-/off-time. The matching to the reactor was done by a Dressler VM1500AW matchbox. Power was set to 8 W (peak) and matching capacitance settings were kept constant for all pulsed experiments. The pressure in the treatment chamber was 0.8 mbar and the gas flow was controlled by MKS flow controllers at 25 sccm Ar and 4 sccm CHF₃. The reactor was cleaned by O₂ and H₂ plasmas and preconditioned 3 min with the same plasma parameters as used for the following treatment to guarantee a chemical equilibrium in the reactor during the plasma coating. The treated substrates were silicon wafers (0.39 mm thickness) with an oxide layer of about 40 Å, sequently cleaned ultrasonically assisted in water, ethanol, and water. In one series, the pulse-on time was varied from 5 to 200 ms at a constant off-time of 200 ms, in another series the off-time was varied from 5 to 200 ms at a constant on-time of 5 ms. By doing so, the duty cycle was varied in two ways from 0.024 to 0.5. The treatment time in pulsed plasma was kept constant at 60 s; the coatings deposited by pulsed and continuous wave plasmas were compared by surface energy measurements, XPS and AFM.

For the determination of a sample's surface tension, 12 advancing and 12 receding contact angles of each bidistilled water, benzyl alcohol and 1-bromonaphtaline have been measured. The surface energy was determined according to the Owens–Wendt relation for surfaces with polar and disperse surface energy contributions [9] by inserting the mean values of each set of advancing and receding angles. The hysteresis (advancing minus receding angle) was calculated as well.

XPS spectra were acquired on a KRATOS Axis Ultra spectrometer using monochromatic Al K_α radiation (1486.6 eV). Charge neutralization was used for all samples and spectra were calibrated to the centre of the C–C/C–H peak at 284.6 eV.

AFM studies were performed on a NT-MDT Solver Pro instrument. Topography and phase images were taken in semi-contact mode.

3. Results and discussion

The surface tension of the on/off-time variation series is shown in Fig. 1a and b, respectively. To these graphs, the data points of a continuous wave (cw) plasma (duty cycle 1) with the following treatment parameters have been added: 1) 8 W, 60 s; 2) 8 W, 15 s; and 3) 2 W, 60 s. These three coatings exhibit the behavior of closed carbon–fluorine films concerning surface tension and hysteresis with water contact angles of 110°.

Starting from dc=0.07, the two variation series show a decrease in surface tension for both polar and disperse contributions, meanwhile this phenomenon is more pronounced for the polar part. The behavior at higher duty cycles is comparable for both series. At duty cycles lower than 0.2, differences can be observed, as can be seen in Fig. 2. The variation of pulse-off shows a local maximum at dc=0.07 in polar surface tension (water contact angle 40°) due to the domination of surface etching. This maximum is less pronounced in the pulse-on variation series. Starting from dc=0.07 to higher duty cycles, polymer deposition dominates the plasma process. The data points from dc=0.07 to 1 were fitted with an exponential function according to surface tension = $A * \exp(-dc/0.012 \pm 0.002) + c$, $c = 0.25 \pm 0.2 \text{ mN m}^{-1}$ for the polar and $c = 20 \pm 0.1 \text{ mN m}^{-1}$ for the total surface tension. This transition from etching to polymer depositing regime depends only on duty cycle whereas the strength of the etching process is clearly dominated by the pulse off-time, as can be seen in Fig. 2a, resulting in different constants A in the data fit curves.

The disperse contributions to surface tension, which are shown in Fig. 2b, show same behavior for both variations. Here, the onset of polymer deposition can be seen. The

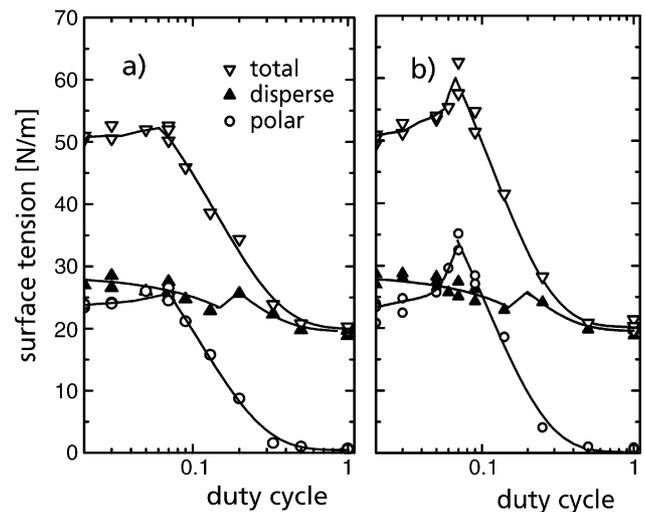


Fig. 1. Surface tensions: variation of a) t_{on} and b) t_{off} . Circles: polar surface tension; filled triangles: disperse surface tension; and unfilled triangles: total surface tension. Polar surface tension shows strong dependence on duty cycle in both series.

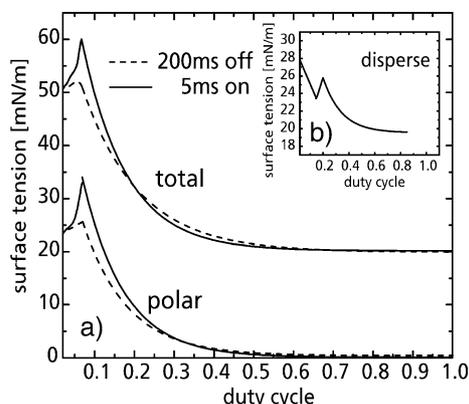


Fig. 2. a) Polar and total surface tensions differ depending on the variation parameter. b) Disperse surface tension shows same behavior in both cases.

effect of coating properties on hysteresis is shown in Fig. 3, where the chemical inhomogeneity caused by domains results in maximal hysteresis, especially for water contact angles.

XPS data reveals an increase in CF_x -groups with increasing duty cycle (Figs. 4 and 5). CF_3 -groups appear in the spectra at a binding energy of 292.6–293.5 eV whereas a small shift to the higher binding energies can be seen with increasing duty cycle (Fig. 4). This peak shift can be attributed to crosslinking or lengthening of $CF_3(-CF_2)_n$ groups according to Ref. [10]. The data indicates that even in the closed layer regime coatings are thinner than 5 nm as can be seen in the intensity of the Si2p and the O1s XPS signals. At the same time, a build-up of $CF_3(-CF_2)_n$ chains for duty cycles larger than 0.4 (almost closed films) can be seen. Angle resolved XPS data indicates an increase of CF_3 -groups at the uppermost surface layer.

The atomic force micrographs shown in Fig. 6 reveal changes due to etching and polymer deposition. The layer

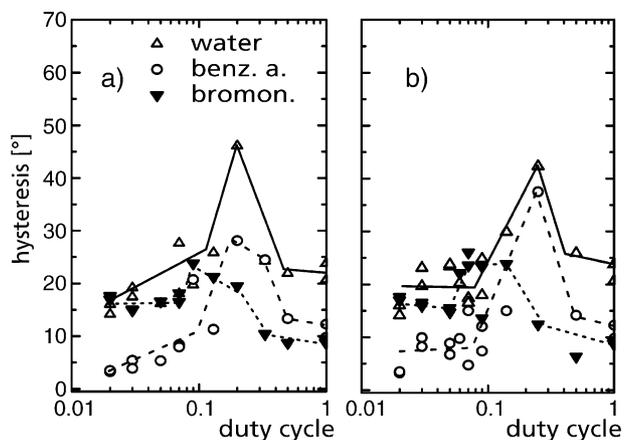


Fig. 3. Hysteresis plots of a) on-time variation and b) off-time variation. Around a duty cycle of 0.1, disperse 1-bromonaphtaline shows increase in hysteresis. Water and benzyl alcohol (polar contributions in surface tension) show a maximum around duty cycle of 0.2–0.3.

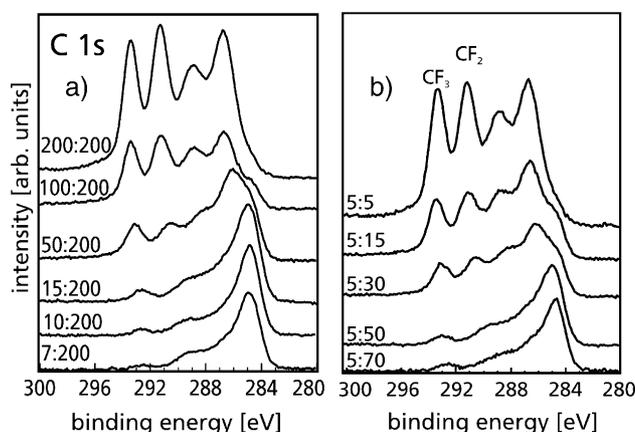


Fig. 4. C1s XPS spectra for on-time (a) and off-time variation (b). Presence of CF_3 can be seen even at low duty cycles. Around a duty cycle of 0.2, the complete structure of C– CF_x groups develops.

thickness is as low as 5 nm. At the same time, different roughness can be observed; maxima in surface tension hysteresis of polar liquids coincide with the surface roughness obtained from AFM measurements.

Concluding, the build-up of domains starting around a duty cycle of 0.1 is visible in the AFM micrographs as well as in surface energy and XPS data. With increasing duty cycle, a closed layer is finally obtained.

4. Conclusion

By varying the plasma on- and off-times, the surface properties of silicon have been changed at low duty cycles drastically from hydrophilic (high polar surface tensions) to hydrophobic at high duty cycles, namely polar surface tensions between 35 and 0.2 mN/m and advancing water contact angles between 40° and 110°. This effect is arising

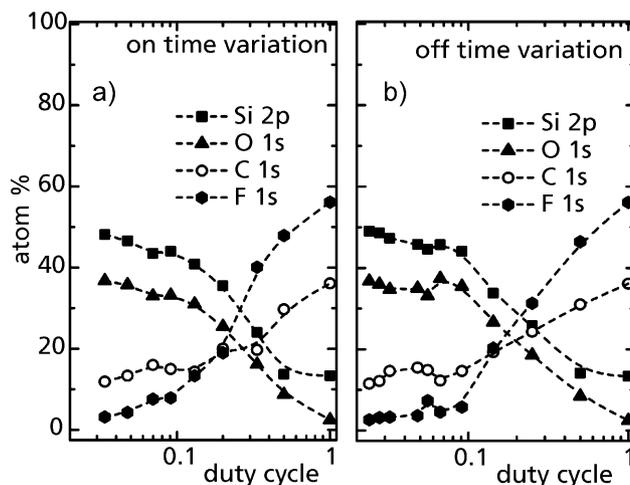


Fig. 5. Atomic concentrations of the deposited plasma polymer layers measured by XPS for on-time (a) and off-time variation (b) at different duty cycles. On axis: values of untreated wafer.

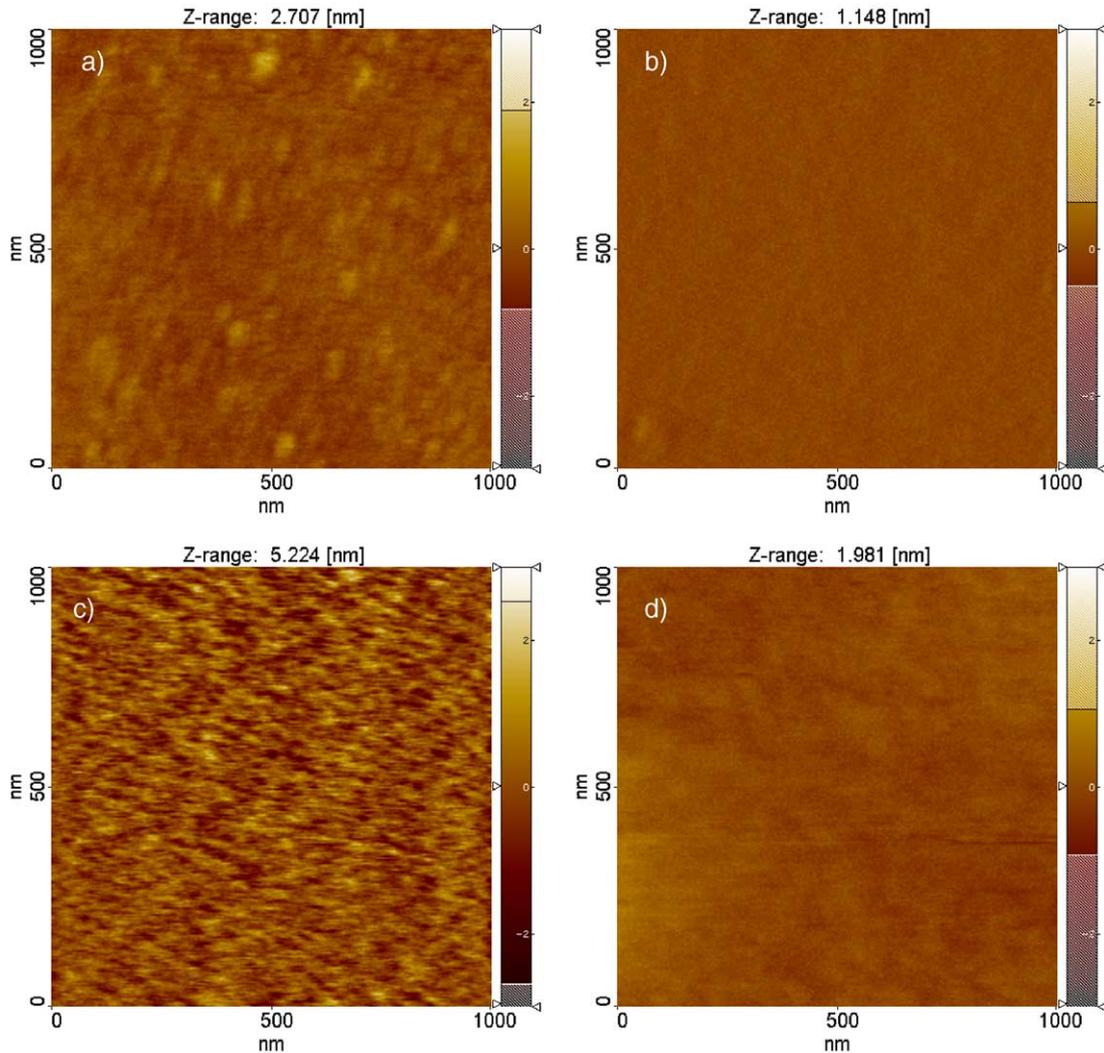


Fig. 6. Atomic force micrographs (topography, $1 \times 1 \mu\text{m}$) of a) untreated SiO_x , b) plasma etched SiO_x (at $\text{dc}=0.07$), c) non-closed plasma polymer layer, and d) closed plasma polymer layer. Notice the decrease in roughness by etching and the increase in roughness until the plasma polymer layer is closed.

from stepwise deposition of plasma polymer in form of domains on the surface until a closed layer is reached. The disperse surface tension changes from 28 to 20 mN/m. The polar surface tensions in the hydrophilic region have a maximum around a duty cycle of 0.07. The maximum is depending on the pulse-on time, most probable at a high amount of F species or a large Ar sputtering effect at this duty cycle. Increasing duty cycle increases the deposition of plasma polymer which can be seen by a slight increase in surface roughness (according to AFM), but even more in an increase in contact angle hysteresis which can be attributed to the chemical roughness effect of a non-closed layer. XPS data show increasing peak intensities of CF, C–CF, CF_2 and CF_3 . Duty cycles higher than 0.3 produce closed layers, which can be seen in the minimum in hysteresis. AFM still detects roughness in this regime, but roughness parameters are almost the same of an uncoated wafer (the ultrathin closed polymer layer shows mainly the topography of the

underlying substrate). As shown with all methods, the surface properties were changed by pulsing the plasma, resulting in polymer domains or closed polymer films.

Acknowledgements

This work was supported by the Federal Ministry for Education and Research BMBF, grant no. NMT/NKQN03138102.

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