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Plasma polymerization of tetrafluoroethylene – towards CF_2 dominated fluorocarbon films

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Abstract: Fluorocarbon films with an exceptionally high CF_2 content were obtained by plasma polymerization using a low pressure radio frequency discharge operated with a mixture of argon and tetrafluoroethylene. Substrates were placed in a remote position downstream the discharge. Gas pressure, discharge power, substrate position, gas composition and substrate temperature were changed to alter the chemical structure of the plasma polymers. The properties of the films were characterized by X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry and contact angle goniometry. A pronounced increase of the CF_2 content was obtained for elevated substrate temperatures and increased amounts of tetrafluoroethylene in the process gas. Applied as a model surface in studies of interfacial phenomena on polytetrafluoroethylene (PTFE), transparent PTFE-like thin films enable the use of numerous optical techniques not applicable to common PTFE foils.

Introduction

Plasma polymerization is a versatile technology for the preparation of functional coatings on solid surfaces [1-4]. Among the current trends in the field of plasma polymerization [5] there are processes that allow to retain a particular functional group [6-8], ring structures [9,10] or chain segments [11,12] of the precursor molecule. Strategies to reach this goal include the use of monomers with polymerizable double bonds and/or the use of exceptionally mild plasma conditions. In the latter case the energy flux can be reduced by means of a pulsed plasma excitation or a remote substrate position. The work presented here aims at the retention of a high percentage of CF_2 groups during the plasma polymerization of tetrafluoroethylene (TFE).

Among the precursor molecules used for plasma polymerization, fluorocarbons are an important class of materials. The properties of the obtained films comprise a low surface energy, a good optical transparency and a low dielectric constant supporting a wide range of demanding applications. However, the particular properties of a fluorocarbon film e.g. with respect to the wetting behaviour [13] or the protein adsorption [14] were found to substantially vary in dependence on the structure of the plasma polymer. This structure is characterized by the atomic composition, the relative abundance of CF, CF_2 and CF_3, the degree of cross-linking and the orientation of linear chain segments with respect to the surface.

The structure of plasma polymerized fluorocarbon films is addressed in many publications. Among those presenting XPS spectra, it become obvious, that the plasma polymerization often results in cross-linked structures with a high percentage of species other than CF_2 [15-19] which may be acceptable or even necessary for a particular application. Beyond that, there are some approaches to obtain a more defined fluorocarbon structure retaining parts of the precursor molecule. For the fabrication of CF_2 dominated fluorocarbon films, precursors like heptadeca-fluorodecene [12] or perfluorocyclohexane [20] were used. Another route to reach this goal is plasma polymerization of TFE.

Among the reports on TFE based plasma polymerization processes [21-30], there are promising results concerning the deposition of CF_2 dominated fluorocarbon films. PTFE-like structures were obtained with a low power continuous wave discharge and remote sample position [23,24], with a pulsed discharge and a sample position on the grounded electrode [25]. In both cases the apparatus was operated at room temperature.

Experimental part

Materials

Tetrafluoroethylene, obtained as a product sample from Dyneon (Burgkirchen, Germany), was used for plasma polymerization with Argon as a carrier gas (99.999 %, Messer Griesheim). Fluorocarbon films were deposited onto silicon wafers 5x5 mm^2 for XPS investigation and 10x20 mm^2 for ellipsometry and contact angle goniometry. Substrates were cleaned before deposition with ethanol in an ultrasonic bath. Chloroform (99.8%, Fluka) was used for stability tests.

Plasma polymerization

The plasma polymerization setup is shown schematically in Fig. 1. The vacuum system consists of a quartz tube with an inner diameter of 20 mm and a length of 300 mm on top of a cylindrical part with an inner diameter of 200 mm and a length of 800 mm connected to a rotary vane pump. The resulting base pressure is 1×10^{-3} mbar. Gases are introduced into the chamber by a gas flow control system. Pressure is measured by a capacitive vacuum gauge. The control unit is connected to a butterfly valve between the pump and the chamber and allows to set a particular pressure for a given gas flow. For plasma generation electrodes are attached to the quartz tube. The electrodes are connected to a 13.56 MHz radio frequency (RF) generator (Hüttinger PFG300RF) via an automatic matching network. This leads to an argon discharge operated in the small diameter tube with a TFE flow fed into the system close to the downstream end of the plasma excitation volume. The bottom part of the chamber houses a grounded substrate holder with a variable vertical position. The distance between the discharge and the substrate holder can be set from 10 cm to 60 cm. The substrate holder can be heated up to 200^{o} C.

For the investigations of this work a total gas flow of 100 standard cubic centimeter per minute (sccm) and deposition times from 300 s to 1200 s were used. The discharge power P, the pressure p, the C_2F_4 fraction in the process gas, the distance from the discharge to the substrate d and the temperature T were varied. Before every deposition experiment, the chamber was evacuated to the base pressure for 10 min and purged with argon for another 10 min.

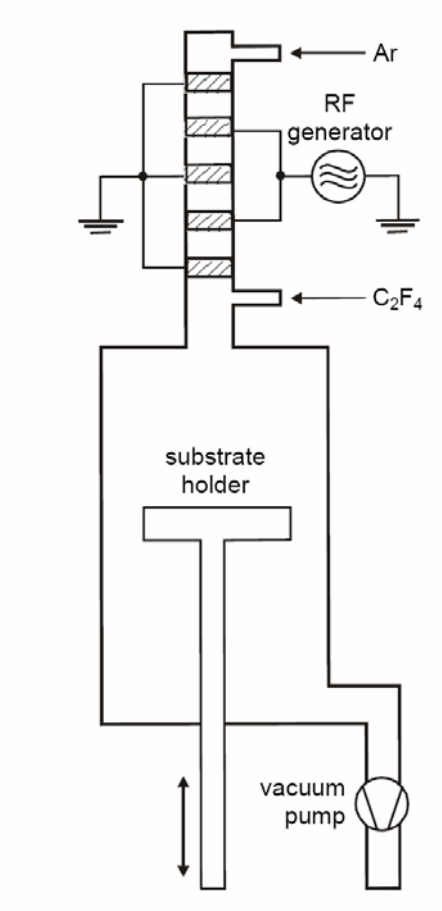

Fig. 1. Plasma polymerization setup.

X-ray photoelectron spectroscopy

XPS was carried out using an Amicus spectrometer (Kratos Analytical, UK) equipped with a non-monochromatic Mg K_α X-ray source operated at 300 W and 10 kV. The kinetic energy of the photoelectrons was determined using an analyzer with pass energy of 75 eV for survey spectra and high-resolution spectra. The take-off angle between sample's surface normal and the electron optical axis of the spectrometer was 0°. In this case, the information depth is about 8 nm. Spectra were referenced to the C_{1s} peak of $–CF_2–$ at 292.6 eV. A satellite subtraction procedure was applied. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function [31]. High-resolution spectra were deconvoluted by means of CasaXPS (Casa Software Ltd., UK). The sample transfer time from the plasma apparatus to the high vacuum of the XPS machine was about one hour.

Ellipsometry

Ellipsometric measurements were performed using a variable angle spectroscopic ellipsometer M-2000VI (J.A. Woollam Co., Inc.). It is a Diode Array Rotating Compensator Ellipsometer (DARCE™) in polarizer compensator sample analyzer configuration equipped with an automatic computer-controlled goniometer and a horizontally mounted sample stage. The light source is a 50-W mercury lamp. The angle of incidence was set to 65°, 70° and 75°. The M-2000VI measures 500 wavelengths simultaneously covering the spectral range from 370 – 1700 nm.

Accurate measurements over the full Δ and Ψ range were acquired (Δ= 0° - 360°; Ψ= 0° - 90°).

To obtain the thickness and the optical properties of the plasma polymer films, the ellipsometric data sets were used in a fit procedure based on an optical three layer model consisting of the bulk silicon layer, the silicon oxide layer, and the fluorocarbon layer. The deposition rate was determined for every set of process parameters by dividing the obtained thickness of the fluorocarbon film by the corresponding deposition time.

Contact angle goniometry

Dynamic water contact angles were measured with a G40 apparatus by Krüss, Germany, using the sessile drop method. For every sample the results obtained from five individual droplets were averaged.

Results and discussion

Gas pressure, discharge power, substrate position, gas composition and substrate temperature were changed systematically to unravel the impact of the varied parameter on the structure of the obtained plasma polymers.

Based on ellipsometric measurements, the refractive index and the film thickness of the plasma polymer films were determined. For all deposition parameters discussed below, the material was found to be transparent, i.e., no absorption occurs in the wavelength range investigated (k=0). The wavelength dependence of the refractive index was fitted using a two-parameter Cauchy equation $n(\lambda) = A_n + B_n / \lambda^2$ (n: refractive index, λ: wavelength, A_n, B_n: Cauchy parameters [32]). The best fit of ellipsometric data provided A_n =1.36...1.41 and $B_n \leq$ 0.003.

XPS survey spectra prove the absence of elements other than carbon and fluorine in the plasma polymer films (Fig. 2). To characterize the chemical structure of the obtained fluorocarbon films, high resolution C_{1s} spectra were recorded. It was found, that the spectra consist of five components corresponding to aliphatic carbon (285.0 eV), –<u>C</u>–CF– (288.3 eV), –<u>C</u>F– (290.4 eV), –<u>C</u>F_2– (292.6 eV) and –<u>C</u>F_3 (294.7 eV). These values are close to those obtained by other authors for similar fluorocarbon systems [30]. To evaluate the C_{1s} spectra of the fluorocarbon films obtained under different deposition parameters, a peak deconvolution procedure was applied. Five component peaks with a given shape (Gaussian-Lorentzian ratio 50:50) were set to the energy values mentioned above. The fit procedure was allowed to vary the component energies except 285 eV within a range of $\pm$0.3 eV, the component intensities and a common value for the full width is obtained at half maximum. From the result, the percentage of the –<u>C</u>F_2– signal with respect to the total carbon content was determined and used as a criterion for the process optimization. An example is shown in Figure 3.

The following figures show the –CF_2– content and the deposition rate of the obtained fluorocarbon films as a function of one particular process parameter. All other parameters were kept constant. The values are mentioned in the figure caption. Estimated error bars are +/-2% for the –CF_2– content and +/-0.5 nm/ min for the deposition rate. The experiments from Figure 4–7 have one parameter set in common (P=50 W, p=0.3 mbar, 5% C_2F_4, d=24 cm, T=20^o C), i.e., these graphs intersect at a single point in the multi-dimensional parameter field of the plasma polymerization process.

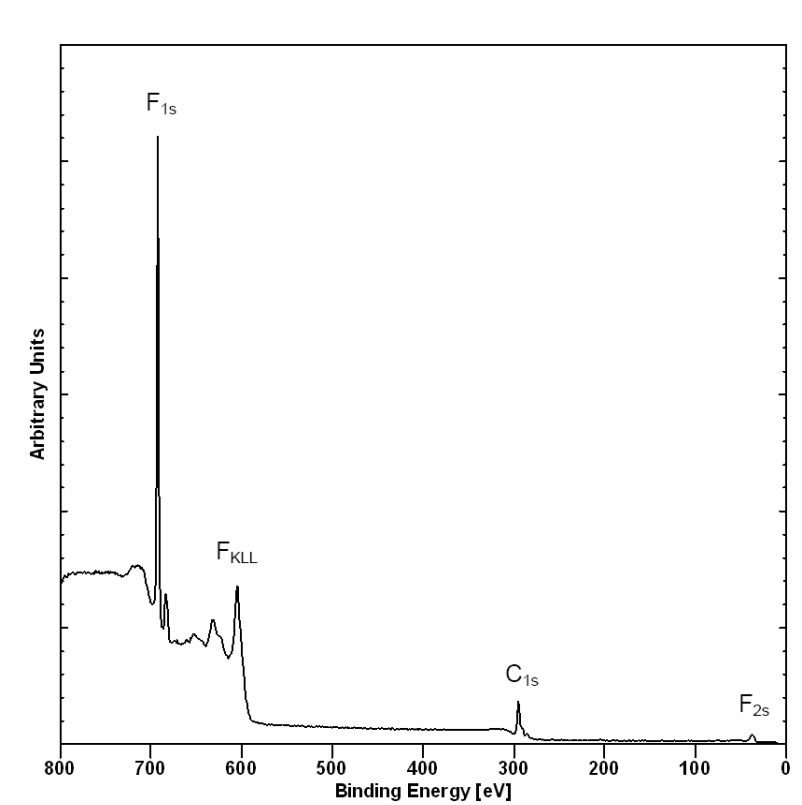

Fig. 2. Typical XPS survey spectrum obtained for the plasma polymer films.

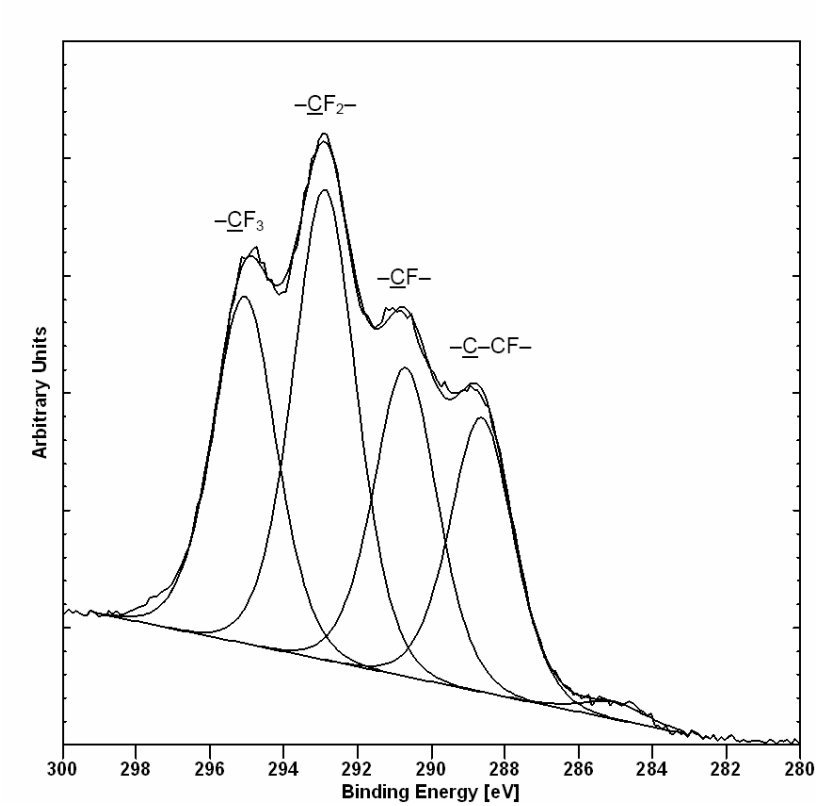

Fig. 3. XPS C_{1s} spectrum (P=50 W, p=0.3 mbar, 5% C_2F_4, d=24 cm, T=20^o C) with 33 % –$\underline{C}F_2$– as determined from the peak deconvolution.

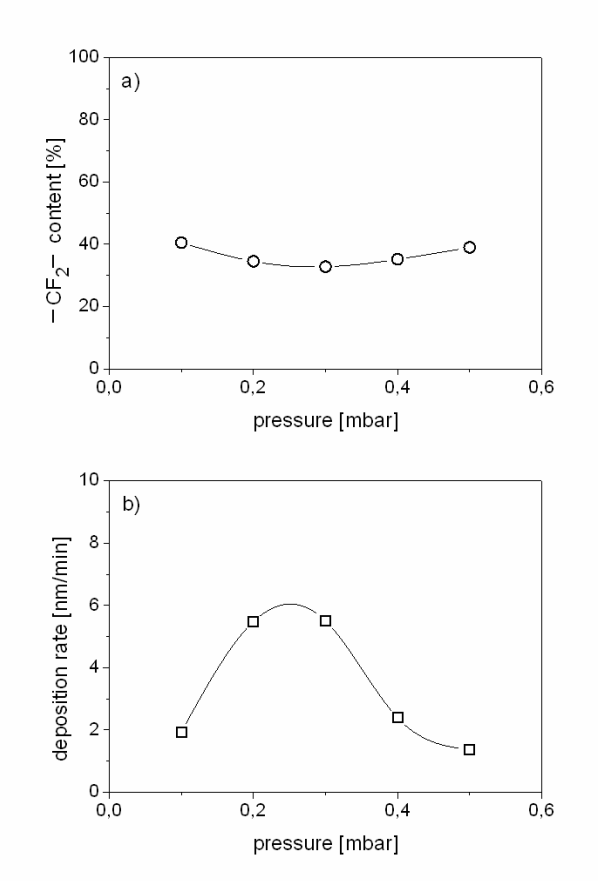

Fig. 4. –CF_2– content (a) and deposition rate (b) as a function of the total operating pressure of the discharge (P=50 W, 5% C_2F_4, d=24 cm, T=20° C).

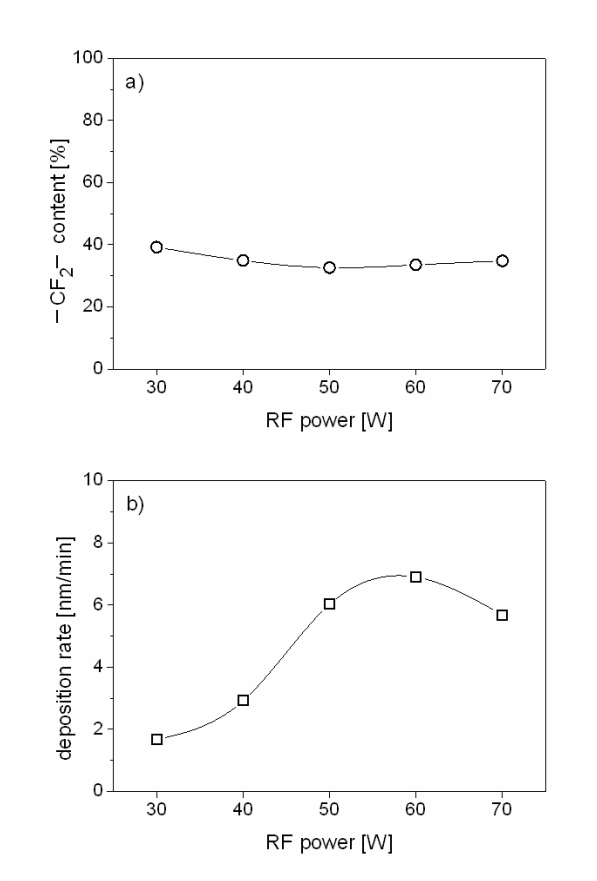

Fig. 5. –CF_2– content (a) and deposition rate (b) as a function of the discharge power (p=0.3 mbar, 5% C_2F_4, d=24 cm, T=20° C).

Figure 4 and 5 show the effect of pressure and power on the properties of the fluorocarbon films and the deposition process. While in both cases the –CF_2– content remains almost unchanged at about 40%, the deposition rate exhibits maxima at 0.25 mbar and 60 W respectively. This general behaviour of the deposition rate as a function of pressure and power agrees well with data given in the literature [3].

Figure 6 illustrates the effect of the sample position. For an increasing distance between the plasma excitation volume and the sample position, it is expected, that the variety of activated species contributing to the deposition process, the mean energy of the impinging particles as well as the intensity of ultraviolet radiation from the discharge decrease which possibly leads to major changes in the chemical structure of the plasma polymer film. However, this is not the case at least for the particular geometry of the plasma polymerization setup used in this work. The –CF_2– content remains almost unchanged when moving the sample away from the discharge while the deposition rate drops by an order of magnitude.

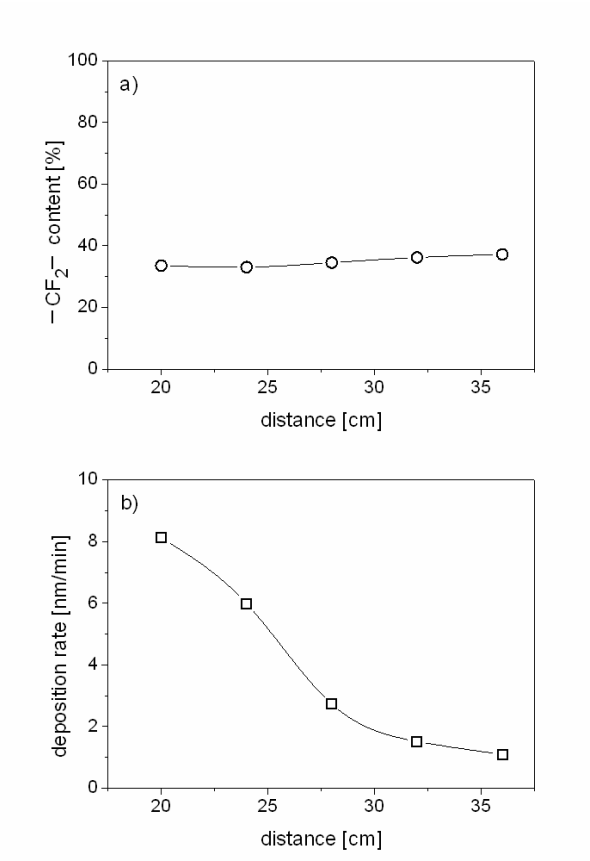

Fig. 6. –CF_2– content (a) and deposition rate (b) as a function of the distance between the plasma exitation volume and the substrate position (P=50 W, p=0.3 mbar, 5% C_2F_4, T=20° C).

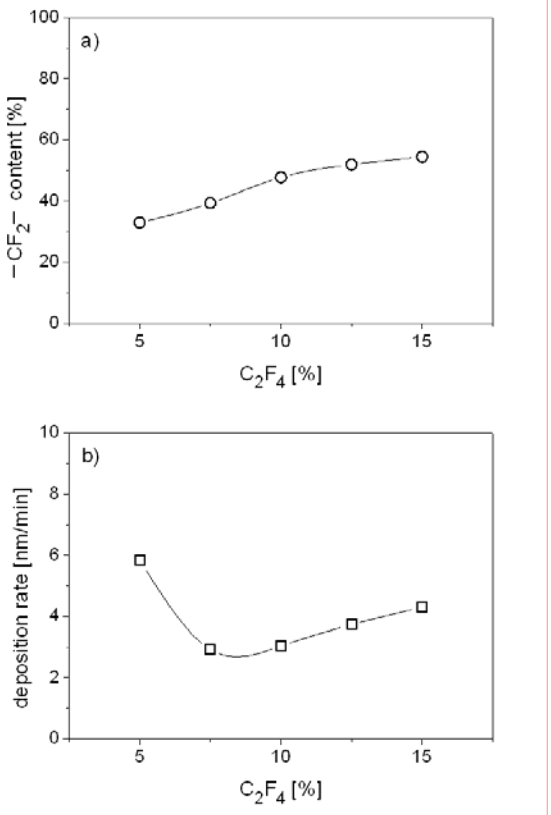

Fig. 7. –CF_2– content (a) and deposition rate (b) as a function of the C_2F_4 flow with respect to the total gas flow (P=50 W, p=0.3 mbar, d=24 cm, T=20° C).

A pronounced step towards the fabrication of –CF_2– dominated structures is observed for the gas composition. An increasing C_2F_4 fraction in the process gas significantly increases the –CF_2– content. A value of 54% was obtained for a C_2F_4 fraction of 15% (Fig. 7). Finally, the effect of elevated substrate temperature was investigated for the parameters represented by the rightmost data point in Figure 7. The temperature was increased up to 85°C. This leads to another pronounced increase in the –CF_2– content up to 66% (F/C ratio 1.86), while the deposition rate drops significantly (Fig. 8). The corresponding high resolution C_{1s} spectrum is shown in Figure 9.

Advancing and receding water contact angles of 120±1° and 92±1° respectively were determined for plasma polymer films deposited with the optimized parameters mentioned above. Furthermore, the stability against organic solvents was investigated. For that purpose samples with a known film thickness were rinsed in $CHCl_3$ for 20 min. No changes were found within the accuracy of ellipsometry.

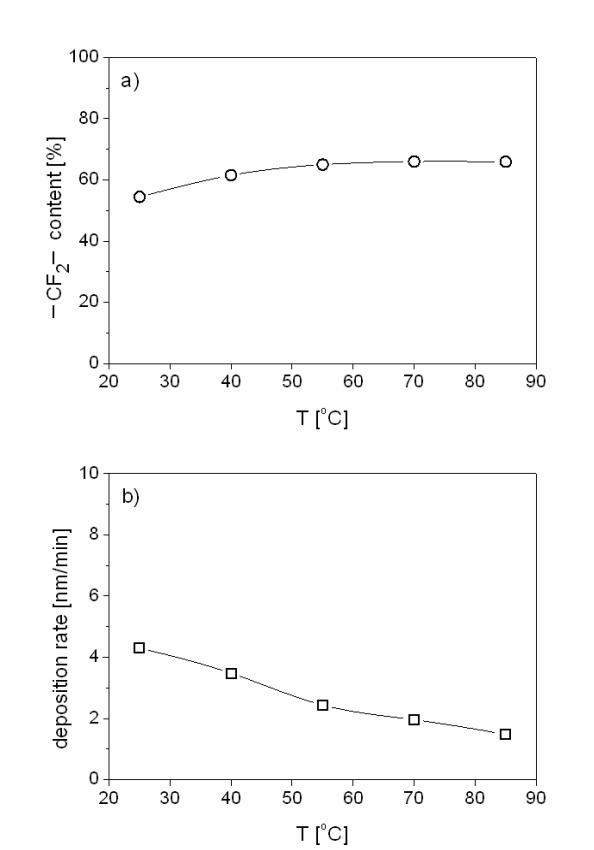

Fig. 8. –CF_2– content (a) and deposition rate (b) as a function of the substrate temperature (P=50 W, p=0.3 mbar, 15% C_2F_4, d=24 cm).

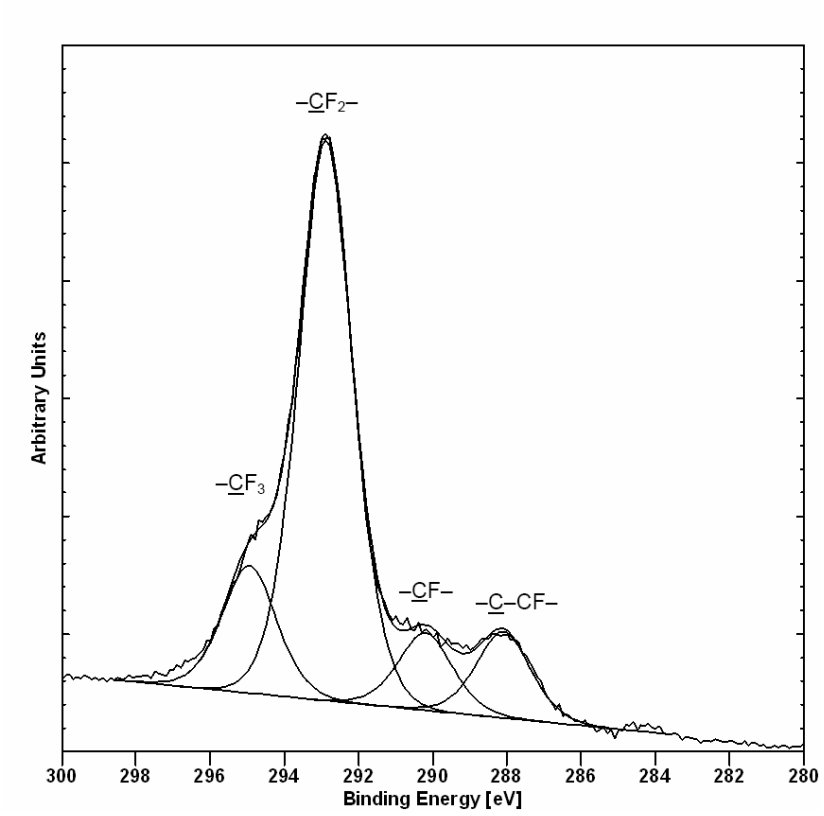

Fig. 9. XPS C_{1s} spectrum (P=50 W, p=0.3 mbar, 15% C_2F_4, d=24 cm, T=85^o C) with 66 % –$\underline{C}F_2$– as determined from the peak deconvolution.

Conclusions

Stable and optical transparent fluorocarbon films with an exceptionally high $–CF_2–$ content of up to 66% were obtained by continuous wave plasma polymerization using a mixture of argon and tetrafluoroethylene as process gas. For process optimization, a variation of gas pressure, discharge power, substrate position, gas composition and substrate temperature was investigated. Depending on the deposition parameters, only small variations were found for the refractive index. A pronounced increase of the $–CF_2–$ content and increased amounts of C_2F_4 in the process gas was obtained for elevated substrate temperatures while the other parameters caused minor changes of the chemical structure. The obtained films can be applied as model surfaces closely resembling PTFE. Transparent thin films prepared either on reflecting or on transparent substrates, allow the investigation of surface modification procedures and interfacial phenomena by numerous optical techniques not applicable to common PTFE foils.

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