

WETTABILITIES OF PLASMA DEPOSITED POLYMER FILMS

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We have investigated the wettability of hydrocarbon films deposited in capacitively coupled He, Ar/C₂H₂ rf discharges. Depending on the discharge pulse lengths we obtained hydrophobic films with contact angles either between 80° and 86° or between 100° and 140°. By treating the latter class of hydrophobic films in Ar or He discharges the film surfaces became hydrophilic with a contact angle not distinguishable from 0°. The investigated films were non-hygroscopic.

(Received February 12, 2005; accepted September 22, 2005)

Keywords: Polymer film, Wettability, Plasma deposition method

1. Introduction

During the last decades large efforts have been devoted to the search for better medical implants. For this purpose two main requirements must be considered: the compatibility of a solid to the biological environment and the suitability of its mechanical, electrical or other properties to the implant applications. Materials fulfilling both demands are rarely found, since the biocompatibility is mainly controlled by the surface characteristics of the solid, whereas the functional properties are largely determined by the bulk. Therefore, the trend for future medical implants is the development of implants made of a recognized and stable engineering material covered by a thin coating. Amorphous carbon films deposited on metals have been studied as possible candidates for biomedical applications mainly because of their chemical inertness and the presence of the constituting elements in the human body [1,2]. The properties of carbon films depend on the fraction of sp³ bonding and H content [3]. Different deposition methods have been developed to produce films extending from 100% sp² bonding to approximately 85% sp³ bonding [3]. Graphitic carbon films have a disordered graphitic structure presenting extremely low hardness and an optical gap close to zero. The so-called tetrahedral amorphous carbon (ta-C) is a semiconductor that may have a high mechanical hardness and a wide optical band gap. Hydrogenated carbon films with a high percentage of H and a high sp³ fraction - called 'polymeric-like a-CH' films - have a wide band-gap but the hardness is as much as 8 times lower than in the ta-C. Up to now mainly work on the biocompatibility of a-CH, ta-C films and carbon nitride (CN) films has been reported. Biological tests of a-CH films demonstrate its good bio-tolerance, its efficiency against corrosion and metalosis in the biological fluids [4,5]. The material is not cytotoxic [6], it is suitable for blood interface applications since it inhibits thrombus formation [7], and in the oral cavity it shows a good bio-integration [8]. Previous studies have shown that the biocompatibility is related to the interfacial tensions, which correlate to the wettability of surfaces [9,10]. The wettability of a-CH films deposited in rf discharges containing hydrocarbons can be controlled by the plasma parameters.

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Thin films deposited in rf discharges containing hydrocarbons were recently also used as protecting layers on tools. Large wetting angles ($>90^\circ$) are indicative of a desired weak interaction between the liquid and the film. Small wetting angles ($<30^\circ$) (strong adhesion) due to chemical interaction occurring at the interface (film dissolution, discontinuity) may result in film failure and loss of its protective properties.

The aim of our work is a parametric study of the contact angles of water on a-CH films deposited in Ar,He/C₂H₂ rf discharges and their variation with the change of the discharge conditions. Besides the wettability the hygroscopic property of hydrocarbon films is also important and therefore further investigated.

2. Experiment

Hydrocarbon films have been deposited in pulsed 13.56 MHz plane-parallel capacitively coupled rf discharges in Ar,He/C₂H₂ mixtures. The discharge chamber used is a horizontally mounted Duran-glass cylinder closed by two aluminum plates with showerheads serving as electrodes. One electrode is capacitively coupled to an rf generator, the second one is grounded - see Fig. 1. The inner diameter of the Duran cylinder is 80 mm and the distance between the electrodes is 190 mm. The gas mixture is admitted through the rf-powered electrode and pumped out with a rotary pump through the grounded electrode. The minimum pressure prior to the deposition has been approximately 10^{-2} mbar. The flow rate of Ar is set to 10 sccm, that of He to 15 sccm. The flow of C₂H₂ varies in the range 0.2-0.7 sccm. The total pressure during the discharge amounted to 0.35 mbar. The pulse lengths are in the 50-200 ms range, the rf power is 20 W. The pulse repeat frequency is 0.5 Hz to completely exchange the source gas between two successive discharge pulses. The thin films are deposited on the silicon holders placed in the central part of the discharge. Prior to every deposition we sputter-cleaned the substrates for 15 min in a cw oxygen discharge of 20 W and after that in a cw argon discharge for 5-10 min.

Using infrared absorption spectroscopy (FTIR spectrometer type Bruker 55) we identified the functional groups in the deposited films. The thickness of the films and their refractive index in the visible range we determined via ellipsometry. The wettability of the deposited hydrocarbon films we characterized by measuring the contact angle of water drops using a DSA 10 MK2 drop shape analysis system (Krüss). Additionally we determined the advancing and receding contact angles by the dynamic Wilhelmy technique. The surface roughness of the films we studied with an atomic force microscope (AFM) type Autoprobe cp (Parker Scientific Instruments). The structure of the film surfaces as well as the film cross-sections we studied further with a scanning electron microscope.

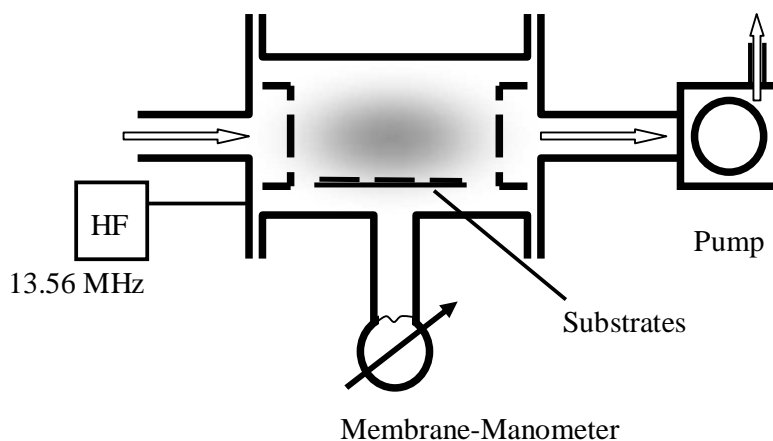


Fig. 1. Discharge chamber.

3. Results

As stated in the introduction an important characteristic of films is their hygroscopic property. The water absorbing ability of films we investigated by means of infrared absorption spectroscopy. We exposed the films to water after measuring their infrared spectra and after that we measured their spectra again. In the infrared spectra the OH groups of water in the film usually show a broad absorption band around 3300 cm^{-1} . Comparing the spectra measured before and after water exposure we observe no increase of the OH absorption, as shows Fig. 2. From this observation we conclude that our films are non-hygroscopic. However, the transparency increased after water exposure. The reasons for this increase are not clear to us.

The functional groups present in the films determine their properties. The IR absorption spectra of films show an absorption band in the $2800\text{ cm}^{-1} - 3100\text{ cm}^{-1}$ spectral range (see Fig. 2), characteristic for C-H stretching vibrations. We fitted a spectrum calculated using an optical model of the samples [11] to the measured IR spectrum of a typical film deposited at 50 ms pulse length in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture and calculated with the fitting procedure the complex refractive index of the film. Fig. 3 shows the imaginary part of the refractive index for an a-CH film of 180 nm thicknesses. The real part of the refractive index amounts to 1.6. The error of the method is within 1%.

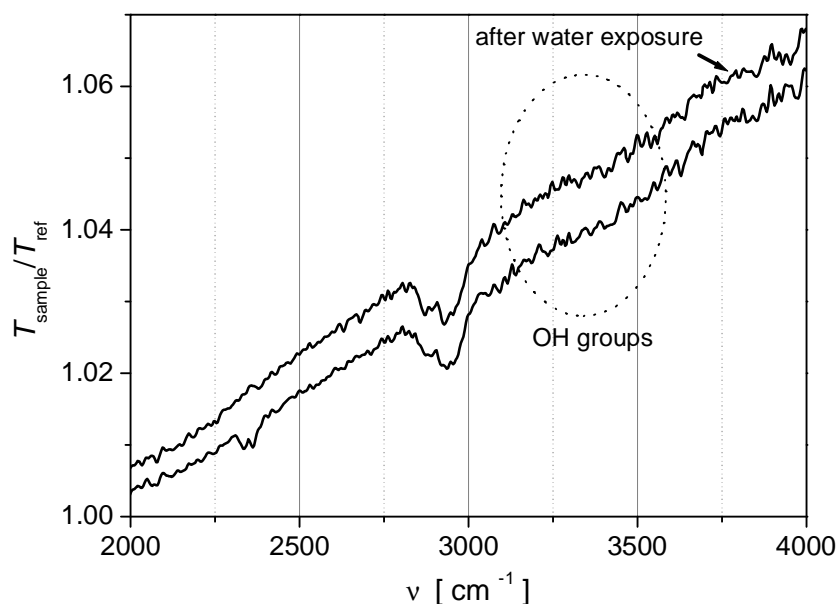


Fig. 2. The infrared absorption spectra measured before and after water exposure. The film has been deposited in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture with 200 ms pulse length.

On the absorption curve the absorption peaks of CH_3 , CH_2 and CH groups can be identified. The absorption of sp^2 groups is visible in the spectral range above 3000 cm^{-1} and the absorption of sp^3 groups in the spectral range below 3000 cm^{-1} . Below 3000 cm^{-1} three obvious absorption peaks can be observed, which are due to the hydrogen in CH_3 (asymmetric, 2960 cm^{-1}), both CH_2 (asymmetric 2930 cm^{-1}) and CH (2915 cm^{-1}), and CH_3 (symmetric, 2875 cm^{-1}), respectively, all bounded to sp^3 -type carbon [12].

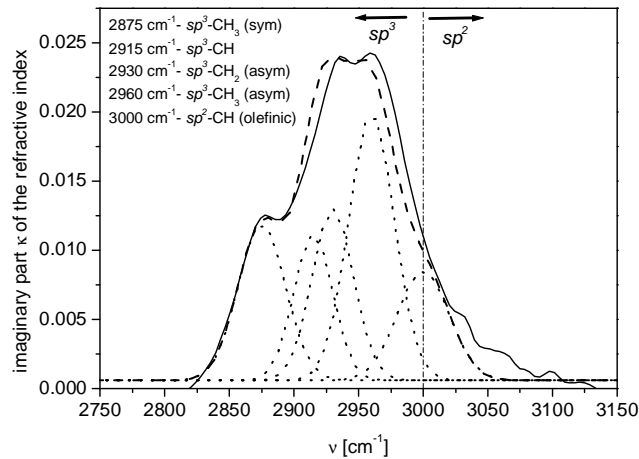


Fig. 3. The imaginary part of the refractive index associated with the C-H stretch absorption bands. The film has been deposited in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture with 50 ms pulse length.

The distinct peaks in Fig. 3 are characteristic for polymer-like a-CH films, the skeleton is less crosslinked than in the case of hard films and consequently the hardness and the strain are reduced [13]. The deconvolution of the absorption band shows that the sp^3 carbon bonds dominate, however also the presence of sp^2 bonds can be observed at 3000 cm^{-1} . It is well known that hydrogen incorporation in carbon films favors sp^3 bonding by etching sp^2 species [14]. The high dominance of sp^3 bonding suggests that the films contain much hydrogen.

The thickness of the films and their refractive index in the visible range we determined via ellipsometry. Films deposited for 90 min at 50 ms pulse length in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture are around 170 nm thick. Films deposited with the same gas mixture but at 200 ms pulse length for 20 min are too rough for their thickness to be accurately determined by ellipsometry. Figure 4 represents a typical result for films deposited at 50 ms pulse length. The figure shows that in the visible range the refractive index n of the polymer-like films is around 1.7 and decreases slightly with increasing wavelength. This value of the refractive index of polymer-like films is much lower than that of hard amorphous hydrogenated carbon films, which in the visible range varies from 1.9 to 2.3 [15]. In the 300-700 nm range the extinction coefficient κ decays exponentially from 0.12 to 0 – see fit in Fig. 4.

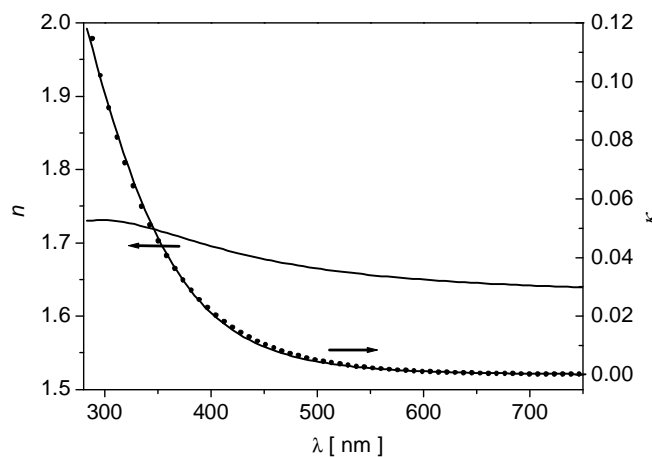


Fig. 4. The real part (n) and the imaginary part (κ) of the complex refractive index in the visible range. The dotted curve is a fit of a decreasing exponential function. The film has been deposited in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture with 50 ms pulse length.

For most applications films should adhere firmly to the underground. This property can be tested by water contact. If the films have pinholes the water can penetrate through the pinholes and creep between the substrate and the film causing detachment. Pinhole-free films can be achieved by treating the surface of films deposited in Ar+C₂H₂ or He+C₂H₂ mixture by an argon or helium discharge, at least for a few seconds.

Films with different contact angles can be deposited when using rf discharges with different pulse lengths. Films deposited in Ar/C₂H₂ and He/C₂H₂ discharges with 50 ms pulse length are only slightly hydrophobic (80°- 87° contact angle). At longer pulse lengths the deposited films become either hydrophobic (100°-140° contact angle) at high C₂H₂ flow rate or hydrophilic at low flow rate of C₂H₂ (<0.3 sccm), see Table 1. The hydrophobic films can be converted to hydrophilic ones by treating them in Ar or He discharges for at least 3-10 s. By this treatment, films with a contact angle of 0° can be achieved. Further, treating the 80°-87° contact angle films in Ar or He discharges, they become hydrophilic, however never reach the 0° contact angle (see Table 1). This fact could be correlated with the surface roughness of the films. It is well known that the hydrophobicity of surfaces is strongly affected not only by the chemical composition but also by their roughness [16-18]. According to Wenzel's equation [16] ($\cos \theta^* = r \cos \theta$, where θ^* is the contact angle for rough surfaces, r is the surface roughness) the surface roughness improves either hydrophilicity ($\theta^* < \theta$ for $\theta < \pi/2$) or hydrophobicity ($\theta^* > \theta$ for $\theta > \pi/2$). The hydrophilic films deposited at 50 ms pulse length are smooth films, r being in the range of 1-1.3. The hydrophobic films deposited with longer pulse length are rougher, with r in the 2.4-2.7 range. When treating the latter films in Ar or He discharges, the surface roughness changes slightly, but the value of r still remains above 2.

Table 1. The measured contact angle and surface roughness of hydrocarbon films deposited at 50 ms and 200 ms pulse lengths in Ar/C₂H₂ gas mixture, using 10 sccm Ar flow.

C ₂ H ₂ flow [sccm]	$\tau = 50$ ms		$\tau = 200$ ms	
	θ [degrees]	r	θ [degrees]	r
0.22	24	1.3	56	1.7
0.6	87	1.3	141	2.7
0.76	82	1.02	143	2.4
After 3 min Ar discharge treatment				
0.6	14	1.3	0	3
0.76	20	1	0	2.4

The influence of the surface roughness as well as the chemical composition on the contact angle is demonstrated in Fig. 5. In pulsed rf discharges the pulse length influences the plasma chemistry [19]. Within the first hundreds of milliseconds after ignition the concentration of C₂H₂ decreases strongly as a result of effective polymerization. Simultaneously increases the density of hydrogen atoms due to H-abstraction. Acetylene molecules are the main quencher of excited rare gas atoms and ions. Therefore, the lifetimes and the densities of excited rare gas atoms and ions increase with increasing pulse duration. With long pulses the surfaces of the deposited films are exposed to a counteraction of fluxes of hydrogen and excited rare gas atoms and ions. The first causing an increase of the hydrophobic character of the surface, the latter an increase of the hydrophilic character. The contact angle shows an increase with increasing surface roughness. If there is no dependence of plasma chemistry on the discharge pulse length the contact angle should decrease with increasing surface roughness, as the smooth surface has a contact angle of 76°, that is below 90°. (The limit between hydrophilic and hydrophobic character is given by the so-called Berg-limit at a contact angle of 65° [10].)

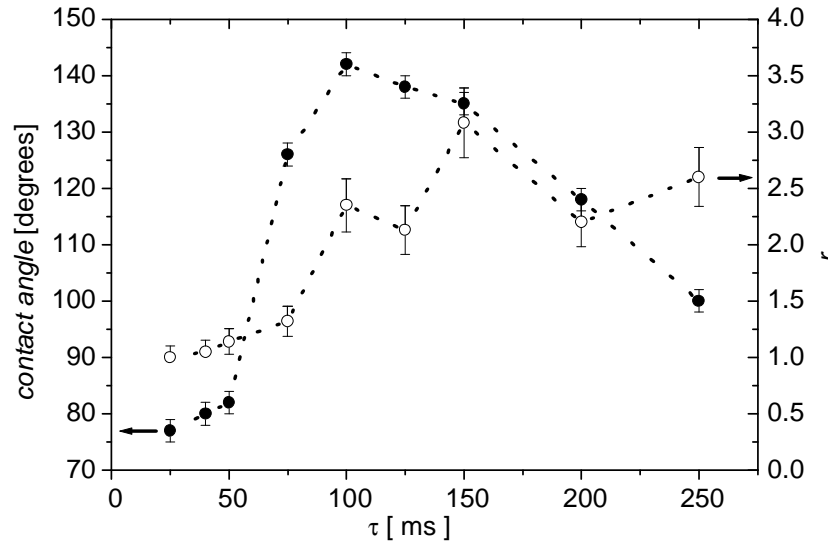


Fig. 5. The measured contact angle (full dots) and surface roughness (open dots) as a function of pulse length. Gas flow: 10 sccm Ar and 0.6 sccm C_2H_2 .

The surface roughness of films has been determined by AFM measurements. In order to make sure that the AFM measured no artifacts the surfaces of the thin films were also scanned by a Scanning Electron Microscope.

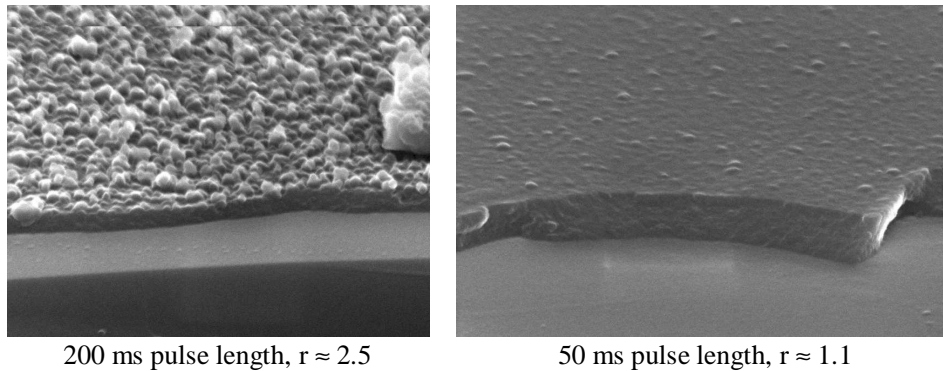


Fig. 6. Scanning Electron Microscope pictures of films. The scale is $1:10^{-7}$ cm. The films have been deposited in 10 sccm Ar + 0.6 sccm C_2H_2 gas mixture.

For many applications not the static contact angle but the dynamic advancing and receding contact angles are important. We, therefore, determined also the dynamic contact angles of numerous films by the dynamic Wilhelmy technique and at the same time checked the changes of the contact angles of thin films by aging. The dynamic contact angles have been determined by measuring the changes of forces, which are present when the solid is brought in contact with water. The advancing contact angle is obtained from data generated as the sample dips into the water, the receding contact angle as the sample retreats from the liquid. A typical force measurement is shown on Fig. 7.

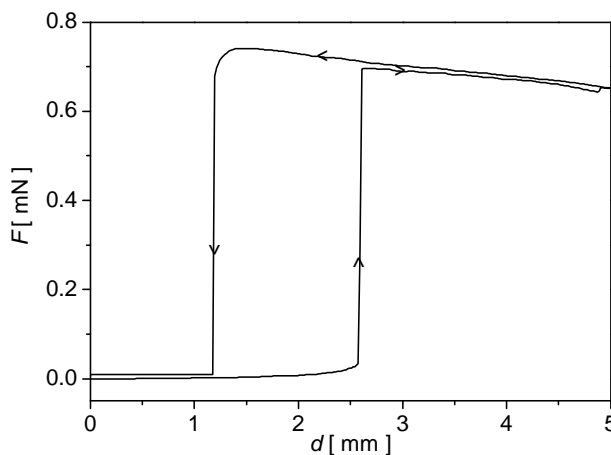


Fig. 7. The force acting on the sample dipped in the water measured with the tensiometer.

The force difference at the position of the up-jump of the force, when the sample first dips into the water (arrow), is a measure of the difference between the advancing and receding angles. For all the investigated films we found no difference between the advancing and receding contact angles. The very small hysteresis visible on Fig. 7 is mainly due to the shift of the zero line caused by the weight of the waterfilm. The dynamic angles also equaled the static contact angles. For hydrophilic films with about 6° contact angle we found that within two weeks storage on air the 6° contact angle can increase up to 20° .

4. Summary

Hydrocarbon films have been deposited in pulsed 13.56 MHz plane-parallel capacitively coupled rf discharges in Ar, He/C₂H₂ mixtures. We have investigated the most important properties – from application point of view – the wettability and the hygroscopic property of films.

The IR absorption spectra of films have shown that in the films the *sp*³ carbon bonds dominate, which suggests that the films contain much hydrogen. From the non-crosslinked skeleton of the C-H stretch absorption band we have concluded that the deposited films are polymer-like a-CH films. The missing of the absorption bands of OH groups from the IR absorption spectra of films measured after their exposure to water has shown that the films do not absorb water, are non-hygroscopic. By treating the deposited films in argon or helium discharges for a few seconds we have achieved pinhole-free films.

Using 50 ms pulse length we have deposited slightly hydrophobic films (80° - 87° contact angle), by using 200 ms pulse length hydrophobic films (100° - 140° contact angle) have been deposited. The treatment of hydrophobic films in argon or helium discharges for 3-10 s resulted in hydrophilic films with 0° contact angle. The same treatment of the slightly hydrophobic films resulted also in hydrophilic films (e.g. change from 80° to 14° contact angle), but never reached a contact angle of 0° . This effect is in correlation with the surface roughness, which besides the chemical composition of films strongly influence the wettability of films. The dynamic contact angle measurements have shown that the dynamic contact angles equal the static ones and with two weeks of storage on air the 6° contact angle can increase up to 20° .

Acknowledgements

This work was financed by a grant of the state Ministry for Science and Research NRW, Düsseldorf, within the project "Plasma gestützte Oberflächenmodifikation von Medizin- und Bio-

technischer Bedeutung – TP4”. We thank Prof. Dr. Herbert P. Jenissen, Institut für Physiologische Chemie, Universitätsklinikum Essen for enabling us to measure contact angles with his Wilhelmy type tensiometer.

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