SURFACE MORPHOLOGY OF AMORPHOUS HYDROCARBON THIN FILMS DEPOSITED IN PULSED RADIOFREQUENCY DISCHARGE

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Introduction

Amorphous hydrocarbon thin films are still very attractive materials for many scientists. They are used in wide range of applications like optical devices, integrated digital circuits, micro-electromechanical devices, biomedical coatings, etc. One of common techniques of preparation of such films is the plasma enhanced chemical vapor deposition[1] (PECVD). The properties of resulted thin films are strongly dependent on deposition parameters. Usually, continuous mode of operation is used in the deposition process, but running the deposition in pulsed mode offers another possibility to vary the material properties[2]. One of the aspects of deposited thin film is the surface morphology, which can play a crucial role in industrial applications of the films. The aim of this work is therefore the investigation of surface parameters like roughness and autocorrelation length of films deposited in pulsed discharge.

Experimental details

Thin films were deposited in pulsed radiofrequency discharge by PECVD technique. The reactor consisted of a horizontally mounted SIMAX glass tube and was closed by two aluminum electrodes. Distance of the electrodes was 186 mm and inner diameter of the tube was 77 mm. Scheme of the apparatus can be found in Fig. 1. Power was delivered via matching unit from Dressler CESAR™ 133 generator operating at 13.56 MHz. Duty cycle and frequency of the cycles were set to 10 % and 1 Hz, respectively. Delivered power during the on-time was 10 W (generator was off during the off-time). Films were deposited in argon-acetylene (C_2H_2) gas mixture. Gases were led into the reactor through drilled powered electrode. Gas flows were controlled by Hastings flowmeters. Flowrate of Ar and C_2H_2 gas was 4 sccm and 1 sccm, respectively. The reactor was pumped through drilled grounded electrode with a rotary pump. Total pressure was measured using Leybold CERAVAC diaphragm gauge. Minimum pressure reached in the apparatus was in the range 1.5–1.8 Pa. Total pressure in the apparatus was in the range from 38.8 Pa to 39.8 Pa (measured immediately before deposition started). Substrates were made from silicon single crystal wafer and had a rectangular shape with dimensions 10 × 15 mm. Silicon substrates were located on a glass holder in the middle of the reactor (see Fig. 1). Prior to every deposition a cleaning of substrate surface in Ar in continuous mode was performed. During this procedure, the delivered power was 5 W and the discharge runned for 5 minutes.

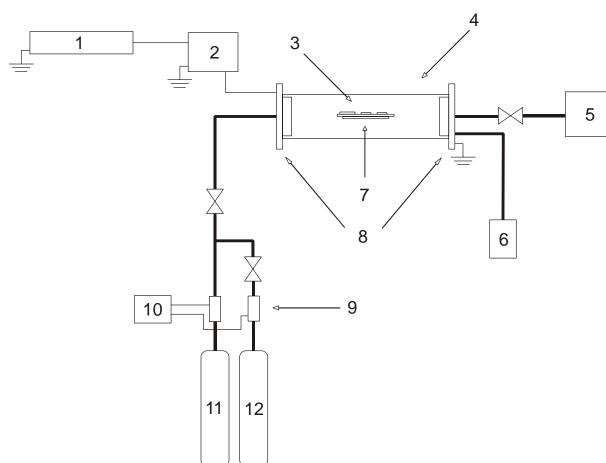

Fig. 1. **Schematic view of the apparatus.** 1 – power source, 2 – matching unit, 3 – samples, 4 – SIMAX glass tube, 5 – rotary pump, 6 – pressure gauge, 7 – glass sample holders, 8 – Al electrodes, 9 – flowmeters, 10 – control unit, 11 – Ar cylinder, 12 – acetylene cylinder

Surface properties were evaluated on a series of samples where total deposition time (also the off-time of the period is counted in) was varied while the rest of the deposition parameters remained fixed at values already mentioned. The total deposition time was changed from 5 to 35 minutes with step of 5 minutes. Thus, the change of surface morphology of thin films with total deposition time was studied.

Film morphology was examined using Topometrix Accurex IIL atomic force microscope (AFM) with silicon nitride contact probes. Scan size was 20 × 20 μm and the resolution in both axes was 500 points. Data were analyzed with open-source program Gwyddion[3]. Scans were taken in the center of the sample as well as in the 3 mm distance from the shorter edge of the sample.

Surface characterization

We will assume that the film surface is randomly (statistically) rough and that the roughness is homogeneous. Furthermore, we will assume that the surface height in a given point x,y can be described by a random function $\zeta(x,y)$ that has given statistical properties.

The heights of surface irregularities are characterized by the root mean square (RMS) value (standard deviation) σ defined as follows:

$$\sigma^2 = \int_{-\infty}^{\infty} (z - \bar{z})^2 w(z) \mathrm{d}z, \tag{1}$$

where $z, \bar{z}$ and $w(z)$ denote a certain value, mean value and one-dimensional distribution of the probability density of the random function $\zeta(x,y)$, respectively (x and y are the Cartesian coordinates in the mean plane of the rough surface. The quantity σ is called the RMS value of the heights.

Another significant statistical quantity is the autocorrelation function G defined by this relation:

$$G(\tau_x, \tau_y) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} z_1 z_2 w(z_1, z_2, \tau_x, \tau_y) dz_1 dz_2, \quad (2)$$

where symbols z_1 and/or z_2 and $w(z_1,z_2,\tau_x,\tau_y)$ denote certain value of $\zeta(x,y)$ in the point $[x_1,y_1]$ and/or the point $[x_2,y_2]$ and the two-dimensional distribution of probability density of $\zeta(x,y)$, respectively. The symbols τ_x and τ_y are given as follows: $\tau_x = x_2 - x_1$ and $\tau_y = y_2 - y_1$.

In practice, however, the autocorrelation function is not widely used. Instead of it the power spectral density function (PSDF) is often calculated from the AFM scans. The two-dimensional PSDF, $W_2(K_x,K_y)$, can be written in terms of Fourier transform of the autocorrelation function

$$W_2(K_x, K_y) = \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(\tau_x, \tau_y) e^{-i(K_x\tau_x + K_y\tau_y)} d\tau_x d\tau_y, \quad (3)$$

where K_x and K_y denote x- and y-component of the wave vector of harmonic component of the certain spatial frequency of roughness. Within the AFM measurements we usually evaluate the one-dimensional PSDF determined only from profiles in the fast scanning axis because these are less affected by the low frequency noise and thermal drift of the sample. This function is defined in the following way

$$W(K_x) = \int_{-\infty}^{\infty} W_2(K_x, K_y) dK_y. \quad (4)$$

The one-dimensional autocorrelation function is often supposed as being Gaussian, i.e. given by the following relation

$$G(\tau_x) = \sigma^2 e^{-\tau_x^2/T^2}. \quad (5)$$

This results in one-dimensional PSDF given by relation

$$W(K_x) = \frac{\sigma^2 T}{2\sqrt{(\pi)}} e^{-K_x^2 T^2/4}, \quad (6)$$

where T is the autocorrelation length and characterizes lateral dimension of the irregularities of the randomly rough surface in its mean plane.

The AFM data are usually represented as a two-dimensional data field of size $N \times M$, where N and/or M represents the number of rows and/or columns within the datafield. Hence, the one-dimensional PSDF can be evaluated by means of the Fast Fourier transform as follows:

$$W(K_x) = \frac{2\pi}{NMh}\sum_{j=0}^{M}\left|\hat{P}_j(K_x)\right|^2, \quad (7)$$

where h is the distance between two adjacent datapoints and $\hat{P}_j(K_x)$ is the Fourier coefficient of the j-th row, i.e.

$$\hat{P}_j(K_x) = \frac{h}{2\pi}\sum_{k=0}^{N} z_{kj} e^{-iK_x kh}. \quad (8)$$

For more details about statistical description of rough surfaces see[4,5].

The surface properties of thin films were characterized by two parameters – RMS value of the heights, σ, and by the autocorrelation length T. These parameters were obtained by fitting one-dimensional PSDF calculated according to eqs. (*7*) and (*8*) with theoretical dependence given by eq. (*6*). The data in the procedure were treated by least-squares method (LSM). The LSM used was based on the Marquardt-Levenberg algorithm[6].

Results and discussion

As already mentioned in previous section, surface parameters of thin films were obtained by evaluating the one-dimensional PSDF. In Fig. 2 can be found a comparison of PSDF calculated from AFM data of a selected sample together with best fit. Note that sharp peak at cca 39 μm^{-1} was filtered using one-dimensional FFT filtering. This peak (and also peaks on other space frequencies) arises from the noise of the electronics of the AFM microscope. The obtained values of σ and T in this case were as follows: σ = 5.50 ± 0.05 nm and T = 137 ± 3 nm. Note that theoretical dependence according to eq. (*6*) fits very well with the experimental data. Therefore, it can be concluded that the assumption of Gaussian form of the autocorrelation function given by eq. (*5*) is substantiated.

The dependences of RMS values of heights σ and autocorrelation length T on total deposition time are carried out in Fig. 3 and 4. Note that data were collected in the center of the sample (in graph denoted as center) as well as in the 3 mm distance from the shorter edge of the sample (in graph denoted as edge).

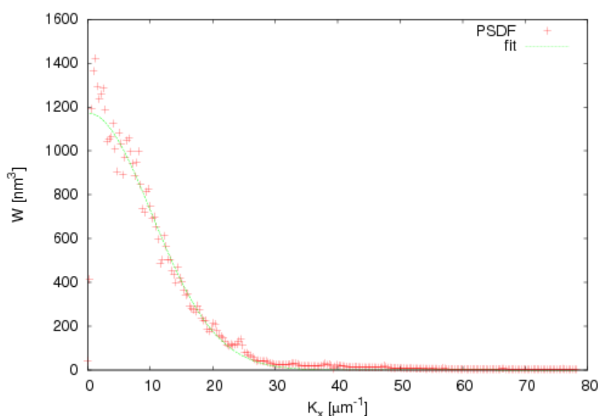

Fig. 2. **Comparison of 1D PSDF calculated from AFM data of a selected sample with corresponding best fit**

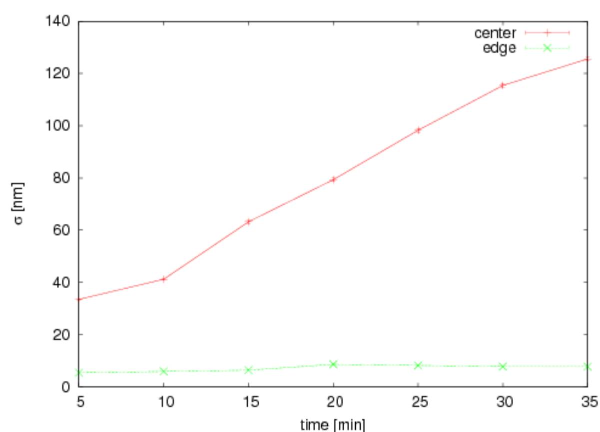

Fig. 3. **Root mean square values of the heights of sample surface irregularities.** The AFM data were taken in the center of the sample and also in the 3 mm distance from the edge

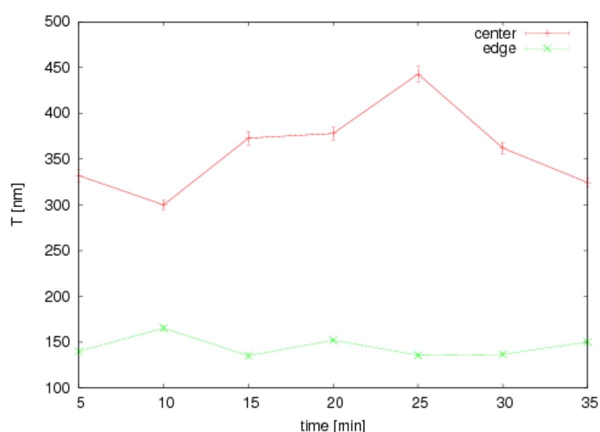

Fig. 4. **Plot of the autocorrelation length resulted from best fits of the AFM data collected in the center and near the edge of the respective sample.** On the abscissa is the total deposition time

It is worth to mention that the samples were oriented in such a way that the side where "edge" data were collected was headed towards powered electrode. Looking at Fig. 3, one can immediately see that in the center of the sample the surface roughness increases linearly, starting at 33.5 ± 0,3 nm. If the total deposition time reaches 35 minutes the roughness increases even up to 125.6 ± 0.9 nm. However, near the edge of the respective sample the roughness remains nearly constant and varies in the range from 5.50 ± 0.05 nm to 8.63 ± 0.04 nm. Increase of surface roughness of thin film with deposition time was reported in work by Lue et al[7], where also a tubular type reactor was used for deposition. This would be in agreement with the development of surface roughness in the center of the sample. However, near the edge the surface roughness exhibits behavior usually seen on films deposited in bell jar type of reactors, i.e. roughness is only slightly dependent on film thickness and values of the roughness are on the order of units of nanometers[8,9] or even on sub-nanometer scale[10]. Normally, very good film uniformity over large area reactors is reported[11]. Nevertheless, the film uniformity can be strongly affected by the design of electrode, gas inlet and pumping[12]. Hence, non-uniformity of thin films deposited within this work may come from reactor design and sample position within the reactor. Of course, the deposition parameters play also an important role in the deposition process. For instance we observed that the roughness in the center of the sample is significantly reduced by lowering the peak power to 5 W.

Different are also values of autocorrelation length T in the center and near the edge of the sample as can be deduced from Fig. 4. However, in this case there is no evident dependency on the total deposition time. Mean value of the autocorrelation length in the center of the sample is 359 nm and in the 3 mm distance from the edge of the sample the respective value is 145 nm.

In Figs. 5 and 6 can be seen AFM images of the thickest sample, where total deposition time took 35 minutes. The scans were taken again near the edge (Fig. 5) and in the center (Fig. 6) of the sample. Note that there is a difference of one order of magnitude in the z-scale. The resulting RMS values

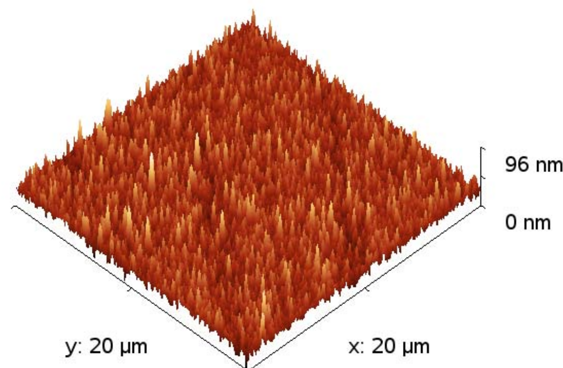

Fig. 5. **AFM image taken in the 3 mm distance from the edge of the thickest sample (35 min).** RMS roughness and autocorrelation length are σ = 7.72 ± 0.04 nm and T = 150 ± 2 nm, respectively

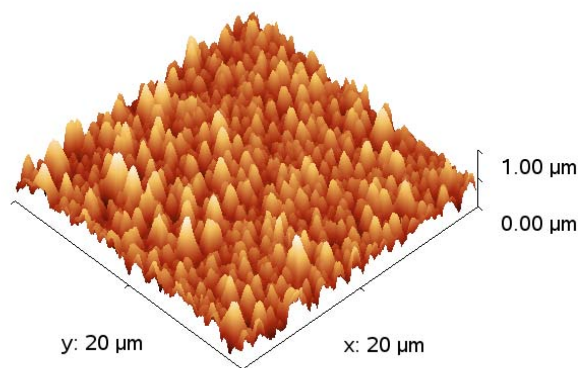

Fig. 6. **AFM image taken in the center of the thickest sample.** RMS value of roughness and autocorrelation length are as follows: σ = 125.6 ± 0.9 nm and T = 324 ± 5 nm

of roughness differ accordingly. While near the edge of the sample the respective value is only $\sigma = 7.72 \pm 0,04$ nm in the center of the sample the value is more than 16 times higher, i.e. $\sigma = 125.6 \pm 0,9$ nm. A difference can be observed also in the autocorrelation length. The value obtained near the edge of the sample is $T = 150 \pm 2$ nm. In the center the respective value is $T = 324 \pm 5$ nm. The autocorrelation length is a measure of lateral dimension of the irregularities of the rough surface. Hence, the increase of this quantity reflects the increase of the particle size deposited on the top of the sample.

Conclusion

We studied in this work surface morphology of thin amorphous hydrocarbon films by means of atomic force microscope. The AFM data were collected in two regions on the sample. We observed a significant difference in roughness parameters between these regions with increasing total deposition time. RMS values of the heights near the edge of the sample did not exhibit any significant change with the total deposition time and in the mean are equal to approximately 7 nm. However, RMS values of the heights in the center of the sample increased linearly with the total deposition time and reached values up to 125.6 nm. The values of autocorrelation length were independent on total deposition time, but there was a difference in absolute values. The mean value of this parameter near the edge of the sample was 145 nm, while in the center of the sample the respective value was 359 nm. The suggested reason for this surface non-uniformity is the reactor design. However, it is necessary to mention that the deposition conditions also play an important role in the film deposition process and that this difference could be at least partially ascribed to particular deposition conditions.

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