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UV light enhanced oxidation of a-C:H thin film in air. A study of thickness reduction

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This paper deals with the study of thickness reduction of an amorphous hydrocarbon (a-C:H) thin film under UV light irradiation. It is shown that when the thickness of the thin film is above 14 nm, a linear dependence in thickness decrease can be observed. The reduction velocity is in this region 10.1 nm/h. If the values of thickness of the thin film are below approximately 14 nm, the reduction velocity decreases subsequently. Area reflectance measurement consisting in taking reflectance spectra in many points lying along the area of the sample is used to create a map with thickness distribution along this area. This method is very sensitive to small thickness variations. A damage can be clearly observed by this technique which was done by a long-lasting ellipsometrical measurement to the sample having approximately 11 nm at the maxima.

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1. Introduction

Amorphous hydrocarbon thin films (a-C:H) are of great interest because of their outstanding mechanical properties. Depending on deposition conditions, films with high hardness, chemical inertness and chemical stability can be prepared [1]. It is also possible to deposit films with high content of sp^2 hybridized carbon atoms. These so called polymer-like carbon (PLC) films are suitable for applications in microelectronics and are widely studied due to their optical properties [2]. This includes photosensitivity under UV light irradiation where structural and photochemical changes are initiated, resulting in thickness reduction of the film.

Spectroscopic phase-modulated ellipsometry is common technique for determining optical properties of thin films. However, in order to obtain high quality spectra long-standing measurements are necessary. This fact can be a problem when dealing with photosensitive films. As a result properties of the films are changed where the beam was incident. In case of PLC films these changes consist in lowering of the thickness of the film. There are several papers concerning with the changes of film properties under UV light irradiation [3,4]. However, a detailed study of thin film thickness reduction is still missing. In this contribution we used short-lasting ellipsometrical measurements for determining changes made by Hg lamp irradiation. On another sample a slightly modified method originally presented by Ohlídal et al. [5] is used in order to illustrate the damage by long-lasting ellipsometrical measurement. This method is based on taking reflectometrical data in many points laying along the area of the sample.

2. Experimental

2.1 Preparation of samples

The samples marked as 1 and 2 were prepared by plasma enhanced chemical vapor deposition (PECVD) technique in tubular reactor. A schematic view of the apparatus is in Fig. 1. The horizontally mounted SIMAX glass tube was closed by two aluminum electrodes. Distance of the electrodes was 186 mm and inner diameter of the tube was 77 mm. The apparatus was pumped out by a rotary pump. Total pressure was measured using Leybold CERAVAC diaphragm gauge. Gas flows were controlled by Hastings flowmeters. Gases used for deposition were argon and acetylene. Flow rate of Ar and/or C_2H_2 was kept constant at 4 sccm and/or 1 sccm, respectively. Corresponding total pressure in the apparatus was 41.1 Pa in case of sample 1 and 38.8 Pa in case of sample 2. Power was delivered via matching unit from Dressler CESAR^{TM} 133 generator operating at 13.56 MHz. Delivered peak power during deposition was 5 W for both samples. The depositions were performed in pulsed regime, where frequency of the cycles and duty cycle for sample 1 was 500 Hz and 50 %, respectively. In case of sample 2 the conditions were set to 1 Hz for frequency of the cycles and 10 % for the duty cycle. Silicon substrates were located on a glass holder in the middle of the reactor. The deposition time was 5 and 45 minutes, respectively.

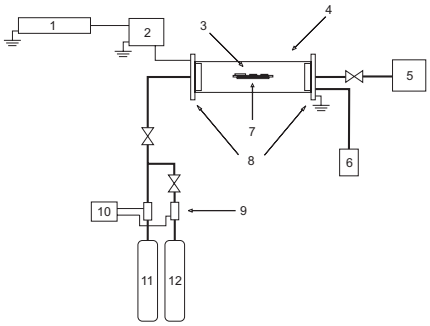

Fig. 1. Schematic view of the apparatus. 1 - power source, 2 - matching unit, 3 - samples, 4 - SIMAX tube, 5 - rotary pump, 6 - pressure gauge, 7 - glass holders, 8 - Al electrodes, 9 - flowmeters, 10 - control unit, 11 - Ar cylinder, 12 - acetylene cylinder.

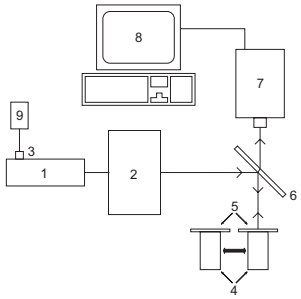

Fig. 2. Schematic diagram of the area reflectance measurement. 1 - Xe lamp, 2 - monochromator Zeiss, 3 - Si photodiode, 4 - sample holder, 5 - Si/studied sample, 6 - beam splitter, 7 - CCD camera, 8 - computer, 9 - voltmeter. sample 1 and 2, respectively. Prior to each deposition a surface treatment in Ar was performed. The treatment of both samples was running for 5 minutes at 5 W in continuous wave regime. After that, deposition was started immediately. Both samples exhibit relatively high thickness non-uniformity in the center of each sample.

2.2 UV light irradiation

Sample 1 was illuminated by Orion Hg(Ar) 6035 pencil lamp. Distance between sample and the pencil was approximately 4 cm. After each of 1 hour irradiation period ellipsometrical measurements took place. This procedure was repeated until nine hours of sample irradiation was reached.

Optical properties of sample 1 were determined by means of spectroscopic ellipsometry. The data were collected using Jobin-Yvon UVISEL phase modulated ellipsometer in the spectral range 0.6-6.5 eV (190-2068 nm) with 0.05 eV step. Angle of incidence was 55°. Only four of possible eight configurations of optical elements of the ellipsometer were used in order to partially eliminate the misalignments of the polarizer and compensator and, simultaneously, to reduce the time needed for data acquisition. Dispersion model of the thin films was based on parameterization of the density of electronic states [6]. Moreover, it was assumed that the three parameter dispersion model was the most suitable one. Hence, parameters A_f, E_g and E_h are used to parameterize the dispersion model. The quantity A_f is proportional to the valence electron density of the material, E_g is the band gap energy and E_h is the high energy limit (for details see [6]). The structural model was considered to be as follows:

- The ambient of the sample-substrate system is formed by a non-absorbing, homogeneous and isotropic material.
- The film is formed by a homogeneous isotropic material from the optical point of view.
- The substrate is formed by silicon single crystal. The optical constants are assumed to be fixed in values published in [7].
- Neither overlayer nor transition layer were considered.

Within this structural model it was further assumed that the upper boundary, i.e., air-film boundary, is slightly rough and hence the Rayleigh-Rice theory can be used [8]. In the process of data evaluation the roughness parameters of the upper boundary were fixed at values determined using atomic force microscopy. The root-mean square (RMS) value of the heights of the irregularities was fixed at 1.49 nm and autocorrelation length of these irregularities at 128 nm. This structural model has been incorporated into the calculations of the optical quantities of the film using a matrix formalism [8].

2.3 Area reflectance measurement

Reference reflectance spectra of sample 2 were taken using Perkin Elmer Lambda 40 spectrometer. Spectral dependence of index of refraction and extinction coefficient evaluated with the help of these spectra were than used for thickness determination using area reflectance measurement. A schematic view of experimental set-up can be found in Fig. 2. As light source served a 35 W Xe lamp. After passing the monochromator and reflecting from the beam splitter the light beam was incident onto the sample. A snapshot for particular wavelength was than taken using a CCD camera with 640x480 points resolution. This camera was the detector part of the Excel Measuring Center^{TM} 4520 from Micro-Vu Corp. Spectral range was limited by the intensity of the Xe lamp to 380-900 nm. After collecting the reflectance spectra in whole spectral region mentioned, sample 2 was replaced by a silicon sample and the same procedure was utilized to measure area reflectance spectra on the silicon sample. By dividing these two spectra and multiplying with absolute reflectance calculated from [7], we obtained an absolute reflectance spectra in individual point on the sample. The final image was cropped to 476×385 pixels.

3. Results and discussion

3.1 UV light irradiation

By illuminating a-C:H thin film with UV lamp, it is possible to reduce the thickness of such a film. As already

presented in [4], surface of thin film is oxidized by UV light irradiation in air creating CO and/or CO_2 molecules. Therefore carbon atoms are photochemically ripped out resulting in a thickness reduction. This process is documented in Fig. 3 where dependence of film thickness on total time of UV light irradiation is shown. First point (0 hours of irradiation) refers to the state before UV light irradiation. It can be seen that the thickness reduction in the first hour of irradiation is not so extensive as for, e.g., 3rd or 4th hour of irradiation. The reason for this could be explained by higher starting thickness of the overlayer (native film). Between particular irradiation period and ellipsometrical measurement period only several minutes elapsed which is not enough time for the overlayer to grow to its saturated value. Thus, following ellipsometrical measurements were performed on film with much thinner overlayer. For up to six hours of irradiation the thickness decrease shows linear dependence with reduction velocity of 10.1 nm/h. When thin film thickness is in the range from 11.5 to 16.6 nm the reduction velocity begins to decrease subsequently. This suggests that the effective volume of the film was reduced and accordingly the photochemical reactions do not proceed with the original rate. Parameters describing the dispersion model, namely A_f, E_g and E_h are plotted as functions of total time of UV light irradiation in figures 4 and 5. Dependence of index of refraction for wavelength of 600 nm is depicted too (extinction coefficient for this wavelength is negligible). It can be seen that the dispersion parameters exhibit some non-constant dependence. The first point (before irradiation process) is logically shifted because of omitting overlayer in structural model of the film. But also in the rest of the data points can be seen some non-constant dependence. For example the band gap energy increases from 2.9 to 3.3 eV. Again, this could be due to the insufficient structural model, but it is also possible that the bulk of the film has changed somehow because of the UV light irradiation.

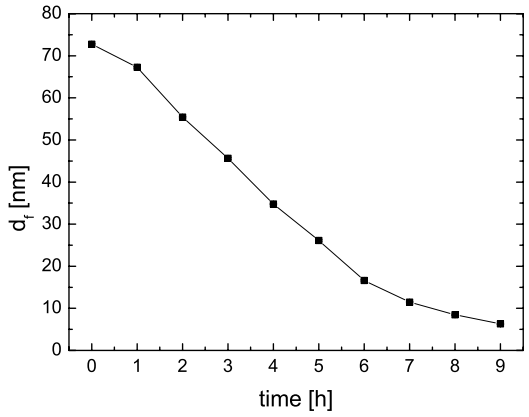

Fig. 3. Dependence of thickness of the thin film (sample 1) on the total time of sample irradiation.

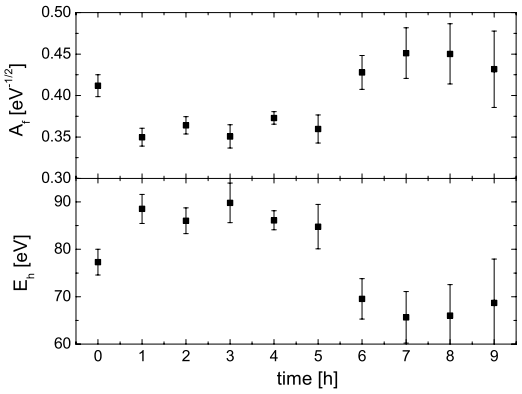

Fig. 4. Dependence of dispersion parameters A_f and E_h on total time of sample irradiation.

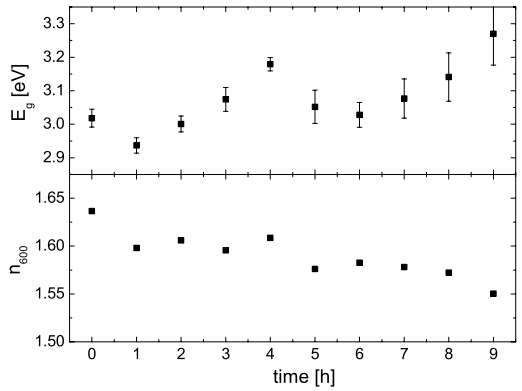

Fig. 5. Dependence of bang gap energy E_g and index of refraction for a wavelength of 600 nm, n_{600}, on total time of sample irradiation.

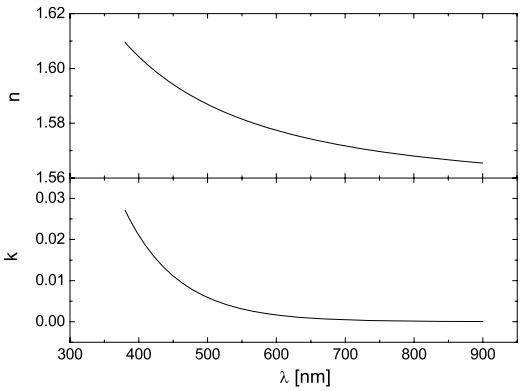

Fig. 6. Spectral dependences of index of refraction and extinction coefficient of the thin film (sample 2) calculated from the reflectance spectra taken by Perkin Elmer spectrometer.

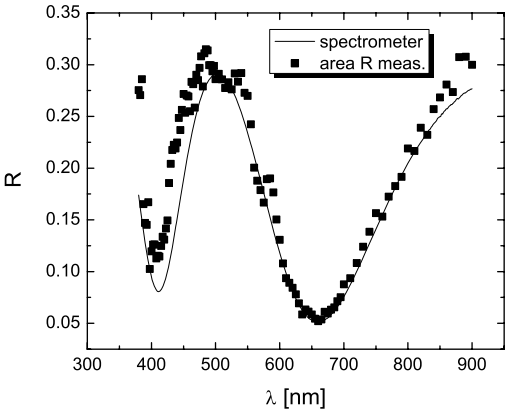

Fig. 7. Comparison of the reflectance spectra taken at the center of the sample using Perkin Elmer spectrometer and a spectra acquired by the area reflectance measurement in some selected point.

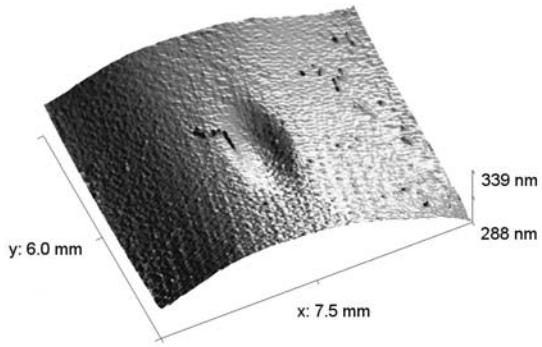

Fig. 8. 3D image of the thickness distribution along the area of sample 2.

Most probably some structural changes in the film consisting in variation of the sp^3/sp^2 ratio were made by the irradiation process. Influence of the UV light irradiation by the ellipsometer itself can be neglected as will be shown later.

3.2 Area reflectance measurement

Within this method a thickness value distribution was determined in many points lying along the area of sample 2. The structural model was nearly the same as for sample 1, i.e., simple homogeneous isotropic thin film on silicon substrate. On the contrary to the structural model of sample 1, no roughness of the upper boundary was taken into account. The dispersion model was considered in the form of Cauchy formula in case of index of refraction and in an exponential form in case of extinction coefficient, namely

$$n = A + \frac{B}{\lambda^2}, \quad k = a\mathrm{e}^{-b\lambda}. \tag{1}$$

In the spectral region where experimental data were evaluated (380-900 nm), the film absorption is not very high (see Fig. 6) and, hence, use of the dispersion model described by eq. (1) is substantiated. A comparison is depicted in fig. 7, where spectra from area reflectance measurement in some selected point and spectra obtained by Perkin Elmer spectrometer at the center of the sample are compared. The spectrometer measurement was preceding to the ellipsometrical measurement which caused damage to the sample (valley in the center of the sample). For wavelengths above 500 nm very good agreement can be observed. However, coming near to UV region the agreement between this two spectral dependences is not so good anymore. This discrepancy could be explained by the thickness non-uniformity of the thin film. The diameter of the light beam used in spectrometer is about 1 mm and, hence, non-negligible thickness variation arises along the area covered by the beam.

When evaluating map of thicknesses along the area of the sample, the dispersion parameters were fixed in values determined independently by reflectance measurement taken by Perkin Elmer spectrometer. Spectra were acquired at the position on the sample where no or very slight thickness non-uniformity can be expected. The parameters evaluated are shown in Table 1.

Corresponding spectral dependences of index of refraction and extinction coefficient are plotted in Fig. 6. A 3D image of resulting map of film thickness as obtained using the area reflectance measurement can be found in Fig. 8. In the center of the image can be clearly seen a damage.

Table 1. Parameters of dispersion model (1) determined by reflectance measurement using Perkin Elmer spectrometer.

A	1.556 ± 0.001
B (nm^2)	7700 ± 300
a	3.4 ± 0.7
b (nm^{-1})	0.0127 ± 0.0005

This sample was damaged with a long-lasting ellipsometrical measurement which took cca 9.5 hours. It was selected in order to demonstrate the sensitivity and usefulness of the area reflectance measurement. Selected profile of the film thickness along the x axis can be found in Fig. 9. Maximum value of the damage is approximately 11 nm and is depicted by an arrow in the figure. This means that ellipsometer itself reduces the film thickness by cca 1.2 nm/hour. A consideration can now be done on the ellipsometer influence in the UV light irradiation experiment. The short-standing ellipsometrical measurements took only 28 minutes which means that a damage of at most 0.6 nm per measurement could be made. Furthermore, the thickness decrease in the linear part of the dependence (see Fig. 3) was on average 10.1 nm. This implies that systematic error in this case is below 6 %.

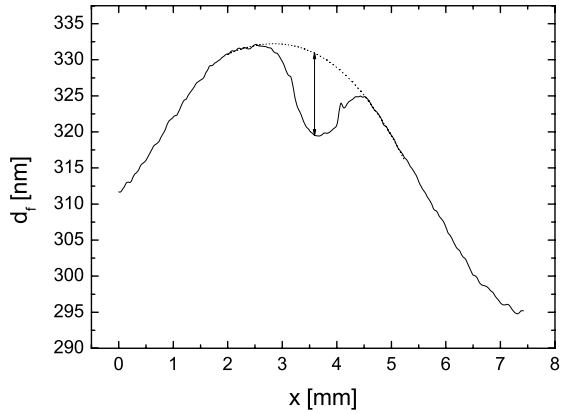

Fig. 9. Selected profile of the thickness of the thin film along the x axis. Maximum value of the damage is depicted by an arrow (approx. 11 nm).

4. Conclusions

In this paper the thickness reduction under UV light irradiation is studied. It was shown that the thickness decrease exhibits linear dependence until the thickness of the film reaches value of approximately 14 nm. Then a decrease in reduction velocity can be observed. The dispersion parameters show some systematic change with time spent for UV light irradiation of the sample. Most probably some structural changes are induced in the bulk of the thin film consisting in variation of the sp^3/sp^2 ratio.

A map of thickness distribution is shown on another sample using area reflectance measurement. A damage done by long-lasting ellipsometrical measurement can be clearly observed by this technique. This example demonstrates the sensitivity and the clearness of this method. It was shown that also a thickness variation of only several nanometers can be observed.

Acknowledgements

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