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Thermal stability of the optical properties of plasma deposited diamond-like carbon thin films

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Abstract

In present paper we studied the optical constants of the diamond-like carbon (DLC) films and their changes with annealing. The multisample modification of combined variable angle spectroscopic ellipsometry and near normal spectroscopic reflectometry was used. The optical constants of the DLC films were simulated by our recently published six-parameter dispersion model employing a parameterization of the density of electronic states (DOS). Based on the dispersion model parameters the density of π and σ electrons were evaluated. We showed that from our model and the independently determined hydrogen atomic fraction of the films before and after annealing the ratio between momentum matrix elements of $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions and the correct sp^3-to-sp^2 carbon bonding configuration ratio can be calculated. It is worth to notice that the first quantity is usually assumed to be equal to unity but we showed that this assumption may cause a significant error in the determination of the sp^3-to-sp^2 ratio. Therefore, our suggested method represents a novelty in this field.

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Keywords: Thermal stability; DLC; Optical constants; Electronic structure

1. Introduction

The classification of various types of hydrocarbon films can be performed through their hydrogen content, on the one hand, and the sp^3-to-sp^2 carbon bonding configuration ratio, on the other hand [1]. These two parameters determine, among others, the mechanical properties of the films and distinguish soft polymer-like and hard diamond-like carbon (DLC) films. It has been already showed that the optical methods are suitable for study of the sp^3-to-sp^2 ratio in amorphous (hydro)carbon films. Various dispersion models of the optical constants were applied for this purpose [2–8].

It is well known that the beneficial properties of the DLC films deteriorate at elevated temperatures [9] and thermal stability of DLC is often a key parameter for the applications. In this paper the effect of annealing of the DLC films on their optical constants will be presented. For these studies our recently published dispersion model [5–8] of the optical constants of the DLC films based on parameterization of the density of electronic states (DOS) will be utilized.

2. Preparation of samples and experimental arrangements

The DLC films were prepared by plasma enhanced chemical vapor deposition (PECVD) on silicon crystal substrates. The deposition conditions were as follows: r.f. power $P = 50$ W, d.c. negative self-bias $U_b = -325$ V, pressure $p = 17.9$ Pa, flow rate of methane $Q_{CH_4} = 2.85$ sccm, flow rate of hydrogen $Q_{H_2} = 1$ sccm and deposition time $t = 10$ min. The detailed description of sample preparation and the deposition reactor was presented in our earlier papers [10,11].

Thermal stability of the films was investigated by means of sample annealing in a quartz chamber pumped down to pressure of 10−5 Pa. Temperature of the chamber was subsequently increased up to the final temperature with the rate of 10 °C/min. The desorption of hydrogen was studied by a thermal desorption spectroscopy (TDS), i.e., the desorbed hydrogen was detected with a mass spectrometer during the sample heating. The as deposited and annealed films were

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Table 1
The parameters of the dispersion model corresponding to the as deposited and annealed DLC films together with relative changes of the film thicknesses and calculated quantities α and β characterizing the structural changes

Parameter	As deposited	280 °C	325 °C	406 °C	460 °C	510 °C
A_π [eV$^{-1/2}$]	1.033	1.230	1.286	1.417	1.462	1.539
$E_{g\pi}$ [eV]	0.949	1.109	1.104	1.104	0.957	0.791
$E_{h\pi}$ [eV]	6.71	7.33	7.65	8.07	8.33	8.04
A_σ [eV$^{-1/2}$]	0.551	0.532	0.517	0.490	0.447	0.423
$E_{g\sigma}$ [eV]	1.584	1.611	1.633	1.674	1.604	1.546
$E_{h\sigma}$ [eV]	51.7	51.7	51.7	51.7	51.7	51.7
$d_f^{(t)}/d_f^{(0)}$	–	1.021	1.038	1.068	1.103	1.114
α (κ=0.7)	0.0354	0.0510	0.0608	0.0802	0.1012	0.1086
α (κ=1.0)	0.0248	0.0357	0.0426	0.0562	0.0708	0.0760
α (κ=1.3)	0.0191	0.0274	0.0327	0.0432	0.0545	0.0585
β (κ=0.7)	–	0.9997	0.9956	0.9860	0.9509	0.9167
β (κ=1.0)	–	0.9954	0.9886	0.9740	0.9343	0.8989
β (κ=1.3)	–	0.9930	0.9848	0.9675	0.9252	0.8893

studied ex situ by ellipsometry and spectrophotometry. The spectral dependences of ellipsometric quantities were measured using a spectroscopic ellipsometer Jobin Yvon UVISEL within the spectral region 230–850 nm. The spectral dependences of the reflectance were measured by a spectrophotometer Perkin Elmer Lambda 45 within the spectral region 190–1000 nm.

3. Measurement of the optical constants

For measuring the optical constants of the DLC films studied the multisample modification of the combined method of variable angle spectroscopic ellipsometry (VASE) and near-normal spectroscopic reflectometry (NNSR) was used.

Within this method all the ellipsometric and reflectometric experimental data were treated for all the samples simultaneously. The spectral dependences of the optical constants were parameterized by our six-parameter dispersion model presented in our earlier papers [5–8]. This dispersion model is based on parameterization of the densities of electronic states (DOS) corresponding to both the π and σ bands. Each of the bands is parameterized by the three parameters with the clear physical meaning. These parameters are as follows: the minimum energy transitions (band gap) E_g, maximum energy transitions E_h and parameter proportional to the total density of the states inside the valence band A. Thus, for both the π and σ bands there are six parameters, i.e., A_π, $E_{g\pi}$, $E_{h\pi}$, A_σ, $E_{g\sigma}$ and $E_{h\sigma}$. This dispersion model was used to characterize five samples annealed to different temperatures from 280 to 510 °C. We made two assumptions, (i) all the five samples had the same optical constants before annealing and (ii) the annealing does not influence the parameter $E_{h\sigma}$. This latter assumption appears reasonable because it is expected the annealing effects only the weak bonds corresponding to the states close to the Fermi energy. Thus, only the first five parameters mentioned above were allowed to change as an effect of the annealing. These dispersion parameters together with the remaining parameters characterizing the films studied were determined by means of the least-squares method (LSM). We employed the structural model of the DLC films including the transition layers between the silicon substrate and DLC films. Within this model it was also assumed that the DLC films exhibited the optical anisotropy caused with the stresses inside the films. In this case the agreement between the experimental and theoretical data was very good. This statement is illustrated by the small value of quantity χ=1.93 (for the definition of χ see Refs. [6,7,11]). The detailed description concerning this structural model will be presented in a forthcomming paper.

The values of the dispersion parameters are summarized in Table 1. From this table one can see that the values of parameter A_π increases whereas the values of parameter A_σ decreases with increasing annealing temperature. This fact is caused by increasing amount of the π electrons to the detriment of decreasing σ electrons. The thicknesses of the DLC films before annealing were $d_f^{(0)} \approx 130$ nm and they increase after annealing as seen from their ratios $d_f^{(t)}/d_f^{(0)}$ in Table 1.

The spectral dependences of the DLC optical constants calculated from the parameters found within our model are plotted in Fig. 1. The influence of annealing on this dependences is evident. Especially, we can see a significant increase of the absorption peak corresponding to π→π* transitions with an increase of annealing temperature.

4. Determination of the sp^3-to-sp^2 ratio

The advantage of our model lies in the fact that we can simply define the following quantity proportional to the total density of states N_π and N_σ of the corresponding π and σ electrons:

$$N_j \propto \frac{A_j}{|p_{vc,j}|}\left(E_{hj} - E_{gj}\right)^2, \quad j = \pi, \sigma, \tag{1}$$

where $|p_{vc,\pi}|$ and $|p_{vc,\sigma}|$ represent the momentum matrix elements of the corresponding transitions, i.e., probability of

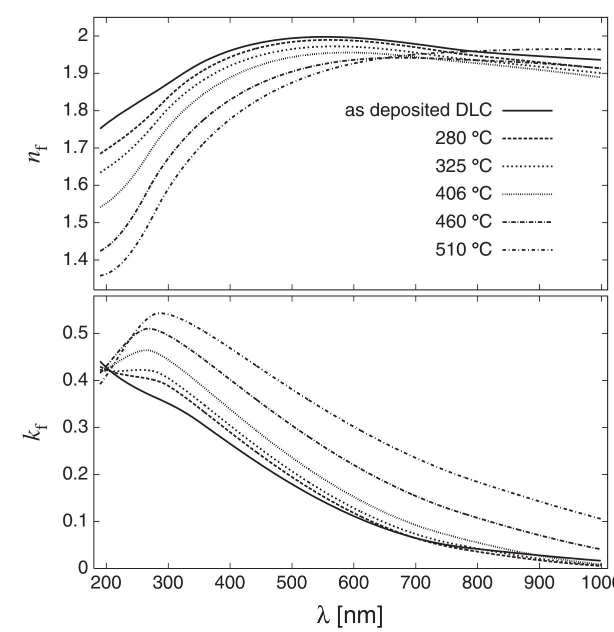

Fig. 1. Dispersion of refractive index and extinction coefficient for as deposited and annealed DLC films. The annealing temperature is given in figure legend.