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The method of optical investigations of the nanostructural diamond-like a–C:N films

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A complex technique has been proposed for optical investigations of nanostructured diamond-like a–C:N films. To determine the thickness d, refractive index n_0 and extinction coefficient κ_0, the refraction ellipsometry at fixed wavelength λ_0 = 632.8 nm with different incidence angles has been used. Proceeding from the n_0, κ_0 and d values, the $n(\lambda)$, $\kappa(\lambda)$ dependences have been restored basing on the optical transmission curves within the 280–1200 nm range, and, as a consequence, the dependence of the imaginary part of dielectric constant, ε'', on the photon energy near the fundamental absorption edge. The band gap width E_g and the Tauc coefficient B have been determined for the films obtained under various technological conditions and preliminary conclusions have been drawn for the contributions from sp^2 and sp^3 phases depending on those conditions.

Предлагается комплексная методика оптических исследований наноструктурных алмазоподобных a–C:N пленок. Для определения толщины d, показателя преломления n_0 и коэффициента экстинкции κ_0 используется метод отражательной эллипсометрии на фиксированной длине волны λ_0 = 632,8 нм при различных углах падения. По значениям n_0, κ_0 и d из кривых оптического пропускания в диапазоне длин волн 280–1200 нм восстанавливаются зависимости $n(\lambda)$, $\kappa(\lambda)$ и, как следствие, зависимость мнимой части диэлектрической функции ε'' от энергии фотонов $h\nu$ вблизи края фундаментального поглощения. Определены ширина запрещенной зоны E_g и коэффициент Тауца B для пленок, полученных в разных технологических режимах, сделаны предварительные выводы о вкладах sp^2 и sp^3 фаз в зависимости от этих режимов.

During last two decades, diamond-like a–C:H and a–C:N nanostructural films excited a great interest due to the development of planar technologies, the need for protective coatings of high strength with controllable heat and electric conductance control, etc. The doping of carbon films with either hydrogen or nitrogen makes it possible to increase the contribution of the diamond-like phase as compared to the graphite one and to regulate the film physical properties. In this connection, transparency of the films in the IR and partially in the visible spectral range should be mentioned.

Well known is the considerable effect of nitrogen on the properties of diamond-like nanostructural a–C:H films when it is added in the process of deposition. At the same time, due to variety of methods and conditions of the film deposition, the nitrogen influence mechanism is not finally ascertained. The results presented in [1, 2] are rather contradictory. Still more problematic

are the investigations of a–C:N films because of more complex atomic bonds in these films. That is why detailed optical investigations of a–C:N films and, in particular, the analysis of the fundamental absorption edge depending on the methods and conditions of the film preparation, are of great interest. In this work, presented are the results of a–C:N diamond-like film optical investigations in UV, visible and near IR spectral regions for films obtained in different technological conditions by magnetron sputtering of a graphite target in nitrogen atmosphere.

In general, the optical study methods of multilayer thin film coatings directed to study their electron structure are based on the refractive ellipsometry method in combination with the analysis of spectral dependence of transmission coefficient for weak-absorbing layers. The ellipsometric angles Δ and ψ measured at the fixed wavelength λ_0 of the incident polarized light are functions of the incidence angle φ_i, optical parameters of the layers and substrate and also thicknesses of the layer.

For one-layer covering

$$\psi = \psi(\lambda_0,\varphi_i,n,\kappa,d,n_s,\kappa_s),$$
$$\Delta = \Delta(\lambda_0,\varphi_i,n,\kappa,d,n_s,\kappa_s),$$

where n and k are refractive index and extinction coefficient of the layer; n_s and κ_s, the similar parameters of the substrate; d, the layer thickness.

From the known ellipsometric angles measured at the different incidence angles, it is possible to determine optical parameters of the film coating by solving the inverse ellipsometry problem with respect to $e^{-i\delta}$ ($\delta = 4\pi/\lambda_0 Nd\cos\varphi$ is the layer phase thickness; $N = n - ik$, the complex refractive index). We have developed the algorithm and calculation program to solve the inverse ellipsometry problem. Those are based on the determination of $\delta^{(j)}$ value for a pair of $n^{(j)}$ and $\kappa^{(j)}$ values from the specified data set following by selection of the solution having a physical sense [6]. It should be mentioned that at high sensitivity of the measured ellipsometric angles to changes in the optical parameters, the absolute values of these quantites for nanostructural carbon films cannot be determined at high accuracy [2, 9–13] due to surface inhomogeneities of the deposited films.

The found values $n(\lambda_0)$, $\kappa(\lambda_0)$ and d make it possible to calculate the transmission coefficient T. For the case of a weakly absorbing film and transparent substrate, it may be presented in zero approximation as

$$T \approx \left[\frac{8nn_s}{(1+n)(n+n_s)(n_s+1)}\right]^2 \exp(-4\pi\kappa d/\lambda_0) = A\exp(-4\pi\kappa d/\lambda_0). \quad (1)$$

Reflections at the air/film, film/substrate interfaces and interference in the film are not taken into account in that expression. Such an approach can be justified by the fact that the film refractive index is determined only at an accuracy to one decimal sign. Besides, interference does not manifest itself in the transmission curves within the considered wavelength range, which is also typical of a–C:H films [9].

The transmission coefficient value at $\lambda = \lambda_0$ is considered as a reference point for subsequent restoring of the $n(\lambda)$ and $\kappa(\lambda)$. It is obviously that the transmission coefficient T_{exp} obtained experimentally by direct measurements at the wavelength $\lambda = \lambda_0$ should coincide with the value obtained from (1). We propose the following algorithm for determination of $n(\lambda)$ and $\kappa(\lambda)$ based on the perturbation theory:

— experimental dependence $\ln T(1/\lambda)$ is approximated by polynomial $P_n(x)$ where $x = 1/\lambda$;

— the value of $\frac{P_n(x_i)}{x_i} = \frac{\ln A(x_i)}{x_i} - 4\pi k(x_i)d$ is determined in the points x_j, $x_j + \Delta x$ and $x_j + 2\Delta x$;

— difference $\frac{P_n(x_i+\Delta x)}{x_i+\Delta x} - \frac{P_n(x_i)}{x_i} = \Delta\left(\frac{\ln A(x)}{x}\right) - \frac{4\pi}{\lambda}\Delta k$ is formed;

— $\Delta\left(\frac{\ln A}{x}\right) = 0$ value is determined as a zero approximation at $\Delta\kappa^{(0)}$;

— difference $\frac{P_n(x_i+2\Delta x)}{x_i+2\Delta x} - \frac{P_n(x_i+\Delta x)}{x_i+\Delta x} = \frac{\ln A'(x_i+2\Delta x)}{x_i+2\Delta x} - \frac{\ln A(x_i)}{x_i+\Delta x} - \frac{4\pi}{\lambda}\Delta k^{(0)}$ is formed and $\ln A'(x_i + 2\Delta x)$ is found;

— the value of

Table.

N	Substrate temp.t, °C	Sputtering durat. τ, min	U_p, V	J_p, mA	d, Å	n_0	k_0	T, %	T_{exp}, %	E_g, eV	B
1	320	80	600	100	650	2	0.11	72	70	1.23	1.8
2	100	60	440	10	500	1.6	0.23	66	68	1.53	3.9
3	100	15	470	40	1100	1.7	0.17	48	42	1.01	1.8
4	100	60	470	40	4900	1.8	0.23	10	10	1.5	3.9

$\ln A(x_i + \Delta x) = \dfrac{\ln A(x) + \ln A'(x + 2\Delta x)}{2}$ is determined in the point $x_i + \Delta x$, and then $\Delta\kappa$ value is corrected in this point.

The transmission curves processed in such a way provide spectral dependences $n(h\nu)$ and $\kappa(h\nu)$ related to real ε' and imaginary ε'' parts of the dielectric function. According to the optical absorption theory for amorphous films d eveloped by Tauc [7], the fundamental absorption edge is described by the relationship

$$(h\nu)^2\varepsilon'' \sim (h\nu - E_g)^2 , \qquad (2)$$

where E_g is the optical energy gap width, the proportion coefficient B called Tauc coefficient determining density of the electron states. Thus, optical energy gap width E_g and the density of electron states can be determined near the fundamental absorption edge using the dependence of $(h\nu)\sqrt{\varepsilon''}$ on the photon energy $h\nu$.

The a–C:N films were grown using magnetron sputtering of a graphite target in nitrogen atmosphere with deposition on the substrates composed of Stoletov pile plates and melted quartz. A standard magnetron attachment for VUP-M unit was used as a basic one in the technological process. The films obtained at the substrate temperatures of 100 to 300°C at sputtering duration from 10 to 80 min at different voltages, gas discharge currents and fixed nitrogen pressure were studied. To determine the film thickness, ellipsometric measurements of refractive index and extinction coefficient were carried out at the helium-neon laser wavelength $\lambda_0 = 632.8$ nm and angles of incidence varying from 45° to 70°. The transmission spectra were measured using a SF-4 spectrophotometer in the wavelength range 280–1200 nm (1 to 4.4 eV). The experimental data were processed according to the above-mentioned procedure. The main results for some of the examined

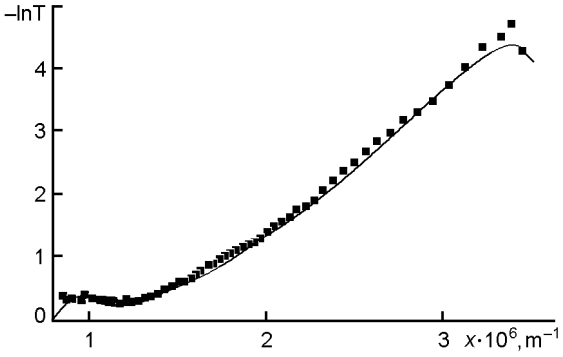

Fig. 1. Effectiveness of the $\ln T(x)$ interpolationby polynomial $P_n(x)$.

samples prepared at different technological conditions are summarized in Table.

Results of ellipsometry (n_0, k_0, d) shown in Table were obtained by the sum-total averaging of all angles of incidence at which measurements were carried out; the transmission coefficient T was calculated according to (1) using n_0, k_0 and d obtained from ellipsometry. As is seen from the Table, the directly measured transmission coefficient T_{exp} at the wavelength λ_0 correlates well enough with the calculated one.

Fig. 1 illustrates the effectiveness of the $\ln T(x)$ interpolation by polynomial $P_n(x)$ taking of one of the samples (sample 1 in Table) as an example. The calculated dependences $\varepsilon'(h\nu)$ and $\varepsilon''(h\nu)$ correlate well with Kramers-Kronig formalism [14].

Studies of the fundamental absorption edge according to Tauc made it possible to determine optical energy gap width E_g and coefficient B for the a–C:N films obtained under different technological conditions. Table presents E_g and B values for some of the examined films obtained using the proposed investigation technique. Fig. 2 shows $\varepsilon''(h\nu)$ dependence for two films obtained at different substrate temperatures and discharge voltages (samples 1 and 2). Fig. 3 demonstrates fundamental absorption edge according to Tauc for some samples. As is seen from Figs. 2 and 3 and the data from

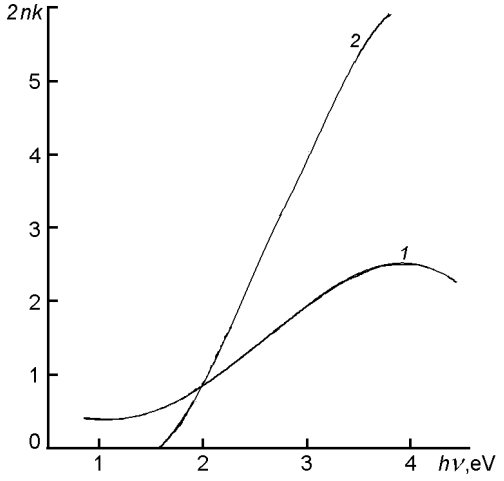

Fig. 2. Dependence of the dielectric function imaginary part on photon energy for Samples *1* and *2*.

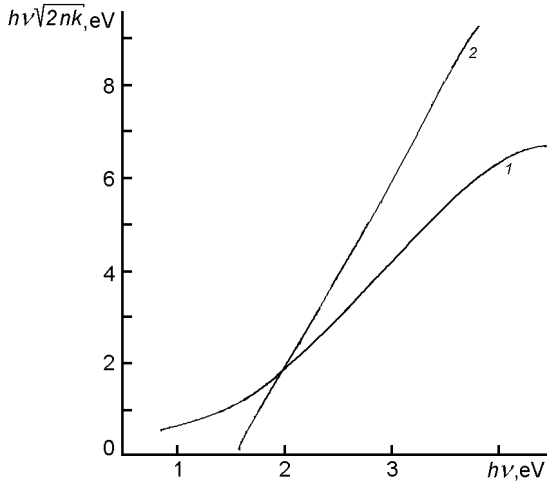

Fig. 3. Fundamental absorption edge as a function of photon energy for Samples *1* and *2*.

Table, the increase of the substrate temperature and discharge voltage during the deposition results in the increased graphite phase contribution (decrease of E_g) which is typical of a–C:H films, too.

In accordance with model conceptions of amorphous carbon energy spectrum [8–13], the fundamental absorption edge is defined by the presence of graphite clusters where carbon atom sp^2-hybridization is realized under involvement of π-electrons. The so-called diamond phase appears to be a matrix of sp^3-hybridized carbon atoms with partial substitution by nitrogen (hydrogen) atoms. Besides, the films are considered to contain an insignificant number of carbon atoms with sp^1 bonds. The bound nitrogen (hydrogen) atoms are deposited also at the cluster boundaries. The cluster (graphite phase) size defines the density of π-electron states, i.e. the forbidden zone width and the slope of the $h\nu\sqrt{\varepsilon''}$ dependence on photon energy. An increase in the graphite phase amount in the film must lead to E_g decrease and B rise. Increase of $2nk$ in this case is obvious, while as for refractive index, its increase in carbon films containing hydrogen is caused by the film density increase due to increasing size of the graphite clusters. In films containing nitrogen, such behavior is not obligatory. Besides, we should mention that in the examined films with nitrogen, a correlation between increase of E_g and decrease of Tauc coefficient B is not always observed, as is seen in Figs. 2, 3. This fact needs a further study. All the basic regularities mentioned above which are connected with the model conceptions about carbon films structure can be traced as a whole in the a–C:N films examined during our work and that is also can be seen from the data of Table. Thus, the general regularities in a–C:N films properties do not differ substantially from the similar ones in a–C:H films.

A considerable difference of a–C:N films from a–C:H films consists in the presence of three Gaussian contours inserted into $\varepsilon''(h\nu)$ dependence for some of the examined a–C:N films as compared to two contours which are characteristic of a–C:H films (those are not shown in Figs. 2 and 3). The presence of the low energy (1–3 eV) contour in the films of both types is associated with π-electrons and the presence of a contour in the domain of higher energies (3–4 eV) is connected hypothetically with σ-electron contribution [8, 9, 12]. We identified in some of examined a–C:N films the third weakly pronounced Gaussian contour in the energy range of 1.5–2.5 eV [14] but its explanation requires further studies.

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Метод оптичних досліджень наноструктурних алмазоподібних плівок a–C:N

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Запропоновано комплексну методику оптичних досліджень наноструктурних алмазоподібних a–C:N плівок. Для знаходження товщини плівки d, показника заломлення n_0 і коефіцієнта екстинкції κ_0 використовується метод відбивної еліпсометрії при фіксованій довжині хвилі λ_0 = 632,8 нм для різних кутів падіння. За значеннями n_0, κ_0 і d з кривих оптичного пропускання в діапазоні довжин хвиль 280–1200 нм відновлюються залежності $n(\lambda)$, $\kappa(\lambda)$ і, як внаслідок, залежність уявної частини діелектричної функції ε'' від енергії фотонів $h\nu$ поблизу фундаментального поглинання. Знайдено ширину забороненої зони E_g і коефіцієнт Тауца B для плівок, що отримані у різних технологічних режимах, зроблено попередні висновки щодо вкладів sp^2 та sp^3 фаз у залежності від цих режимів.