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Optical properties of linear-chain carbon film deposited on a steel sample

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The optical constants of a linear chain carbon (LCC) film in the spectral range from 248 to 1100 nm (1.13−5.0 eV with a step of 0.1 eV) were obtained by the Beatty ellipsometric method, and its thickness was determined. The LCC film was deposited on a pre-polished mirror surface of a massive steel sample using the technology of pulsed carbon plasma with ion stimulation. It was found that in the measured range of the spectrum the refractive index of the film varies from 2.35 to 2.73, and the value of k varies from a value close to zero to 1.02. The effective film thickness is determined to be $d = 92 \pm 2$ Å. According to the type of conductivity, the LCC film is a dielectric ($E_g = 4.1$ eV). A simplified method for determining the band gap of nanosized semiconductor and dielectric films is proposed.

Keywords: ellipsometry, optical properties of a carbon film, linear-chain carbon, band gap.

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Introduction

It is known that carbon can exist in three valence states, which correspond to $sp3$-, $sp2$- and $sp1$-hybridization of atomic orbitals. So, there are three pure allotropic forms corresponding to three valence states [1]. The first state ($sp3$) corresponds to three-dimensional (spatial) polymer of carbon — diamond. The second state ($sp2$) corresponds to two-dimensional (planar) polymer of carbon — graphite, and the third valence state ($sp1$) corresponds to unidimensional (linear) polymer, which is named carbyne. Carbyne is the linear-chain carbon (LCC) for the first time discovered (synthesized) in 1960 in A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS) by the method of dehydropolycondensation (stitching) of acetylene molecules ($sp1$-bond). Today, there are physical grounds of the methods for production of films of various carbon phases at low temperatures and pressures by means of ion beams; unique ion sources have been created for the implementation of such methods; new experimental procedures and devices were used to study these films; ion, ion-plasma and laser methods have been developed for production of thin nanocrystalline films [2]. Materials containing linear-chain carbon have unique physical and chemical properties and are widely applied in different areas of the science and engineering. These materials have already been applied in electronics, medicine, space and aero engineering. Very promising applications are optics, microwave technologies and electrics. Today, the technologies have been developed for production of high-efficient adsorbents with a low cost, based on the linear-chain carbon [3]. High efficient cold thermal and secondary electron emitters have been made with record-breaking characteristics [4], thus allowing to create devices of new generation, based on the vacuum electronics. Light-emitting devices of new generation have been developed. The work [5] presents the results of application of nano-size coatings made of 2D-ordered linear-chain carbon in medicine. In all applications, high stability of relevant operational characteristics of these materials are of a key importance.

The data obtained by using spectral methods are essential for creation, study and forecasting the properties of coatings made of linear-chain carbon. As a rule, in order to resolve certain tasks, the researchers record the spectra of reflection, passage or absorption within narrow regions of X-ray, visible or IR radiation. The purpose of this work was to study the complex of optical properties of the linear-chain carbon film applied onto steel sample, within a wide range of wavelengths, from ultraviolet to near infrared radiation. The data obtained in the work can be used for creation and verification of theoretical models of the light interaction with various types of nano-size structures. Moreover, due to record-breaking values of optical constants

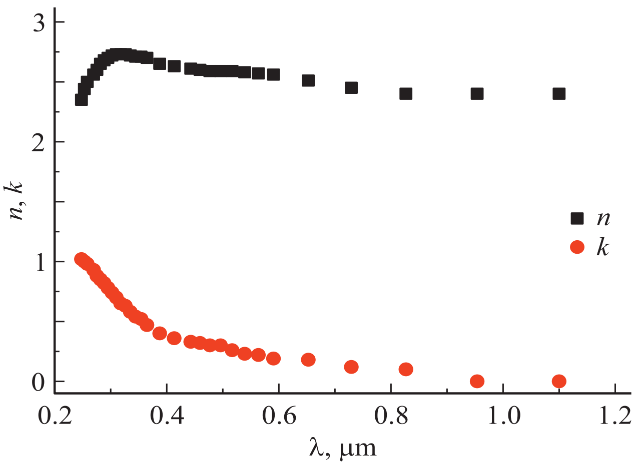

Figure 1. Dependences of the refraction index n and absorption coefficient k of the LCC film on the wavelength λ.

of diamond-like materials, the presented results can be used for simulation of composite nano-structures with unique optical characteristics.

Experimental procedure

Deposition of linear-chain carbon films onto a surface of a solid sample made of the steel 09G2S, with preliminary polishing, was made in vacuum ion-plasma set „URM.3.279.070 Diamond" in vacuum of $\sim 10^{-1}$ Pa according to the procedure described in [6]. These films were produced by using the technology of pulse carbon plasma with ion induction. A good homogeneity of the film thickness was controlled by means of optical microscopy.

For determination of optical constants of LCC film, we used a classic ellipsometric method described in the works [7,8]. The parameters Δ and Ψ determined therein were found by means of spectral ellipsometer by Beatty method. The measurements were performed on the samples of base material (polished steel without film) and with the film on it at the light beam falling angles 72° and 76° within the region of wavelengths 248 to 1100 nm (1.13–5.0 eV with the pitch of 0.1 eV). Ellipsometer was created on the basis of spectral complex KSVY-12 and a goniometer GS-5. Based on the obtained ellipsometric parameters Δ and Ψ by resolving main equation of ellipsometry for each wavelength, were determined optical constants of the base material n_2, k_2. Measurements at the wavelengths of 1100 and 950 nm allowed to calculate optical constants of the film n_1, k_1, as well as its thickness d according to [9]. This value of thickness was used in calculations of optical constants of the film within the whole spectral range.

Results and discussion

According to the solution of main equation of ellipsometry, the film refraction index within the used range of spectrum varies from 2.35 to 2.73, and the value k changes from zero to 1.02, wherein the film thickness is equal to $d = 92 \pm 2$ Å, and the film is nano-sized and dielectric (Fig. 1). The absorption coefficient k of LCC film at the wavelengths $\lambda = 953.9$ nm (1.3 eV) and $\lambda = 1100$ nm (1.13 eV) is equal to zero. The film reflectivity within the specified range of spectrum varies from 17 to 26% (Fig. 2), by reaching the maximum at $\lambda = 269.6$ nm (4.6 eV).

It is known that the optical spectrum of absorption in visible and near UV range allows to calculate the band gap (optical energetic slot) of wide gap materials with the use of the known Tautz ratio:

$$(\alpha h\nu)^2 = A(h\nu - E_\mathrm{g}), \tag{1}$$

where $\alpha = 4\pi k/\lambda$ — absorbance, $h\nu$ — energy of photons, E_g — band gap, A — constant. When building the function $(\alpha h\nu)^2$ of $h\nu$ (eV) the value E_g is derived by extrapolation of straight line in the high-energy part of the spectrum, wherein the crossing point of that straight line with abscissa axis corresponds to the optical band gap.

The work [10] uses ellipsometric method for the measurement of spectral dependences α on λ for thin films CdS with subsequent calculation of optical band gap. The authors in the mentioned work determined the band gap, by using the spectral ellipsometry method, for the films CdS made by magnetron spraying onto silicon and glass base materials. Determination of disperse dependences k_1 (coefficient of film absorption) and α on $h\nu$ was done as follows. First, we measured the spectra of ellipsometric parameters Δ and Ψ within the range from 1 to 5 eV. Next, we made an optical model (film/base material), which contains optical parameters, such as n_1, n_2 — refraction indices of the film and base material, k_1, k_2 — absorption coefficients of film and base material, d — the thickness of studied film. Within the selected optical model, by resolving the base equation of ellipsometry ($R_\mathrm{p}/R_\mathrm{s} = \mathrm{tg}\,\Psi\, e^{i\Delta}$, where R_p and R_s are Fresnel reflection coefficients) we calculated ellipsometric parameters, that coincide to the maximum extent with the experimentally measured parameters, determining the

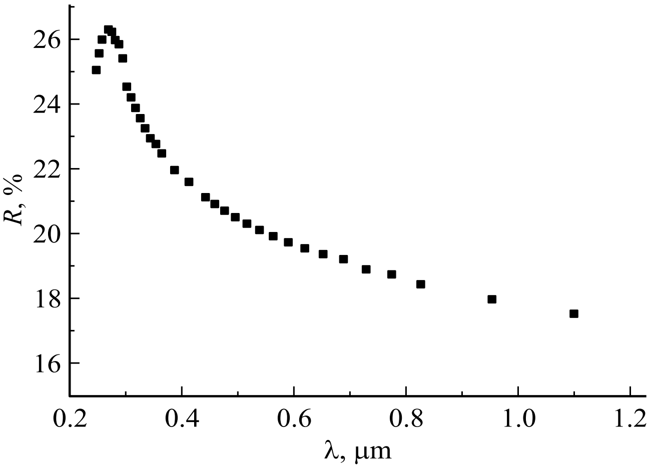

Figure 2. Reflectivity R of film of LCC.

spectra of n_1 and k_1 in this way. Main fault of that approach is the need for cumbersome arithmetic with selection of relevant models and optical parameters, which is quite challenging.

We proposed much simplified approach to determination of the optical band gap of nano-size semiconductor and dielectric films by using the method of ellipsometry. We found that for small, nano-size thicknesses, with the increase of the absorption coefficient k of film, the decrease of ellipsometric parameter Ψ is typical. It is clearly seen when building nomograms $\Delta - \Psi$ for poorly absorbing film on metallic base (Fig. 3, $\lambda = 6526\,\text{Å}$, falling angle $\varphi = 72°$, $n_2 = 1.82$, $k_2 = 3.11$, $n_1 = 2.4$, $k_1 = 0-1.0$, $d = 100\,\text{Å}$,

LCC film, base material — steel 09G2S). The point at $\Delta \approx 104°$ and $\Psi \approx 31°$ corresponds to the film thickness $d = 0$ (no film), and the lines mean six areas of nomogram for different values of k. The calculations were performed, by starting from the near IR region, where the value of $(\Psi_c - \Psi_f)$ is minimum.

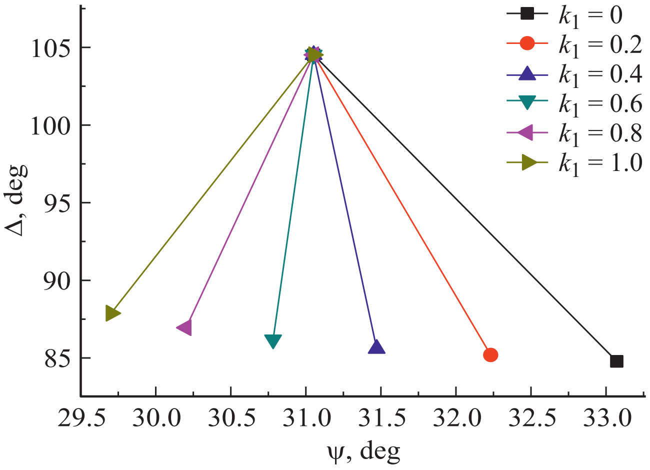

Figure 3. Nomogram $\Delta - \Psi$, $\lambda = 6526\,\text{Å}$, $\varphi = 72°$, $n_2 = 1.82$, $k_2 = 3.11$, $n_1 = 2.4$, $k_1 = 0-1.0$, $d = 100\,\text{Å}$.

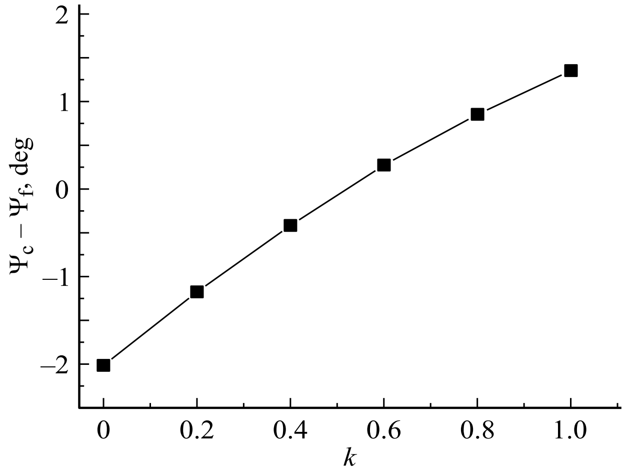

Figure 4. Dependence of $\Psi_c - \Psi_f$ on the absorption coefficient k of film.

Figure 4 shows that with the increase of the absorption coefficient k1, the difference $\Psi_c - \Psi_f$ is rising (Ψ_c is ellipsometric parameter of pure base material, and Ψ_f refers to the base material with film). It appears that the spectrum $\Psi_c - \Psi_f$ is similar to the spectrum k_1 of the film, and the spectrum $\Delta_c - \Delta_f$ corresponds to the spectrum n (Δ_c is ellipsometric parameter of a pure base material, Δ_f refers to base material with film) (Fig. 1, 5). Therefore, experimentally measured values Ψ_c, Ψ_f, Δ_c, Δ_f allow to determine the nature of change of optical constants of nano-sized films on the wavelength without any additional calculations and selection of a reflecting model. In particular, when building the dependence $\left((\Psi_c - \Psi_f)h\nu\right)^2$ on $h\nu$ (eV) the extrapolation of straight-line in high-energy part of the spectrum to the abscissa axis results in the value of optical band gap.

As can be seen in Fig. 5, the differences $\Delta_c - \Delta_f$ and $\Psi_c - \Psi_f$ are rising, as far as the wavelength is decreasing, wherein the difference $\Delta_c - \Delta_f$ is reaching the maximum $\lambda = 269.6\,\text{nm}$ (4.6 eV), as reflectivity R at this wavelength (Fig. 2). Based on the foregoing, we build the dependence $\left((\Psi_c - \Psi_f)h\nu\right)^2$ on $h\nu$ (eV) (Fig. 6), as well as the curve $(\alpha h\nu)^2$ on $h\nu$ (eV) (Fig. 7), obtained from the spectra of optical constants. Both these figures demonstrate that the crossing point corresponding to the optical band gap, is near to 4 eV on both dependences. Based on the dependence $\left((\Psi_c - \Psi_f)h\nu\right)^2$ on $h\nu$ it is $E_g = 4.1\,\text{eV}$, and based on $(\alpha h\nu)^2$ on $h\nu$ we get $E_g = 3.94\,\text{eV}$. For the sake of comparison, crystalline diamond has the band gap $E_g = 5.5\,\text{eV}$.

Conclusion

For the first time we obtain the optical constants by using the Beatty ellipsometric method for the linear-chain carbon film within the spectral range from 248 to 1100 nm (1.13−5.0 eV with the pitch of 0.1 eV) and its thickness is determined. LCC film was deposited onto the surface of a solid sample made of steel 09G2, with preliminary polishing, by using the technology of pulse carbon plasma with ion induction. According to the solution of main equation of ellipsometry, the film refraction index within the used range of spectrum varies from 2.35 to 2.73, and the value k changes from zero to 1.02, wherein the film thickness is equal to $d = 92 \pm 2\,\text{Å}$, and the film is nano-sized and dielectric. The film reflectivity within the specified range of spectrum varies from 17% to 26%, by reaching the maximum at $\lambda = 269.6\,\text{nm}$ (4.6 eV).

Optical band gap of the LCC film was determined, which is equal to $E_g = 4.1\,\text{eV}$. Based on the analysis of ellipsometric parameters obtained from the base material with and without film, we proposed a simplified method for determination of the band gap of nano-sized semiconductor and dielectric films, which does not require cumbersome

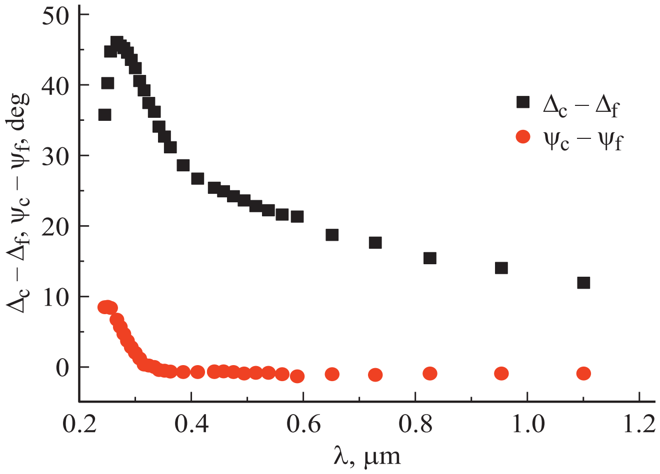

Figure 5. Dependences $\Delta_c - \Delta_f$ and $(\Psi_c - \Psi_f)$ on the wave length λ of LCC film.

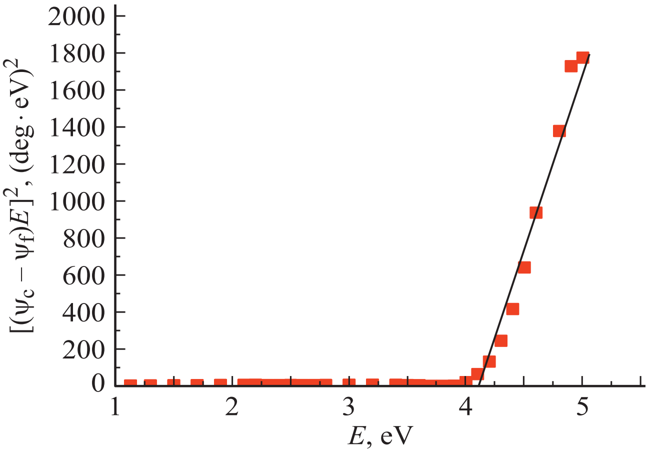

Figure 6. Dependence $[(\Psi_c - \Psi_f)h\nu]^2$ on the energy of photons of LCC film.

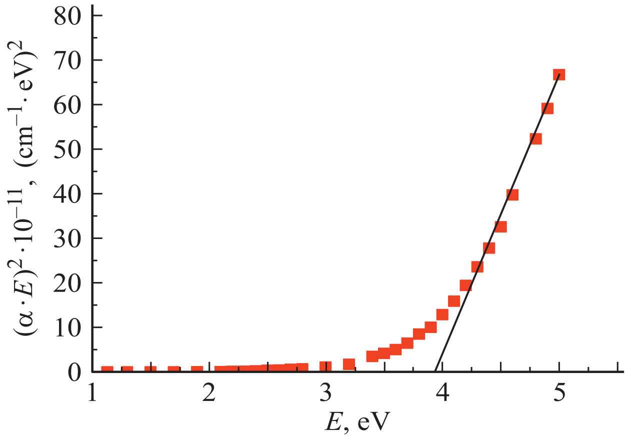

Figure 7. Dependence $(\alpha h\nu)^2$ on the energy of photons.

arithmetic with selection of relevant models with necessary optical parameters.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Yu.P. Kudryavtsev, V.G. Babaev, M.B. Guseva, V.V. Khvostov, N.F. Savchenko, A.F. Aleksandrov. Nanoteknologii: razrabotka, priminenie, **2** (1), 27 (2010) (in Russian).
[2] V.G. Babaev, M.B. Guseva, N.F. Savchenko, V.V. Khvostov, S.G. Bugrov. Poverkhnost?. Rentg., sinkhr. i neitr. issled., **6**, 100 (2005) (in Russian).
[3] N.F. Savchenko, V.V. Khvostov, M.B. Guseva, O.Yu. Nishchak, A.F. Aleksandrov, V.G. Babaev. Nanoteknologii: razrabotka, priminenie, **2** (2), 3 (2010) (in Russian).
[4] V.G. Babaev, V.V. Khvostov, M.B. Guseva, N.F. Savchenko, Yu.G. Belokoneva. Poverkhnost?. Rentg., sinkhr. i neitr. issled., **5**, 89 (2007) (in Russian).
[5] V.T. Kostava, N.M. Anuchina, N.P. Bakuleva, M.V. Zelivyanskaya, Zh.E. Kondratenko, I.G. Lyutova, D.A. Popov. Meditsinskaya tekhnika, **6** (300), 3 (2016) (in Russian).
[6] P. Flood, V.G. Babaev, V.V. Khvostov,N. D. Novikov, M.B. Guseva. Polyynes. Synthesis, Properties, and Applications (CRC Press, Boca Paton, FL, 2006). p. 219–252. DOI: 10.1201/9781420027587
[7] A.V. Rzhanov. *Osnovy ellipsometrii.* (Nauka, Moskva, 1979) (in Russian).
[8] R. Azzam, N. Bashara. *Ellipsometry and polarized light.* (Mir, Moskva, 1981) (in Russian).
[9] *Algoritmy i programmy dlya chislennogo resheniya nekotorykh zadach ellipsometrii*, ed. by A.V. Rzhanov. (Nauka, Novosibirsk (1980) (in Russian).
[10] N.S. Das, P.K. Ghosh, M.K. Mitra, K.K. Chattopadhyay. Physica E, **42** (8), 2097 (2010). DOI: 10.1016/j.physe.2010.03.035