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Investigation of the optical properties of carbon nanofilms in sp, sp^2, sp^3-hybridized states and their use to determine the phase composition of carbon

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Abstract. The optical properties of carbon nanofilms in the sp (linear-chain carbon, LCC), sp^2 (amorphous carbon) and sp^3 (diamond-like carbon) hybridized state have been studied. The films were synthesized by the ion-plasma method and subjected to heat treatment (annealing) at various temperatures in air. Optical properties were measured by spectrophotometry and Raman scattering. Methods are proposed for determining the phase composition of carbon films of various sp hybridization states based on measurements of transmission spectra in the visible region of the spectrum.

Keywords: amorphous carbon, diamond-like carbon, linear-chain carbon, phase composition, spectrophotometry, Raman spectroscopy, decision trees, data mining

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Материалы конференции
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Исследование оптических свойств нанопленок углерода в sp, sp^2, sp^3- гибридизированных состояниях и их использование для определения фазового состава углерода

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Аннотация. Исследованы оптические свойства нанопленок углерода в sp (линейно-цепочечный углерод), sp^2 (аморфный углерод) и sp^3 (алмазоподобный углерод) – гибридизированном состоянии. Пленки были синтезированы ионно-плазменным методом и подвергались термической обработке (отжигу) при различных температурах в среде воздуха. Оптические свойства измерялись методами спектрофотометрии и комбинационного рассеяния света. Предложены методы определения фазового состава углеродных пленок различных sp-состояний гибридизации на основе измерений спектров пропускания в видимой области спектра.

Ключевые слова: аморфный углерод, алмазоподобный углерод, линейно-цепочечный углерод, фазовый состав, спектрофотометрия, рамановская спектроскопия, деревья решений, интеллектуальный анализ данных

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Introduction

Carbon films are of interest as functional layers for third-generation organic and hybrid photovoltaic converters, transparent conductive electrodes in electronics, protective and antireflection layers in optics, and structural materials [1–3].

To study various forms of carbon, for example, analysis of the phase composition, the presence of defects or impurities, electron microscopy (scanning and transmission) and spectroscopy (XPS, Auger spectroscopy), Raman spectroscopy (Raman), spectroscopy in the UV, visible and near IR regions are used. spectra, thermogravimetry, probe microscopy. Each of the methods has certain capabilities, advantages and disadvantages [4]. For example, thermogravimetry requires a significant mass of samples, and Raman spectroscopy in the visible range shows the presence of only the sp^2 phase (its fraction in diamond-like carbon (DLC) is up to 30–50%), analysis of the sp^3 phase requires UV Raman spectroscopy.

Depending on the ratio of the fractions of carbon atoms with sp^3, sp^2, sp in the state of hybridization, nano- and microfilms of diamond-like, amorphous, and linear-chain carbon can be formed. The structure, mechanical and optical properties of carbon coatings depend on the ratio (sp/sp^2/sp^3) and vary widely depending on the method and technological parameters of synthesis [5].

For most film amorphous carbon materials, optical analysis methods are based on the analysis of ellipsometric data and the calculation of an energy parameter called the Tauc edge or optical band gap E_g. As a result of the analysis of optical spectra, extensive experimental material has been accumulated on the relationship between the microscopic structure of amorphous carbon and the values of E_g. There are a number of extrapolation formulas used for the analysis of spectra, which makes it possible to develop methods for the analysis of various allotropic forms of carbon by the optical method [7].

Due to differences in chemical bonds in the sp, sp^2, sp^3 - hybridized state, thermal oxidation of films of different forms of carbon should occur differently. The kinetics of the oxidation process is described by the Deal-Grove model and, depending on the conditions, can be described according to a linear or parabolic law. For thin films, one can use the linear approximation $d = A \cdot (t + t_0)$, when the rate-limiting stage is the kinetic stage of the reaction itself, since an excess amount of oxidant is delivered to the air/carbon film interface and the oxidation rate is controlled by the reaction rate constant, which is included in A.

Annealing is significantly affected by impurities in carbon films, in particular, their doping with metal or hydrogen atoms during synthesis.

This work is devoted to identifying the distinctive characteristics of the optical spectra of various forms of carbon, which would ensure their identification by optical spectrophotometry.

Materials and Methods

The deposition of films of linear-chain and diamond-like carbon was carried out on a modernized vacuum ion-plasma installation “UTM.3.279.070 Almaz” at a vacuum of ~ 10^{-1} Pa according to the procedure described in [2] on substrates made of K-8 glass. The formation of a linear-chain carbon film is stimulated by irradiation with Ar ions. Diamond-like carbon films were formed under the same conditions as linear-chain carbon films, but without ion stimulation by argon. The deposition of amorphous carbon films was carried out at the UVR-3M installation in a glow discharge plasma at a voltage of 2 kV, direct current at room temperature and a pressure of ~ 10 Pa in a mixture of argon, propane, butane and isobutane. The thickness of the films was determined by the number of carbon plasma pulses (0.3–0.5 nm per 1 pulse) or the deposition time (amorphous carbon) and was ~ 100 nm.

The optical properties of the samples were studied on a Horiba Jobin Yvon T64000 Raman spectrometer at room temperature in air using a laser at a wavelength of 514 nm and on a Lambda-25 spectrophotometer in the wavelength range of 190−1100 nm before and after annealing. The samples were annealed at a temperature of 400 °C with an interval of 2 minutes in air.

Results and Discussion

Fig. 1 shows the Raman spectra of carbon materials. All spectra are characterized by broad bands D and G. The degree of ordering of such materials is usually described by the ratio of the integral intensity of the D and G peaks. It should be noted that the DLC spectra, when excited in the visible range, show the presence of only the sp^2 phase and, depending on its content and ordering can take the form characteristic of both spectrum 1 and spectrum 2, for example [3].

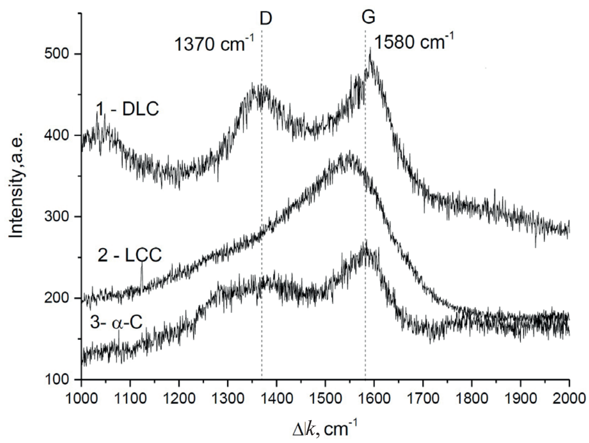

Fig. 1. Raman spectra of films of carbon materials: diamond-like carbon (1 – DLC), linear-chain carbon (2 – LCC), amorphous carbon (3 − α-C)

Figure 2 shows the optical transmission spectra of the films before and after annealing at 400 °C. It can be noted that, after annealing, the effect of film bleaching appears, which is associated with the oxidation and delocalization of free π-electrons of the sp^2 phase, which are responsible for light absorption. The difference between the spectra becomes more pronounced.

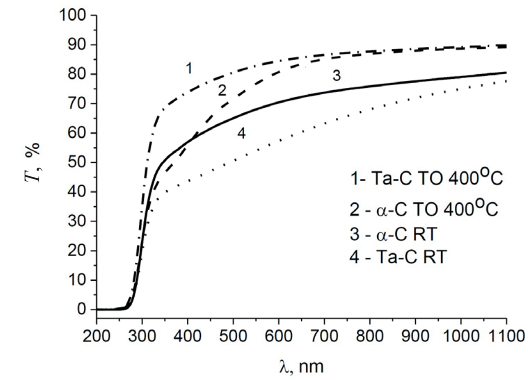

Fig. 2. Optical transmission spectra of an amorphous carbon (α-C) and diamond-like carbon (DLC) film before and after annealing (TO) at 400 °C

Figure 3 shows the dependences of the transmittance of films of amorphous carbon (α-C), diamond-like carbon (DLC) and linear-chain carbon (2 − LCC) at a wavelength of λ = 500 nm after annealing.

As can be seen from the Figure 3, the linear model describes the oxidation process well. The oxidation rate constant *k* depends on the type of film (the type of sp hybridization state). From this constant, it is possible to determine the phase composition of carbon, since the same phases lead to the same *k* (for example, *k* = 0.018 for both cases of ta-C, the highest *k* for LCC films, the smallest for a diamond-like film).

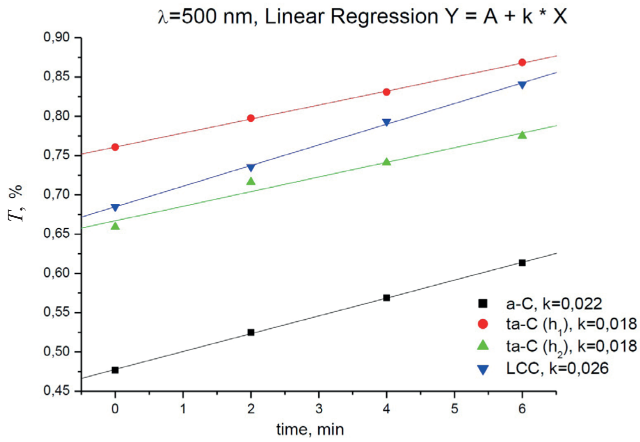

Fig. 3. Graphs of the dependence of the transmittances on the annealing time of a film of amorphous carbon (α-C), diamond-like carbon (DLC) for two different thicknesses (h_1, h_2) and linear-chain carbon (LCC).

At the same time, it should be noted that these dependences of the film transmission coefficients on time, i.e., the *k* values can be determined not only by the phase composition, but also by the density of carbon films, and the diffusion coefficient of oxygen into the film. In addition, the presence of impurities, defectiveness, and crystallite size can affect the oxidation rate. Using the proposed method, it is difficult to determine the composition of a film from different carbon phases and, in particular, to calculate the percentage of the sp^2/sp^3 phase in diamond-like films.

There are possibilities of using the "Decision Tree" method [6] in determining the phase composition of carbon films and for more complex cases, for example, the presence of several phases in films at the same time or the presence of impurities. Additional research is planned to implement it.

Conclusion

It is shown that Raman spectroscopy in the visible excitation region does not allow one to fully identify different phases (sp hybridization states) of carbon. A method is proposed for determining the phase composition of carbon films of various sp-hybridization states based on measurements of transmission spectra in the visible region of the spectrum (linear regression method). A method is proposed for determining the phase composition of a film from the results of only one measurement of the optical transmittance at any wavelength of the visible part of the spectrum at a known temperature and annealing time and a known optical transmittance at the same wavelength for a film not subjected to annealing. The results obtained can also be used to determine the temperature of the onset of thermal oxidation of carbon samples and to determine the mass content of the sp^3 phase in diamond-like carbon films.

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