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Structure modification of carbon nitride films by heat treatment

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The structure modification of carbon nitride films CN_x obtained by dc magnetron sputtering and heat treated under room conditions has been studied by thermogravimetric analysis, optical spectroscopy and scanning electron microscopy after. The repeated short-term heating/cooling treatment results in irreversible transformation of the film structure with predominating disappearance of the amorphous carbon phase. After UV irradiation, the mass and optical density of films having nanosize dense-packed structure become increased.

С помощью термогравиметрического анализа, оптической спектроскопии и сканирующей электронной микроскопии изучена модификация (после термообработки в условиях нормальной атмосферы) структуры пленок нитрида углерода CN_x, полученных магнетронным способом. Процесс последовательного кратковременного нагрева-охлаждения приводит к необратимому преобразованию структуры пленок CN_x с преимущественным исчезновением аморфной фазы углерода. После УФ-облучения обнаружено увеличение массы и оптической плотности пленок, имеющих наноразмерную плотноупакованную колонарную структуру.

1. Introduction

New carbon nanomaterials such as single-walled and multi-walled nanotubes, graphite nanofibers and structures on their basis are of good promise for hydrogen energetics [1]. The basic methods for manufacturing of carbon nanotubes in large quantities are electric arc evaporation of graphite, laser ablation of a graphite target and catalytical thermolysis of carbon-containing compounds. To remove the by-products (catalyst particles, amorphous carbon, etc.) the sample annealing is used followed by treatment in concentrated acids. Magnetron sputtering is usually used to obtain amorphous and fullerene-like carbon films [2]. Recently, the films with columnar nanostructure have been obtained by magnetron sputtering without the use of metal catalyst [3]. Such structures can be applied for hydrogen storage in addition to the above-mentioned nanotubes. Unfortunately, there are many inconsistent literature data about sorption efficiency of the same carbon substance ranging from the tenth parts of per cent up to tens of weight per cents of hydrogen with respect to the sorbent weight [1]. The structural differences of objects being studied could be a reason for such discrepancies. When considering the practical potential of these materials, it is necessary first of all to study their thermal stability and effect of high temperatures on their structure. In this connection, the purpose of this work is to study the structure modification of carbon nitride CN_x films by heat treatment in air.

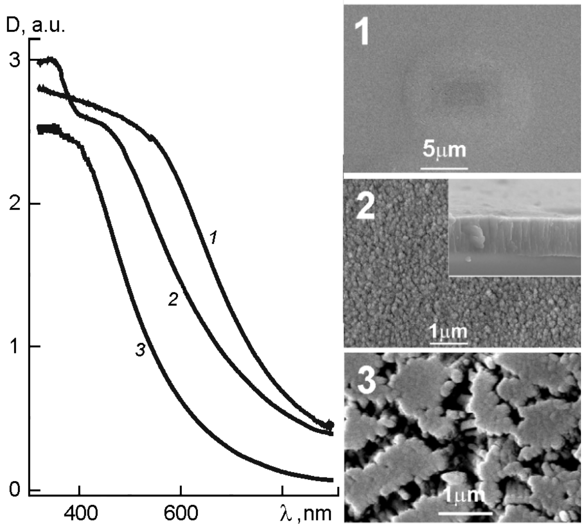
2. Experimental

The carbon nitride CN_x films were grown by a non-catalytic method of magnetron sputtering of graphite target in pure nitrogen atmosphere and nitrogen-oxygen (up to 5 at.%) mixture (in some cases, the ammonia was introduced into the growth atmosphere) onto glass, quartz, and gadolinium-gallium garnet (GGG) single crystal substrates. A planar magnetron with flat cathode and ring anode was used to produce the plasma. The discharge power during the film deposition did not exceed 20.0 W. The substrate temperature was varied from 350 to 570 K. The substrates were previously cleaned in a mixed solvent. The gas pressure in the chamber was 25 Pa. The film growth duration was varied up to 120 min. The films of about 1 μm thickness were chosen to be investigated. Three essentially different types of films (graphite-like, diamond-like and nanostructural) were obtained in the work depending on the growth conditions (the substrate temperature, gas atmosphere composition, intensity of etching processes, etc.).

The carbon nitride films obtained without domination of the etching process (≤0.5 at.% O_2) have the classic graphitelike properties [4]: high conductivity, low hardness, dense amorphous structure, low adhesion. The film color varied from grey to black. The optical gap as estimated from the absorption spectra is less than 1 eV as a rule. The graphite-like films have the highest absorption factor in visible range and a broad plateau in short-wave band (Fig. 1a, curve *1*, surface microstructure is shown in Fig. 1b (photo 1)).

The diamond-like carbon nitride films of the dense columnar microstructure [3] contain a mixture of sp^2- and sp^3-hybridized carbon and nitrogen atoms. These films are formed at higher energy of deposited particles and under moderate etching conditions (~ 1–2 at.% O_2). Those have a high hardness, a larger optical gap than graphite-like films (up to 1.5–1.6 eV), high adhesion, and high refractive index.

The nanostructural films are formed at a high etching component concentration in the growth atmosphere (etching component for type I films is ~ 3 at.% O_2; for type II ones, ~ 7 at.% NH_3) and moderate deposition temperature ~ 470 K. These films have low hardness and low conductivity. The scanning electron microscopy shows a pronounced loose columnar structure consisting of bunches of dense-packed nanofibers 70–100 nm in diameter [3]. The fiber length corresponds to the film thickness, nanofibers grow direction is normal to the substrate (Fig. 1b, photo 3). The nanostructural films have minimal absorption factor in visible range and narrow peak in short-wave range (Fig. 1a, curve *3*).



a) b)

Fig. 1. Absorption spectra (a) and surface microstructure (b) of carbon nitride CN_x films: *1*, graphite-like; *2*, diamond-like; *3*, nanostructural. Inset in photo 2 shows the cross-section view of diamond-like film.

The effect of short-term heating/cooling on modification of absorption spectra in ultraviolet (UV) and visible range was investigated by thermogravimetric analysis (TGA), optical spectroscopy (a Shimadzu UV-2450 spectrophotometer) and scanning electron microscopy (JSM-6490 LV) in normal atmosphere. The sample chemical composition was determined using the X-ray microanalysis in the same JSM-6490 LV electron microscope with an INTA Penta FETx3 energy dispersion spectrometer.

Thermogravimetric measurements were carried out using a TGA setup made in Donetsk Institute for Physics and Techno-logy of NASU to investigate low-mass (< 1 mg) samples. The TGA setup is a version of hermetic beam balance. The sample was placed into heating zone using a long quartz thread; as a result, the high temperature influence on the balance was minimized. During heating, the setup records the sample mass variation at the mode of automatic balance support. The setup allows to carry out the measurements in controlled atmos-

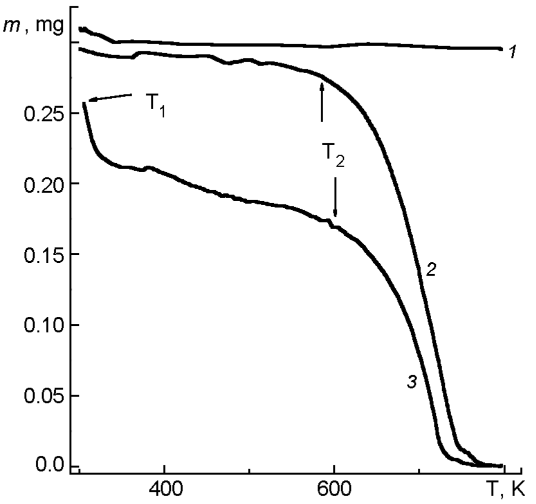


Fig. 2. Thermogravimetric curves of carbon nitride CN_x films: *1*, graphite-like; *2*, diamond-like; *3*, type I nanostructural.

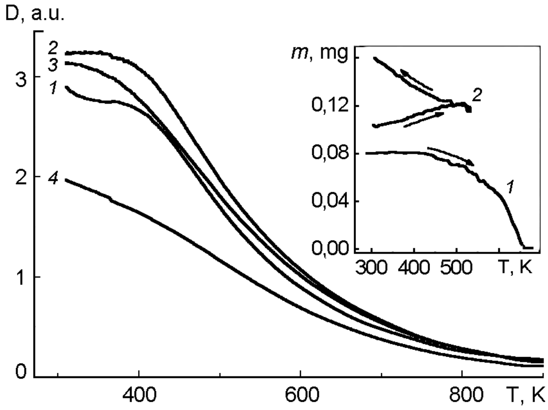


Fig. 3. Absorption spectra of type II nanostructural film: *1*, initial film; *2*, UV irradiated and heated to 540 K; *3*, heated to 628 K; *4*, heated to 643 K. Inset shows thermogravimetric curves: *1*, initial film; *2*, UV irradiated, heated to 540 K and cooled.

phere in temperature range 290–900 K. The minimum recorded mass change is 10^{-6} g.

3. Results and discussions

A smooth increase of optical absorption at decreasing wavelength and two absorption bands in UV range are typical of diamond-like films. The surface microstructure is shown in Fig. 1b (photo 2); insert shows the film cross-section.

Thermogravimetric curves $m = f(T)$ are shown in Fig. 2 for three types of CN_x films: graphitelike, diamond-like, and type I nanostructural ones. It was shown by measurements that in nanostructural films (curve *3*), the mass decreases starting either immediately at room temperature or at about 350 K (this temperature is referred to as T_1). Then in some temperature range the sample mass changes weakly, but at a higher temperature (point T_2) starts an intense mass decrease up to total "evaporation" of the film. The type II nanostructural film does not show the initial section of the curve $m = f(T)$ (point T_1) (see inset in Fig. 3, curve *1*). Only the temperature T_2 is a characteristic one in diamond-like film (Fig. 2, curve *2*), and there is no mass loss for graphite-like film (Fig. 2, curve *1*) within the temperature range studied.

The obtained typical thermogravimetric curves describe absolutely adequately processes that take place during heating the carbon film structures in air. So the point T_2 describes the start of intense oxidation process, that must be ended by total "evaporation" of film material during further heating. As for point T_1, this temperature describes the desorption of gas that was accumulated in interfibre space. It deals with nanofibre structure [3] having a very developed surface that can absorb gas easily. An enhanced thermal stability [5] is typical of all the graphite-like materials.

Experimental procedure was as follows. The absorption spectrum of initial film was measured at first. Then, under continuous monitoring of the mass variations, the sample was heated at a rate of ~ 10 K/min up to temperature when the TGA-setup traces the mass variation. Then the sample was cooled quickly and absorption spectrum was measured again. This procedure was repeated several times up to the moment when the film was completely degraded due to high temperature that was easy traced by TGA, too.

The first result worth of attention relates to diamond-like films. As expected, the absorption spectra confirmed the gradual optical density decrease while film mass decreased that was confirmed by TGA. But the main result is the transformation of diamond-like film absorption spectrum (Fig. 1a, curve *2*) into that of nanostructural film (Fig. 1a, curve *3*) after short-term heating up to 610 K and quenching. As it was mentioned, the initial absorption spectrum of diamond-like film contains two absorption bands near $\lambda = 400$ and 300 nm (photon energy 3.1 and 4.1 eV, respectively) (Fig. 1a, curve *2*). We suppose that two phases included into material of diamond-like film correspond to these two peaks of absorption. One phase has more strong interatomic bonds (corresponds to peak about 300 nm) whiled another one has more weak bonds (corresponds to peak near 400 nm). The formation of ordered structure with sp^2 and sp^3 coordination of carbon and nitrogen atoms starts obviously in first phase while the second one is amorphous. In our case, the heat treatment results in the sample mass loss mainly due to decreasing amorphous phase content (it is seen in Fig. 1a that the peak near 400 nm is absent in the absorption spectrum of nanostructural film (curve *3*)). The transition of diamond-like film into nanostructural state is confirmed by scanning electron microscopy (SEM). The surface structure of initial diamond-like film (photo 2) and the same structure after heat treatment (photo 3) are shown in Fig. 1b. It is seen that the film continuity is disturbed and the loosened columnar structure is formed. SEM of initial film cross-section (inset in photo 2) shows that the diamond-like film consists of dense-packed columns that grow through whole film thickness. Then it is obvious that the column core corresponds to the phase with strong bonds, while the shell to the phase with weak bonds. The shell phase disappears first under heat treatment, and the remaining core phase forms the nanostructure with separated fibers. The properties of this structure repeat the properties of nanostructural films: low hardness, low conductivity, developed surface. Literature data confirm the role of oxygen as the etching component that prevents forming the amorphous carbon. In [6], it is shown, that in the oxygen presence in the growth atmosphere, the diameter of carbon nanofibers decreases, and fibers are separated from each other.

However, the most interesting effects are obtained for type II nanostructural films deposited in an atmosphere containing ammonia as an etching component. These films are nanostructural initially. Thermogravimetrical analysis has shown that heating of the initial film (see inset in Fig. 3, curve *1*) results in gradual mass loss starting from 450 K up to total film evaporation at 670 K. Oxidation of carbon and nitrogen with air oxygen with formation of volatile C–O and N–O compounds is the reason for this effect in the film. At the same time, after ultraviolet (UV) irradiation of that film with a rather low intensity (20 W), its heating in air already to moderate temperatures (about 500 K) results in gradual increase of the film mass. The following cooling results in additional film mass increase (see inset in Fig. 3, curve *2*). Total increase is near 60 % of initial mass. It is to note that the repeated complete thermogravimetry of this film gives a curve similar to a curve *1*, but already at a new film mass level.

As to absorption spectra of the type II nanostructural film, Fig. 3 shows that after a UV irradiation and primary heating-cooling, an appreciable increase of absorption peak in short-wave band (curve *2*) is observed. This indicates that an additional structure is formed. Such behavior seems to be a consequence of some C–C and C–N bonds destruction under UV irradiation and additional connection of air nitrogen atoms thereto. During further heat treatment, the oxidation of the film material resulting in decreasing its mass and optical density takes place. We have carried out an experiment with heat treatment of similar unirradiated films in pure nitrogen atmosphere (99.99 %) to confirm the fact of air nitrogen connection and formation of additional solid-state structure in the type II nanostructural films. After heating up to 700 K and subsequent cooling down to room temperature, the film mass increased approximately twice. The absence of oxygen has prevented a premature oxidizing of films and the mass addition has taken place due to the nitrogen implantation. It should be noted that in this case the effect was attained not due to UV irradiation but due to thermo-activation processes.

4. Conclusions

The scanning electron microscopy and thermogravimetry of the carbon nitride diamond-like film CN_x shows that this material consists of two phases: nanostructural and amorphous. The short-term heat treatment of diamond-like film in air at 610 K results in etching of the amorphous phase and formation of the separated columnar nanostructure. The increasing mass and optical density of the CN_x film attained in an atmosphere with ammonia impurity is revealed. This film has the column structure initially. The effect is attained after preliminary UV\irradiation of initial film and following heating it in air up to 540 K due to absorption of air nitrogen with formation of the additional solid-state structure.

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Модифікація структури плівок нітриду вуглецю під впливом теплової обробки

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За допомогою термогравіметричного аналізу, оптичної спектроскопії та сканувальної електронної спектроскопії досліджено модифікацію (після термообробки в умовах нормальної атмосфери) структури плівок нітриду вуглецю CN_x, отриманого магнетронним способом. Процес послідовного короткочасного нагріву-охолодження призводить до незворотнього перетворення структури плівок CN_x із зникненням, головним чином, аморфної фази вуглецю. Після УФ-опромінення виявлено збільшення маси та оптичної щільності плівок, що мають нановимірну щільноупаковану колонарну структуру.