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Influence of intensive etching processes on structure and properties of carbon nitride films

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The influence of electromagnetic radiation and oxygen impurity in the growth atmosphere on the growth processes of nanostructured carbon nitride CN_x films has been studied. The oxygen impurity in the gas mixture and an UV irradiation has been found to decrease the thickness and refraction index of carbon nitride films, while increasing the optical band gap width. The intensive etching processes result in the formation of close-packed columnar film nanostructures of carbon nitride.

Представлены результаты исследований влияния электромагнитного излучения и примесей кислорода в ростовой атмосфере на процессы роста наноструктурных пленок нитрида углерода CN_x. Обнаружено, что примесь кислорода в газовой смеси и УФ облучение уменьшают толщину и коэффициент преломления пленок нитрида углерода и увеличивают ширину запрещенной зоны. Интенсивные травящие процессы приводят к образованию плотноупакованных колонарных пленочных наноструктур нитрида углерода.

Nanosized carbon-nitrogen materials with the columnar nanotube structure having unique properties and application fields (as hydrogen storage media, electrodes for fuel cells, electron emitters, ultrafiltration membranes, etc. [1, 2]) are under intense study at present. Such materials can be prepared by both catalytic and non-catalytic methods that require, however, complex and expensive preparation, separation and purification techniques of the material. Research of the material properties depending on deposition conditions is an important technological problem.

The carbon nitride materials are known to be inhomogeneous structures containing both tetrahedral structure elements consisting of C and N atoms in the sp^3 hybridized state, and structure elements of triple-coordinated C and N atoms in the sp^2 state within an amorphous medium [3]. The phase composition and properties of the films so obtained depend appreciably on the ratio of sp^3- and sp^2-hybridized states. The structure elements ratio depends on the film preparation conditions, in particular, on the intensity of etching and rearrangement processes on the growth surface. The role of etching processes during the growth of nanostructured carbon films is studied insufficiently to date. The etching processes play no doubt as important role at structure growth as the deposition processes. Also it is known that electromagnetic irradiation of the film growth surface (as well as of the gas phase near to the growth surface) influences largely the growth processes and therefore the characteristics of the obtained material [4, 5]. Studies of low-power UV radiation influence on the structure of al-

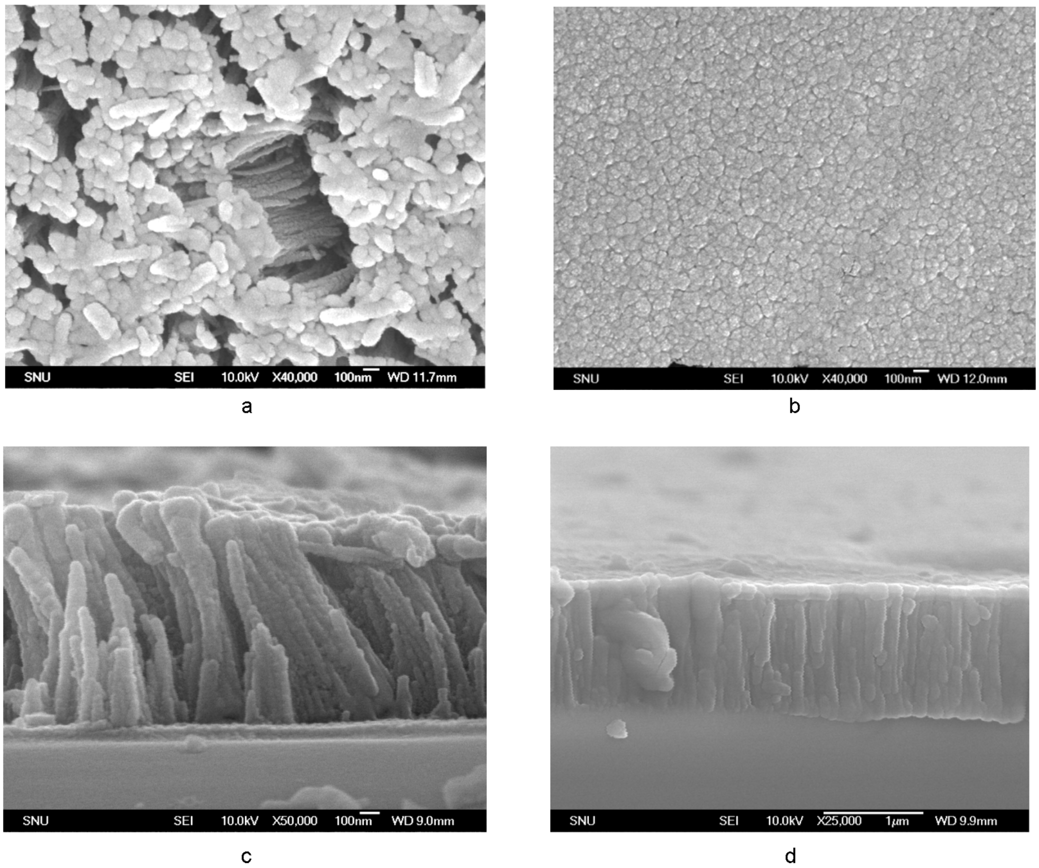

Fig. 1. SEM-image of surface and cross-section of nanostructured (a, c) and diamond-like (b, d) CN_x films.

ready grown amorphous carbon nitride films [6, 7] are known. Structural modification of the obtained films was observed after an irradiation of the sample surface by UV radiation of a high-pressure mercury lamp during many hours. For the UV irradiated films, a reduced intensity of absorption band connected with hydrogen was observed in the IR-spectra. This phenomenon is connected with photoinduced decomposition of such bonds under irradiation and removal of the bound hydrogen from the film structure. When the UV-photo processing time was increased, the band gap of the obtained films widened. That effect is explained by the reduction of the graphite-like sp^2 cluster size under irradiation. The mechanisms of low-power radiation influence on the film growth directly during the deposition process are no doubt of other nature than simply thermal phenomena (heating, graphitization, evaporation). In this case, it is reasonable to draw an analogy with gas-phase etchings processes (selective absorption of radiation, excitation of certain bonds and structure components and their further removal from the growth surfaces).

In this work, influence of oxygen impurity in the growth atmosphere and effect of UV range radiation on the growth processes, structure and properties of nanostructured carbon nitride films was studied. The nanostructured CN_x films were grown by a non-catalytic method using the magnetron sputtering of a graphite target in the atmosphere of pure nitrogen and a nitrogen-oxygen mixture (up to 6 at % O_2). Quartz glass and NaCl single crystal substrates were used. The plasma was generated using a planar magnetron with flat cathode and ring anode. The magnetron discharge power did not exceed 20 W. A modified radiating heater of the standard magnetron attachment was used to provide the simultaneous irradiation of the substrate surface with electromagnetic radiation during the growth. The film growth surface was irradiated with the focused radiation of a DRSH-250 mercury lamp. A UFS-5 light filter was used to select the preset frequency range. The power density of UV radiation reached

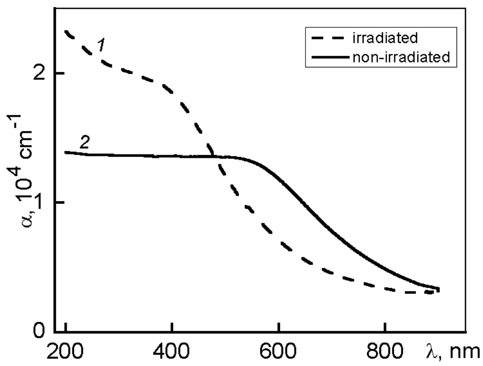

Fig. 2. Absorption spectra of CN_x films under various irradiation conditions: non-irradiated (*1*) and irradiated at q = 0.5 W/cm^2 (*2*).

up to 0.5 W/cm^2. The substrate temperature varied within 80 to 450°C range. The substrates were preliminary purified in a mixed solvent. The gas pressure in the chamber was controlled by instruments of a vacuum unit and was about 25 Pa. The film growth time was up to 120 min. Several series of films were grown on various substrates under varying the irradiation conditions of growth surfaces [8] and composition of gas atmosphere [9].

Spectroscopic examination of CN_x films (grown on quartz glass) in UV and visible spectral range was made using a Shimadzu UV-2450 spectrophotometer (λ = 200–900 nm). The studied electron spectra allow to estimate various important parameters of the amorphous material, in particular, the optical band gap width, and thus provide the information on changes in electron structure of the samples. The reflectance of the samples was measured, too. Ше фддщцы to calculate the material extinction factor, the refractive index, the real and imaginary part of permittivity using the known formulas [10]. The film thickness was determined by multi-beam interference using a MII-4 micro-interferometer and varied within limits of 0.2 to 1.5 μm depending the growth duration, the composition of atmosphere and irradiation conditions. The structure of the obtained films was examined by X-ray analysis (the photo method using an URS-55 unit) and electron microscopy of the surface (JEOL JSM-6330F field emission scanning electron microscope). The scanning electron microscopy allows to estimate the surface morphology of the obtained nanostructural films and its change under external influences on the growth processes.

The absorption spectra of films are typical spectra of usual diamond-like amorphous carbon films: a gradual smooth growth of absorption factor with increasing photon energy. Depending on the growth condition (the substrate temperature, intensity of etching processes, spectral composition of the radiation used), three fundamentally different types of films were obtained: diamond-like, graphite-like and nanostructural. The graphite-like films are characterized by [9] the highest absorption factor in the whole spectral range and a wide plateau in short-wavelength region. As to the diamond-like ones, a smoothly growing absorption with increasing photon energy and an absorption bands in the UV region corresponding to σ- and π-bands are typical. The nanostructured films have a characteristic structure consisting of vertically aligned nanofibers (Fig. 1a, 1c).

The X-ray diffuse dispersion analysis specifies mainly amorphous structure the carbon nitride films. The scanning electron microscopy shows a strongly pronounced columnar structure of the material obtained under the intensive etching, consisting from close-packed nanofibers of about 60 to 80 nm average diameter (Fig. 1a, 1c). The fiber length corresponds to the film thickness, and nanofibers grow normal or at a small angle to the substrate. The fibers are combined in blocks by several tens of units. Thus, the obtained material can be attributed to a nanostructured class. The CN_x films obtained without dominating etching processes show classical diamond-like properties with good adhesion, a high refractive index and dense structure according to SEM images (Fig. 1b). The cross-section image shows columnar structure of material (Fig. 1d), typical of polycrystalline diamond films [11]. Those structures have been obtained without any special preparation of substrates. In our opinion, of key importance is the magnetron sputtering of graphite used here and the substrate surface covering with graphite particles forming the growth centers during the initial deposition stage.

The nanostructured columnar films formation was observed under active etching processes on the growth surfaces. In this case, there are continuous competitive processes of deposition and etching and this fact allows to control the material growth to a considerable extent. The thickness measurements of the obtained samples show a sharp decrease of the carbon nitride film growth rate at increasing O_2 concentration in the

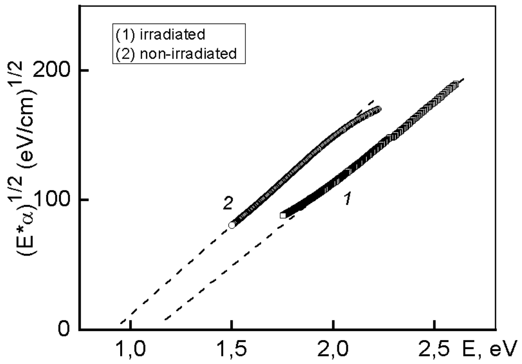

Fig. 3. Change of optical band gap width of CN_x films at the substrate irradiation: non-irradiated (*1*) and irradiated at $q = 0.5$ W/cm^2 (*2*).

growth atmosphere up to 6–7 at. %. We observed an essential absence of the material growth at oxygen concentrations exceeding 7 % [9]. The films grown up at 2–3 % oxygen concentration demonstrate a characteristic structure (Fig. 1a, 1c). The same structure is observed at the growth surface irradiation with an UV spectral component of the radiation source (UFS-5 filter). The films show an enhanced transparency both in visible and in near IR spectral ranges (Fig. 2). A reduced growth rate of such samples (by a factor of 3 to 5 times as compared non-irradiated ones) is noted, too. This fact testifies to an intensification of reconstruction and etching processes on the growth surfaces of films under the UV radiation.

The absorption edge of studied CN_x films is well described by Tauc equation [12], like other amorphous semiconductors. Therefore, the optical band gap width E_g was determined by extrapolating the energy dependence of $(\alpha E)^{1/2}$ (Fig. 3). The non-irradiated films are characterized by the optical band gap of about 0.9 to 1.0 eV, that is a usual value for such diamond-like films. It has been shown that the growth surface irradiation with UV light results in the optical band gap width increase up to 1.2–1.3 eV. When the oxygen concentration in the growth atmosphere is increased up to 5 %, the optical band gap width tends to increase, too [9]. This fact evidences changes in the sample phase composition, namely, intensified etching of the graphite-like sp^2-carbon clusters at growing oxygen concentration in the chamber atmosphere.

According to the Robertson structure model for diamond-like films [3], σ- and σ*-states in electron structure of amorphous carbon form valence and conduction bands

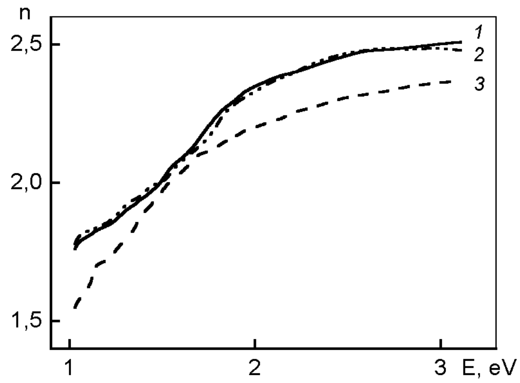

Fig. 4. Dispersion of refraction index *n* of CN_x films at various concentration of oxygen C and substrate temperatures T_s: C = 0.5 %, T_s = 80°C (*1*); C = 0.5 %, T_s = 350°C (*2*); C = 5 %, T_s = 350°C (*3*).

while π- and π*-states of sp^2-combined graphite-like elements (laying inside the σ-σ*-gap) form the band gap edge and control the optical band gap width. Thus, the optical band gap width correlates directly with the amount of the graphite-like carbon phase in the film and decreases with its growth. The optical band gap width increase in CN_x films irradiated with ultraviolet or grown at high O_2 concentrations in the growth atmosphere evidence the quantitative reduction of the sp^2-state structural elements fraction in such samples.

The same is confirmed by the refractive index n value and dispersion in the photon energy range 1.0–4.0 eV. In Fig. 4, shown is the dependence n on photon energy for CN_x films obtained at oxygen concentrations in the growth atmosphere 0.5 % and 5 %, and substrate temperatures 80 and 350°C. The refractive index was determined by calculation from absorption and reflection spectra data. It is necessary to note that increased oxygen concentration results in evident reduction (by 10–15 %) of refractive index, whereas the substrate temperature practically does not influence the *n* value and dispersion. The behavior of *n* dispersion does not change and is of a normal type, unlike most diamond-like carbon films obtained by magnetron sputtering of graphite target where the dispersion n has an anomalous character [13–15]. The anomalous dispersion in the most of amorphous carbon films may be an additional argument in favor of sp^2-bound structural elements (typical of graphite) predomination in such films. At the same time, the normal dispersion n determined in this work convinces that CN_x films consist predominantly of sp^3-

bound structural elements typical of diamond, where the *n* dispersion has a normal form [13]. The increased etching of graphite-like components in the CN_x films at high O_2 concentrations is confirmed by the decreasing absolute n value when oxygen concentration is increased (Fig. 4). That is obviously caused by density decrease of such films as a result of etching.

Thus, it is revealed in the work that the oxygen impurity in the gas mixture and UV irradiation cause a decrease of thickness and refraction index of carbon nitride films. The films become more transparent simultaneously (photo-blooming effect). The material absorption edge is displaced towards the short-wavelength spectral region and the optical band gap width E_g increases. The revealed change of the film optical properties is due obviously to the set of photochemical and photostructural transformations occuring in the films under intensive etching processes. It is shown also that the intensive etching processes result in formation of close-packed columnar film nanostructures of carbon nitride.

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Вплив інтенсивних процесів травлення на структуру та властивості плівок нітриду вуглецю

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Подано результати досліджень впливу електромагнітного випромінювання і домішок кисню у ростовій атмосфері на процеси росту наноструктурних плівок нітриду вуглецю CN_x. Виявлено, що домішка кисню у газовій суміші і ультрафіолетове опромінювання зменшують товщину і коефіцієнт заломлення плівок нітриду вуглецю, збільшують ширину забороненої зони. Показано, що інтенсивні процеси травлення приводять до утворення щільноупакованих колонарних плівкових наноструктур нітриду вуглецю.