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Influence of UV-radiation on structure and properties of diamond-like α-C:N films

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Study results on effect of a low power (up to 1 W/cm^2) UV and visible radiation on the structure and properties of diamond-like carbon nitride (α-C:N) films during their growth have been presented. The UV irradiation of the growing film surface has been found to be effective for the graphite phase etching and to result in an improved structure ordering of the film and enhanced quality thereof.

Представлены результаты исследования воздействия УФ- и видимого излучения невысокой мощности (до 1 Вт/см^2) на структуру и свойства алмазоподобных пленок нитрида углерода α-C:N в процессе их роста. Обнаружено, что УФ-облучение ростовой поверхности пленок эффективно для травления графитной фазы, ведет к росту структурной упорядоченности пленок и улучшает их качество.

Diamond-like nanocrystalline films are a promise material and attract a great interest due to unique "diamond" properties: high hardness, wear resistance, chemical inertness, biocompatibility, etc. Research of the film properties as functions of conditions of the growth condition is an important technological problem. Influence of electromagnetic radiation on the gas phase near the growth surface and on surface being grown may affect extremely heavily the growth and quality of the material obtained. The radiation influence on structure of diamond and diamond-like thin films directly during their growth is not studied comprehensively enough [1–3]. Such researches are useful in understanding photostimulated growth processes in the films, thus allowing to control effectively the structure growth.

In this work, the influence of UV and visible radiation on structure and property of diamond-like carbon nitride films [4] during their growth has been studied. The α-CN films were grown by magnetron sputtering of a graphite target in pure nitrogen atmosphere on quartz glass substrates. The growing surface of the film (substrate) was irradiated with the focused radiation of a DRSH-250 mercury lamp using UV filters, at power density about 1 W/cm^2. A series of diamond-like films with properties depending considerably on the radiation spectral structure was obtained, thus suggesting photoinduced structuring processes in the formed film. To obtain the diamond-like films, a standard magnetron in combination with an universal vacuum setup VUP-5M was used. A heater was designed which made it possible to irradiate simultaneously the substrate surface with electromagnetic radiation, since the standard heater of magnetron setup did not allow to do it due to its design.

The heater consists of a ceramic base fixed to the central rack of magnetron setup. In the center of the base, a rectangular aperture is situated comparable in size to the substrate. The tungsten heater shaped as a thin plate is fixed on the base, with the same central rectangular aperture. The substrate is pressed to the heater by special clamping plates. Thus, it is possible to irradiate the substrate from above with the lamp light directly during the film growth (Fig. 1). To that end, a metal mirror is fixed to the central rack above the heater at the angle 45^0. Additional optical ele-

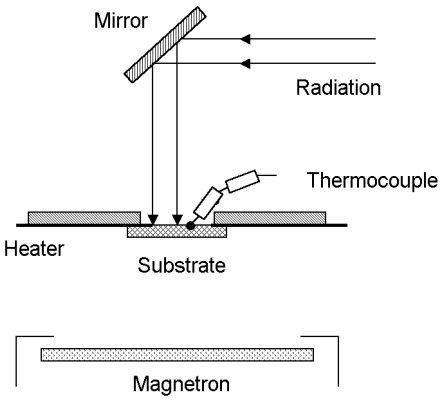

Fig. 1. Schematic view of heater and radiation source.

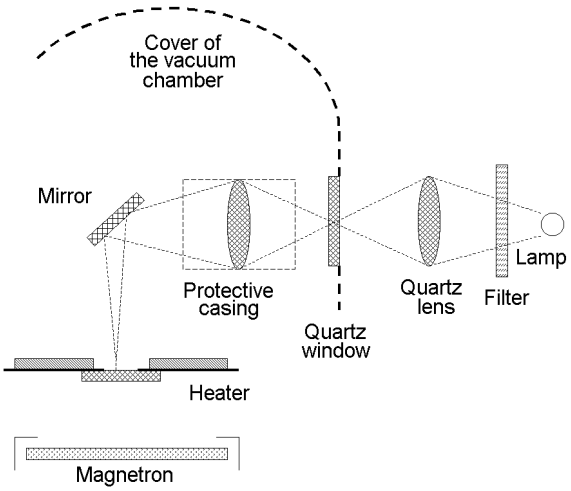

Fig. 2. Optical system using a quartz lamp as radiation source.

ments (quartz lenses) are used to focus radiation on the substrate. The focused spot area on the substrate is 8 to 10 mm^2. A quartz optical window (Fig. 2) was used to pass the radiation into the working chamber of VUP-5M. The spectral structure of the radiation was changed using light filters. The filter was located outside of the chamber in such a manner that the gas environment and a substrate were irradiated at identical density of the radiation beam in all experiments. The substrate temperature was varied within limits of 150 to 450°C and controlled using a chromel-alumel thermocouple positioned at the external side of the heater. The heater was powered using an internal adjustable voltage source of VUP-5M. Quartz glass plates were used as substrates. Substrates were cleaned in a mixed solvent before the growing process. The gas pressure in the chamber was controlled by appropriate devices of the vacuum post and was about 0.2 Torr. The film growing time was 120 minutes.

Amorphous diamond-like carbon nitride films (K and КТ series) were obtained with properties varuing over a wide range. The morphology and thickness of the films were defined by the discharge parameters (gas mix pressure, magnetron current), the substrate temperature, and energy of the electromagnetic radiation incident on the substrate. The film color varied from dark brown up to light brown and orange. Spectroscopic researches of diamond-like α-CN films in visible and near IR spectral region (wavelength range 690 to 1700 nm) were carried out using a ZMR-3MD spectrophotometer. The films of K series irradiated with full spectral range of the lamp, irradiated only with the UV component and unirradiated (Fig. 3) were investigated.

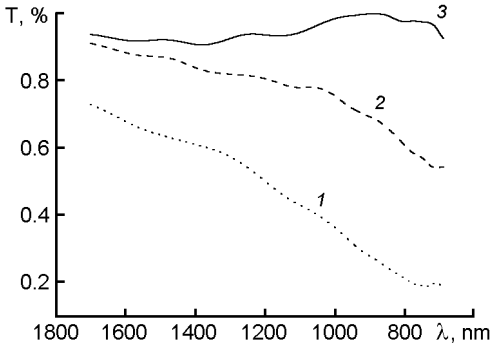

Fig. 3. Absorption spectra of α-C:N films grown under various irradiation conditions (K series): *1* — lamp; *2* — without lamp; *3* — filter.

Spectra of the films grown without irradiation are typical of usual diamond-like amorphous carbon films [5]. The film irradiated with the full lamp spectral range is characterized by a lower transparency both in IR and in visible regions. In this case, the light beam makes additional heating of growing surface (together with resistive heating) that results in the film darkening due to thermal graphitization. At the irradiation only with UV component of the spectrum (using a filter) the film is remarkable for its high transparency both in visible and IR spectral ranges and has a characteristic light brown (orange) shade. We assume that the UV radiation excites additionally the growing surface of the film, thus increasing mobility of growing radicals on the surface and efficiency of the graphite phase etching. All those effects result in

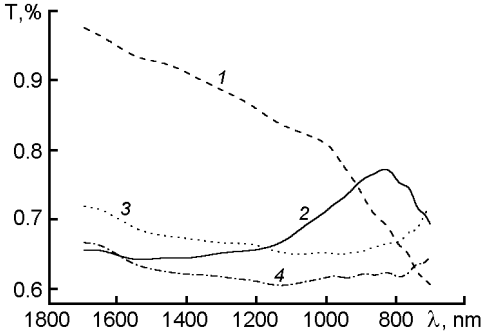

Fig. 4. Absorption spectra of α-C:N films grown at various substrate temperatures (КТ series): *1* — 150 °C; *2* — 200 °C; *3* — 250 °C; *4* — 350 °C.

an increased ratio of sp^3/sp^2 hybridized sites and causes the growth of more ordered and high-quality structures [2]. Spectra of the КТ series films obtained at various substrate temperatures and irradiated only by UV component of the lamp spectrum are shown in Fig. 4. It is seen that as the substrate temperature increases, the film transparency in the IR range decreases considerably. Perhaps this is related to formation of current-carrying clusters in the film structure at temperature elevation. For the film grown at the substrate temperature T = 200°C, a substantial transparency enhancement is observed in the range of 800 nm, that demands a further research.

The work results suggest that the UV-irradiation of the film growing surface is effective in increased mobility (excitation) of radicals that are responsible for the film growth and provides an increased efficiency of graphite phase etching, improved structure ordering, and enhanced film quality without significant complication of the growing technology.

References

1. R.W.Lamberton, S.M.Morley, P.D.Maguire et al., *Thin Solid Films*, **333**, 114 (1998).
2. V.N.Varyukhin, R.V.Shalaev, S.-C.Yu et al., *Jap. J. Appl. Phys.*, **41**, L1393 (2002).
3. G.M.Guro, G.A.Kaluzhnaya, T.M.Mamedov et al., *Zh. Eksp. Teor. Fiz.*, **77**, 2366 (1979).
4. Y.-S.Jin, T.Shibata, Y.Matsuta et al., *Thin Solid Films*, **345**, 18 (1999).
5. B.Dischler, A.Bubenzer, P.Koidl, *Appl. Phys. Lett.*, **42, 636 (1983).**

Вплив УФ опромінення на структуру та властивості алмазоподібних плівок α-C:N

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Представлено результати дослідження впливу УФ- і видимого випромінювання невисокої потужності (до 1 Вт/см^2) на структуру і властивості алмазоподібних плівок нітриду вуглецю α-C:N у процесі їхнього росту. Виявлено, що УФ-опромінення ростової поверхні плівок ефективно для травлення графітної фази, веде до росту структурної упорядкованості плівок і поліпшує їхню якість.