METHODS OF PRODUCTION, STRUCTURE, AND PROPERTIES OF FILM MATERIALS BASED ON THE CARBON—NITROGEN SYSTEM (SURVEY)

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About 50 papers devoted to producing and investigating the properties of carbon nitride films are critically reviewed. It is shown that reasonable experimental confirmation of synthesis of the hypothetical \( \beta\)-C\(_3\)N\(_4\) does not yet exist. Carbon nitride films can be produced practically by all PVD and CVD methods. They may contain up to 50% nitrogen, have an amorphous structure, and atoms in carbon nitride sp\(^2\)-bonded. The microstructure of amorphous CN films is mostly based on two types of clusters—cyanogen polymers and graphite-like domains with carbon atoms partially substituted by nitrogen. The relation between two microstructure types depends on the deposition conditions and crucially influences the film properties. The smaller the graphite-like clusters size and the more chaotically they are oriented in the film the harder will be the film. The factor which influences most the type of film microstructure and properties is the ion bombardment of the film during the deposition. The small friction coefficient, high elasticity, and relatively high hardness of nitride carbon films may make them useful as protective coatings of a storage medium in computers.

There are several forms in which carbon combines with nitrogen. These are: gas cyanogen \((\text{CN})_2 = \text{C}_2\text{N}_2\), which has a linear molecule; paracyanogen, which is a polymer \(-\text{(CN)}_n-\) obtained when cyanogen is polymerized by exposure to ultraviolet light or heating above 500°C; hexacyanogen, another polymer of cyanogen, which consists of plane hexagons alternately containing atoms of N and CCN groups. Finally, there is carbon nitride \(\text{C}_3\text{N}_4\), which is a porous amorphous substance; it can be obtained by the reaction \(2\text{S(CN)}_2 = \text{CS}_2\uparrow + \text{C}_3\text{N}_4\). When heated to the red-hot state (800-850°C), carbon nitride decomposes into cyanogen and nitrogen [1].

In a study reported in the literature in 1990, calculations were performed to determine the parameters of the structure of the hypothetical structural modification of carbon nitride \(\beta\)-C\(_3\)N\(_4\), isomorphic to phase \(\beta\)-Si\(_3\)N\(_4\), as well as some of its mechanical and electrical properties [2]. The calculations showed that the elastic modulus of the hypothetical nitride is comparable to that of diamond. It also followed from the calculations that the interatomic bonds in carbon nitride should be more covalent than in \(\beta\)-Si\(_3\)N\(_4\) and have a high degree of sp\(^3\)-hybridization.

The attractive properties of the new hypothetical compound and the seeming simplicity of synthesizing it were the deciding factors in the start of a scientific marathon to synthesize and study films based on carbon and nitrogen. Today, we know of more than 50 studies devoted to technologies for their synthesis by nearly every possible method of physical and chemical vapor deposition. The properties of the films have also been examined.

In this survey, we critically analyze these investigations. The goal of the analysis is to evaluate the possibilities of various methods of synthesizing films of carbon nitride and their practical use, as well as to determine the feasibility of actually obtaining the \(\beta\)-C\(_3\)N\(_4\) phase by film production methods.

All of the methods of obtaining films of carbon nitride can be conditionally divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD). In the last two decades, chemical methods of deposition have been used more and more with plasma activation of process by inducing an electric discharge in gases (PA CVD — plasma-activated CVD). This development has brought PVD and CVD technologies closer together, since nearly all of the physical methods also
involve the use of an electric discharge in a gas phase. One of the few significant differences in the two types of methods is the presence of undesirable chemical elements in the carrier gases containing the required elements in CVD. This feature has had a marked effect on the composition of CVD films of carbon nitride, since hydrogen invariably also turns out to be present in the film.

**Carbon Nitride Films Deposited by PVD Methods.** We will conditionally divide the physical vapor deposition methods used to obtain films of carbon nitride into three groups: methods based on the principle of cathode sputtering (sputtering methods); methods employing ion sources — IBAD (ion-bombardment-assisted deposition); other, less frequently used methods of film production.

The methods most commonly used to deposit CN_x films are reactive sputtering methods: RF-diode and RF-magnetron, and DC-magnetron (magnetron sputtering on direct current). The popularity of these technologies stems from the fact that they have been studied in great detail and are well-established as film-production methods in industry.

The RF-diode sputtering of graphite targets is done at a working-gas pressure \( P_f = 1.5-6 \) Pa (this gas usually being an Ar—N_2 mixture or pure N_2) and a substrate temperature 600°C \( \geq T_s \geq 80^\circ \)C. According to various studies, the growth rate of the nitride film under these conditions varies within the range 0.01-0.1 nm/sec, while its relative content of nitrogen is within the range 0.1 \( \leq N/C \leq 1.0 \) [3-9] and averages 0.5 \( \leq N/C \leq 0.8 \). Researchers have observed that oxygen is the main impurity in these films. The oxygen content reported in the various literature sources ranges from 1 to 9%.

The use of magnetron sputtering in the DC-modification has made it possible to significantly reduce the pressure of the working gas (\( P_f = 0.2-1.0 \) Pa), which has in turn reduced the oxygen content in CN_x films (oxygen content has usually been lower than the sensitivity threshold of the research methods used [10-12]) and increased film growth rate by a factor of 3-5 on the average [13, 14]. However, the average nitrogen content in CN_x films obtained by DC-magnetron sputtering is lower than in films obtained by RF-diode and RF-magnetron PVD, amounting to N/C \( \sim 0.3-0.4 \) [10-12, 15, 16]. This has been attributed to at least two factors: the greater probability that highly volatile nitrogen will be desorbed from the condensation surface by fast-moving particles of the plasma, whose mean free path has been increased several-fold as a result of the reduced pressure of the working gas with a magnetron-type discharge; the lower efficiency of the processes of dissociation and ionization of molecules (especially molecules of nitrogen, which ensure the formation of the atomic nitrogen that participates in the formation of the nitride film) in the direct-current discharge compared to an RF-discharge.

In studies of the effect of the working gas composition on the composition of carbon nitride films, it has been found that an increase in the relative nitrogen content in the Ar—N_2 mixture has been accompanied by an increase in film growth rate [5, 9, 12, 17, 18]. This effect is related to the fact that physical sputtering is augmented by chemical sputtering (etching) of the carbon target by particles of nitrogen, which increases deposition rate.

The rate of growth of nitride films was also found to depend on the condition of the substrate. Growth rate decreased if the film was formed under ion bombardment of the surface when a negative voltage was supplied to the substrate [19]; growth rate also depended on substrate temperature, with the rate either decreasing to zero at \( T_s > 450^\circ \)C [3] or at \( T_s > 600^\circ \)C [9, 12]. The beginning of a sharp decrease in nitrogen content was also seen at \( T_s = 600^\circ \)C [10, 11, 19].

The structure of carbon nitride films synthesized by sputtering methods generally consists of an amorphous matrix which sometimes contains crystalline inclusions ranging in size from 1 nm [20] to 50 nm [21]. It has not yet been possible to definitely determine the structure of the inclusions [3-8, 20, 21]. The volume of the crystalline phase is no greater than 5% of the total volume of the film. It was reported in [9] that the structure of crystallites seen in the amorphous matrix corresponds to the phase \( \beta-C_3N_4 \), although the composition of the film was only \( \sim C_{0.8}N_{0.2}O_{0.1} \).

The possibility of variation of the microstructure of the amorphous phase of CN_x films was established by high-resolution transmission electron microscopy and infrared, Raman, and photoelectron spectroscopy. For example, transmission electron microscopy [10-12] showed that the microstructure of amorphous CN_x films is similar to that of films of the turbostratic phases of boron nitride or carbon. The authors of [20] arrived at a similar conclusion in studying cross sections of films by the same method. The results of the latest studies of the amorphous phase of CN_x films [22], conducted by high-resolution transmission electron microscopy and electron energy loss spectroscopy, indicate that the structure of these films may be fullerene-like in character.

The infrared spectra of carbon nitride films obtained by sputtering contain lines with maxima of 1370 \( \pm 20 \) cm\(^{-1}\) and 1570 \( \pm 20 \) cm\(^{-1}\), which corresponds to the D- and G-peaks in amorphous carbon films (a-C). The spectra also contain the line 2200 \( \pm 20 \) cm\(^{-1}\), which is related to vibrations of the C≡N chemical bond. The spectra obtained from Raman scattering also contain the D- and G-peaks seen in the spectra of a-C films. This indicates the structural affinity of certain