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Synthesis of Carbon Nitride Films by Double-Pulse Laser Ablation

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Abstract—Carbon nitride films have been synthesized by double-pulse laser ablation of graphite in nitrogen plasma. The films produced in both single- and double-pulse experiments have been studied by X-ray photoelectron spectroscopy and X-ray diffraction. The degree of crystallinity and the content of sp^3-hybridized carbon atoms in the films obtained by double-pulse laser ablation turn out to be higher than in the films deposited by the conventional one-pulse method.

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The possibility of the existence, under normal conditions, of materials based on different modifications of carbon nitride, some of which could have valuable mechanical properties, has been predicted in [1, 2]. For example, the β phase of crystalline carbon nitride C_3N_4 (β-C_3N_4), whose structure is analogous to that of β-Si_3N_4, should be almost as hard as diamond. This prediction has stimulated numerous experimental works dealing with the synthesis of superhard crystalline β-C_3N_4. However, the individual β-C_3N_4 phase has not heretofore been synthesized on a preparative scale, despite the use of different methods. Only powders and films have been synthesized in which different crystalline phases (including superhard β-C_3N_4) exist as inclusions in the amorphous CN matrix [3, 4]. Nevertheless, these films are already used as wear-resistant coatings [5, 6].

An efficient method of synthesis of CN films is laser ablation of graphite in a nitrogen atmosphere followed by chemical vapor deposition on different collectors (substrates) [7]. The formation of gaseous nitrogen–carbon compounds (C_xN_y) during graphite ablation in nitrogen has been demonstrated by time-of-flight mass spectrometry. It turned out that C_3N_4 molecules are the major product of chemical reactions if the second harmonic of a solid-state Nd:YAG laser ($\lambda = 532$ nm) was used for graphite ablation [8]. Low contents of crystalline phases of nitrogen–carbon compounds (including β-C_3N_4) in CN films deposited by laser ablation can be explained as follows: Films with a high degree of crystallinity, for example, diamond films, are obtained by laser ablation of graphite in a vacuum (residual pressure in the reactor is ~10 Pa). Under these conditions, the velocity of the ablated matter (graphite) motion toward the substrate is high and is mainly determined by the power density of laser radiation at the target surface and the distance between the target and the substrate. Therefore, it is possible to choose conditions under which the velocity of particles impinging on the substrate will be optimal for the formation of crystal structures in the resulting film. The role of the kinetic energy of particles on the surface of the substrate in synthesis of films by vapor deposition methods was discussed in [9, 10].

For deposition of carbon nitride films, graphite ablation in nitrogen atmosphere (the pressure in the reactor is ~10–1000 Pa) by short (10^{-8} s) laser pulses is used. As a result of an explosive formation of laser plasma on the graphite surface, a shock wave arises in the gas. This wave propagates from the target (graphite) to the substrate at a velocity that exceeds the velocity of the motion of particles of expanding laser plasma toward the substrate. This shock wave, when reflected from the substrate, changes its direction to the opposite one. The interaction of the reflected shock wave with the particles moving toward the substrate (components of the expanding laser plasma, products of chemical reactions of nitrogen with carbon particles) leads to the deceleration and, sometimes, termination of their motion toward the substrate [11].

Hence, the particles that form films arrive to the substrate surface with considerably lower velocities as compared to the velocities of particles during laser ablation in vacuum. As a result, the kinetic energies of film-forming particles on the substrate surface turn out to be insufficient to ensure their motion across the surface. This leads to the predominant formation of amorphous rather than crystal structures [12].

To increase the velocity of the particles arriving to the substrate during laser ablation, it has been sug-

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gested to use series of double rather than single (conventionally used) pulses, i.e., two successive laser pulses with radiation being focused into the same spot on the graphite surface. In this case, the expanding laser plasma acts as a piston accelerating (giving rise to) the motion of the particles that were formed by the first laser pulse and whose movement toward the substrate was decelerated (terminated) by the reflected shock wave. For the laser plasma and shock wave formed by the second pulse to act as a piston, appropriate time delays between the arrivals of the first and second laser pulses to the target surface should be chosen.

EXPERIMENTAL

Radiation of two solid-state Nd:YAG lasers was focused on the surface of spectrally pure graphite placed in a reactor. The substrate, 10 × 10 mm, was a thin plate of monocrystalline silicon Si(100). Before deposition, the substrate was washed with solvents (acetone and ethanol) in an ultrasonic bath and placed at a distance of 20 mm from the graphite surface. The reactor was evacuated to a pressure of ~10 Pa and filled with spectrally pure argon to a pressure of ~$(4–5) \times 10^2$ Pa. Then, a glow discharge was ignited, the substrate surface serving as the cathode. The substrate was cleaned by sputtering with argon ions for 15 min, and the reactor was again evacuated to ~10 Pa. The reactor was filled with nitrogen (impurity content below 2ppm) to a pressure of ~1.5×10^2 Pa, and a glow discharge was ignited, with the graphite target as the cathode and a graphite electrode as the anode. The current in the discharge was maintained at ~10 mA. Irradiation of the graphite surface with laser pulses leads to the formation of a carbon plasma. The products of the expanding carbon plasma were introduced into the nascent nitrogen plasma. The power density of laser radiation on the graphite surface was ~2×10^8 W/cm^2. The pulse repetition rate was 10 Hz. The time delay of the second laser pulse with respect to the first one was varied from 2 to 50 μs (double-pulse regime). The spectra below were recorded for films obtained by the double-pulse technique with the time delay of the second pulse of 10 μs. The synthesis time was 30 min.

The characteristics of the films synthesized in single- and double-pulse experiments were studied by X-ray photoelectron spectroscopy and X-ray diffraction. X-ray diffraction spectra were recorded on a DRON-4 diffractometer.

The X-ray photoelectron spectra were recorded on a Kratos XSAM-800 spectrometer using MgK_α excitation ($h\nu$ = 1253.6 eV) in the constant relative resolution mode ($\Delta E/E$ = const) at a residual pressure of 10^{-8} Pa. The X-ray tube power during measurements did not exceed 90 W (15 kV, 6 mA).

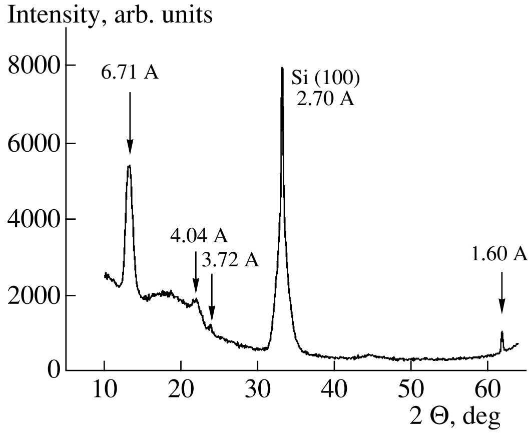

Fig. 1. X-ray diffraction spectrum of a film synthesized by the double-pulse technique.

RESULTS AND DISCUSSION

X-ray Diffraction

The spectra of the films synthesized using the single-pulse technique show only one reflection ($2\theta = 33.2°$) from the Si(100) substrate. The spectra of the films obtained by the double-pulse technique (Fig. 1) show reflections that point to the formation of crystalline phases in the films. However, the number of reflections observed is small and their interpretation turned out to be impossible.

Based on data in [13] where reflection positions and intensities were calculated for all theoretically predicted modifications of carbon nitride [2], we concluded that the synthesized films contain crystalline phases of previously unknown modifications. The possibilities of the existence of new modifications of solid carbon nitride have been discussed in [7].

X-ray Photoelectron Spectroscopy (XPS)

XPS studies were carried out to compare the contents of sp^3 C atoms in the films synthesized in single- and double-pulse experiments. It is worth noting that chemical bonds in the predicted superhard CN material, whose structure corresponds to the crystalline phase β-C_3N_4, are tetrahedral (sp^3 bonds); therefore, a change in the number of sp^3 carbon atoms will point to a change in the degree of crystallinity of the films.

Some difficulties of comparison of the X-ray photoelectron spectra of CN films obtained under different conditions are associated with their insufficient conductivity, which leads to accumulation on their surface of electric charge during measurements. Since the electric characteristics of the films depend on the synthesis conditions, the internal reference method was used for determining the binding energies. The C1*s* peak of the amorphous phase with C–C bonds was used as the internal reference. The C1*s* binding energy was taken to be 285.5 eV.

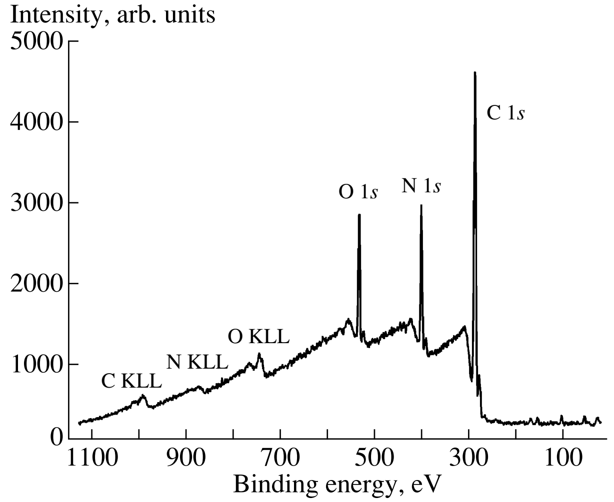

Fig. 2. General X-ray photoelectron spectrum of a film synthesized by the double-pulse technique.

Elemental composition. The elemental composition of the films was calculated by measuring the relative intensities of the spectral lines of the element core levels in general spectra with taking into account the ionization cross sections of the core level of each element. The nitrogen content of the films changed from 10 to 30 at % depending of synthesis conditions. The concentrations of nitrogen in the films synthesized in single- and double-pulse experiments were the same with the experimental error.

The existence of oxygen in the films can be caused by experimental conditions: after the films were synthesized in the reactor, they were placed in an XPS chamber in air. Figure 2 shows the general spectrum for one of the synthesized CN films.

Interpretation of the fine structure of C1*s* and N1*s* lines. In spite of numerous works [3, 14], no unambiguous decomposition of the C1*s* and N1*s* peaks in the CN films is available in the literature. The experimental spectra show broad asymmetric lines, which is evidence of the existence in the films of different types of chemical bonds between nitrogen and carbon atoms. Indeed, both carbon and nitrogen can form different chemical bonds. For example, carbon forms tetrahedral, trigonal, and linear structures, which correspond to sp^3, sp^2, and *sp* hybridization, respectively. Nitrogen atoms can form an even larger number of configurations due to the presence of the lone electron pair and its participation (nonparticipation) in the formation of chemical bonds. Comprehensive analysis of numerous literature data on the influence of chemical environment on the binding energy of core levels of C1*s* atoms in CN compounds allowed the authors of [14] to conclude that the reliable decomposition of the C1*s* peak in the spectrum of CN films obtained by vapor deposition methods should consist of only three components.

We agree that, in the absence of references (the lack of the necessary number of individual phases for changes) and high-precision quantum-chemical calculations of energy levels in CN films, as well as taking into account the possibilities of conventional X-ray photoelectron spectrometers, it makes no sense to consider the interpretation of C1*s* and N1*s* peaks in finer details than it was suggested in [14].

Figures 3 and 4 show the results of decomposition of the C1*s* and N1*s* XPS peaks for the films synthesized by different laser ablation techniques.

Decomposition was carried out using the XPSPEAK41 program. The background was subtracted using the Shirley algorithm. The decomposition results are consistent with the literature data. For example, let us compare the decomposition of the C1*s* spectrum for the film synthesized by the double-pulse technique (A) with the decomposition of the C1*s* spectrum (B) reported in [15] where the C1*s* binding energy of carbon existing in all samples was also taken to be 285.5 eV.

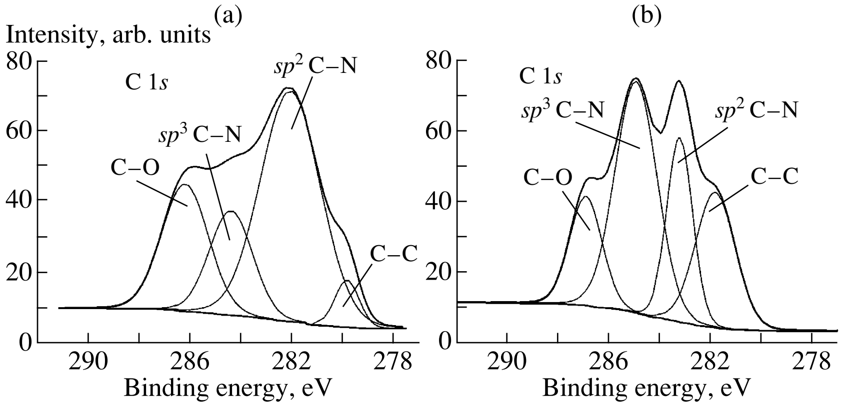

Fig. 3. X-ray photoelectron C1*s* spectra of films obtained by (a) single- and (b) double-pulse techniques.

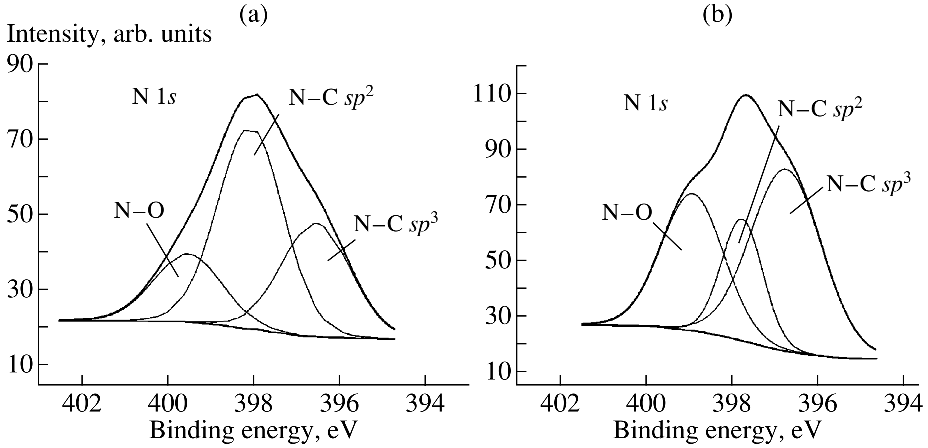

Fig. 4. X-ray photoelectron N1*s* spectra of films obtained by (a) single- and (b) double-pulse techniques.

The binding energies (eV) are

285.5 (C), 286.9 (Csp^2), 288.6 (Csp^3), and 289.9 (C–O) for film A and

285.5 (C), 286.3 (Csp^2), 287.2 (Csp^3), and 289.6 (C–O) for film B.

Assuming that the areas of the components in the decomposition of the C1*s* and N1*s* spectra are proportional to the concentrations of corresponding structural units in the film, we calculated the increase in the concentration of sp^3-hybridized C atoms with respect to the concentration of sp^2-hybridized C atoms in going from the single- to double-pulse mode. This increase is about five.

We also calculated the relative composition of the phase in which the carbon atoms have sp^3 hybridization and the nitrogen atoms are bonded to these carbon atoms. Based on the decomposition results, we calculated that this ratio is 0.54 and 0.56 for the films obtained in the single- and double-pulse experiments, respectively. These values correspond to the N/C ratio. Thus, we can conclude that, under the experimental conditions used, a new phase is formed whose composition corresponds to the formula C_2N. The properties of this phase have to be determined.

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