Photoacoustic detection of the parameters of laser vaporisation of amorphous carbon nitride

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Intense laser vaporisation of amorphous carbon nitride of the composition $C_3N_{4.2–4.3}$ makes it possible to consider it as a promising precursor for obtaining the superhard crystalline phase of this compound, β-C_3N_4, by laser deposition.

Intense attention of researchers in the field of materials science has recently been focused on nitrogen–carbon materials due to the prediction of the existence of the crystalline phase β-C_3N_4,[1] whose calculated bulk modulus and hardness exceed those for diamond.[2]

An important parameter of nitrogen–carbon materials is the nitrogen content;[3] when this is increased to the 57% optimum for β-C_3N_4, the mechanical characteristics of the nitrogen–carbon material improve markedly. However, bonding of nitrogen is still a serious problem due to the necessity of its preliminary activation by plasma-chemical methods.[4,5] In this work, we suggest a way to solve this problem by using a nitrogen–carbon material precursor of the paracyan class, whose chemical composition, $C_3N_{4.2–4.3}$, is close to the optimum one for subsequent chemical modification into the crystalline phase β-C_3N_4.

We studied the possibility of using amorphous carbon nitride, a polymeric material with a *symm*-heptazine type monomer (Figure 1) cross-linked by bridging NH groups, for the laser-chemical synthesis of β-C_3N_4. Samples of amorphous carbon nitride were obtained by thermal decomposition of mercuric rhodanide at 180 °C in an inert gas environment:

$$2Hg(SCN)_2 \longrightarrow CS_2\uparrow + 2HgS\downarrow + C_3N_4\downarrow \qquad (1)$$

It was found by differential thermal analysis that the starting reagent rapidly decomposes with gas evolution and a significant thermal effect. The composition of the gaseous reaction products was determined on a quadrupole mass spectrometer with pulsed gas injection. The gas was found to contain mainly neutral molecules of CS, CS_2 and S_2 with admixtures of H_2O and C_xH_y, which directly indicates that the CS_2 molecule is formed due to reaction (1). The solid residue was purified from HgS by heating at 200–300 °C, so that the presence of the latter was not observed in the X-ray spectra. The structure of the final product with a density of 2.2 g cm^{-3} was studied by IR spectroscopy. The IR spectra obtained display an absorption band at 800–1800 cm^{-1} consisting of separate peaks at 845, 1215, 1290, 1445 and 1580 cm^{-1}, which characterise the monomeric unit of the material, the *symm*-heptazine system (Figure 1). Chemical analysis showed the molecular formula of the amorphous carbon nitride to be $C_3N_{4.25}$.

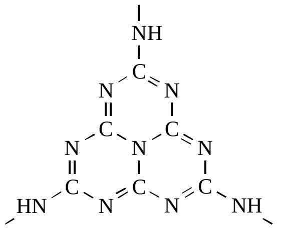

Figure 1 Structural formula of a monomeric unit (*symm*-heptazine system) of amorphous carbon nitride.

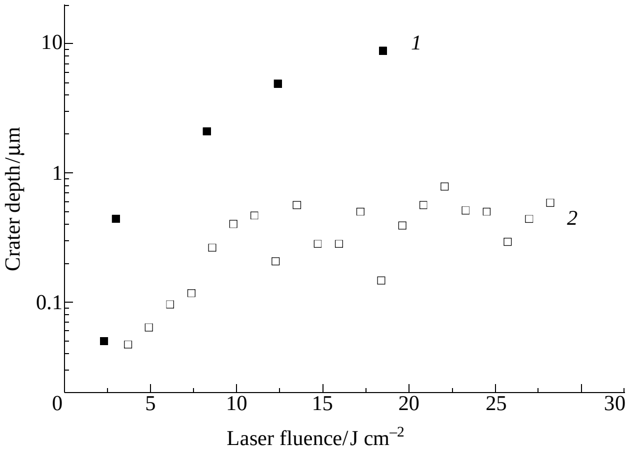

Figure 2 Dependence of the mean crater depth in an amorphous carbon nitride target (*1*) and in polycrystalline graphite (*2*) per laser pulse on fluence (the relative standard deviation is 20%).

A number of parameters were determined by the photoacoustic method, namely, the absorption (extinction) coefficient at the wavelength of laser irradiation and the velocities of ultrasonic waves, which determine the character of the amorphous carbon nitride vaporisation under laser irradiation. In the experiments we used a photoacoustic device,[6] which enabled measurement of the sound velocity and the mean crater depth during a laser pulse. A pulsed Nd:YAG laser provided an output energy of 5 mJ per pulse of the second harmonic irradiation (532 nm) in the TEM_{00} mode at 6% stability, pulse length (FWHM) $\tau_{Las} = 25$ ns and pulse repetition rate $f_{Las} = 12.5$ Hz. A portion of irradiation was fed to a photodiode–pyroelectric system by a beam splitter in order to synchronise the system of recording and control of the laser irradiation energy in each pulse. After reducing the main irradiation to the required magnitude and focusing, it was directed to the target normal to its surface. Bulk absorption of irradiation in the target created a three-dimensional thermoacoustic source of ultrasound, which was recorded on the opposite side of the target in the idle mode by a piezoelectric sensor and an oscilloscope. To make photoacoustic measurements, the powder of amorphous carbon nitride was compressed at a pressure of 50 atm into pellets with a 1.6 g cm^{-3} bulk density.

The propagation velocity of longitudinal acoustic waves in an amorphous carbon nitride target is not only an important characteristic of the latter but also a necessary parameter for the determination of the mean crater depth per laser pulse. Because of the significant penetration depth of optical-region irradiation into amorphous carbon nitride targets, sound velocity measurements were made using a surface acoustic source excited by pulse laser irradiation in a thin copper foil plate [L(Cu) as compared with the target thickness L_0, 0.03 mm << 1.1 mm]. The foil was attached to the front side (the one opposite to the acoustic detector) of the target. As a result, the total time of propagation, T_d, of a longitudinal acoustic wave from the source to the detector in 0.5 and 1.1 mm thick amorphous carbon nitride pellets was 1.4 and 1.6±0.1 μs, respectively. Using the formula

$$T_\mathrm{d} = \frac{L(\mathrm{Cu})}{V_\mathrm{s}(\mathrm{Cu})} + \frac{L_0}{V_\mathrm{s0}} + 1.2$$

and the sound velocity in copper, $V_\mathrm{s}(\mathrm{Cu}) = 3600\ \mathrm{m\ s^{-1}}$, this gives the sound velocity in the amorphous carbon nitride target, $V_\mathrm{s0} = 2700 \pm 300\ \mathrm{m\ s^{-1}}$, with an accuracy to within the constant of wave propagation time in the photoacoustic detector (1.2 μs).

When laser irradiation acts directly on the target surface (without the copper plate), the delay of acoustic wave arrival to the detector (at the level of 5% of the acoustic signal amplitude) decreased by 0.15 μs with respect to the irradiation pulse, which determined the acoustic source size in the target $V_\mathrm{s0} \times 0.15\ \mu\mathrm{s} = (3\text{–}4) \times 10^{-4}\ \mathrm{m}$ $[(3\text{–}4)\alpha^{-1}]$ and the extinction coefficient at the wavelength of 532 nm, $(1.0 \pm 0.1) \times 10^4\ \mathrm{m^{-1}}$.

The mean crater depth per laser pulse, X, was measured by a procedure used in previous work,[6] in which X was expressed through the sound velocity in the target and the decrease ΔT_d (over N irradiation pulses during laser irradiation time Δt) in the propagation time of the acoustic wave through the target from the acoustic source at the crater bottom to the detector as the crater deepens

$$X = \frac{V_\mathrm{s0} \Delta T_\mathrm{d}}{\Delta t\, f_\mathrm{Las}}$$

The results of calculating X at various magnitudes of laser fluence ε ($\mathrm{J\ cm^{-2}}$) show that the bulk character of irradiation absorption in the depth region (α^{-1}) up to 100 μm determines the threshold character of destruction of the amorphous carbon nitride target with a threshold value $\varepsilon_\mathrm{thr} = 2\ \mathrm{J\ cm^{-2}}$ (Figure 2). Above the destruction threshold, the magnitude of X rapidly increases with increasing fluence due to an increase in the temperature of specimen destruction.

The mean crater depth per pulse, and hence the amount of vaporised material, are more than one order of magnitude higher for amorphous carbon nitride than the corresponding parameters determined by the photoacoustic method[6] for polycrystalline graphite (Figure 2) widely used for deposition of carbon nitride films under nitrogen discharge conditions.[4] This suggests that amorphous carbon nitride undergoes intense vaporisation under laser irradiation and has low thermal stability in comparison with elementary carbon in the form of graphite.

Thus, owing to the high efficiency of laser vaporisation of amorphous carbon nitride in comparison to the graphite materials widely used at present for laser deposition of β-C_3N_4 films, and considering the similarity of the molecular formula of this compound, $C_3N_{4.2\text{–}4.3}$, to the desired composition, it may be regarded for now as the most promising precursor for obtaining the crystalline phase of superhard carbon nitride by this method. On the other hand, the practical application of amorphous carbon nitride for this purpose still requires a study of the composition of the products of laser vaporisation of this material and its effect on the composition and structure of the carbon nitride films deposited.

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