Thermodynamic characteristics of the laser evaporation of amorphous carbon nitride

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A study of the thermodynamics of laser evaporation of amorphous carbon nitride makes it possible to predict the optimum conditions for the laser deposition of crystalline films of superhard carbon nitride.

Numerous recent studies into the synthesis of nitrogen–carbon materials, initiated by the prediction of the existence of a superhard crystalline phase of β-C_3N_4,[1] touch on fundamental problems of the thermodynamics of evaporation and condensation of these compounds, such as the deposition temperature of films, vapour composition, *etc*.[2–4] However, such studies are still really scant and generally not focused, thus on the whole the problem of synthesising the crystalline phase of β-C_3N_4 remains as yet unsolved.

In this work, we used laser evaporation and the photoacoustic method for detecting its parameters, to study over the range 400–800 K the evaporation curve of amorphous carbon nitride, a polymer with a *symm*-heptazine monomeric moiety and a molecular formula $C_3N_{4.25}$. We also determined the temperature dependence of the heat of evaporation of the material and calculated the probable vapour composition. The data obtained allowed us to make assumptions about the range of optimum conditions for the laser deposition of crystalline films of superhard carbon nitride.

Using the photoacoustic method,[5] the following physical characteristics of an amorphous carbon nitride specimen with a bulk density of $\rho_s = 1.6$ g cm^{-3} were determined: the propagation velocity of acoustic waves, 2700±300 m s^{-1}; the extinction coefficient, α(532 nm) = (1.0±0.1)×10^4 m^{-1}; and the dependence of mean crater depth $X(\varepsilon)$ per laser pulse on the fluence (Figure 1). The reflection coefficient of the material, R(532 nm) = 0.07±0.02, was determined by reflectometry.

In the case of pulse laser evaporation, the experimentally measured crater depth per laser pulse, X, depends on the rate of movement of the evaporation frontier in the target, V_{ev}, by a differential equation:

$$V_{ev}[T(t)] = \frac{dX}{dt} \quad (1)$$

On the other hand, the absolute rate theory gives the following formula for the rate of movement of the evaporation frontier:

$$V_{ev}(T) \approx C\frac{kT}{h}\exp[-\Delta\nu H(T)/kT] \quad (2),$$

where C is a constant and $\Delta\nu H(T)$ is the evaporation heat of amorphous carbon nitride.

The evaporation temperature for a weakly absorbing surface can be calculated by the equation

$$T(t) = T_0 + \frac{(1-R)\alpha V_m \varepsilon(t)}{C_p} \quad (3),$$

in which the first term is the starting temperature of the specimen (293 K), and the second corresponds to temperature

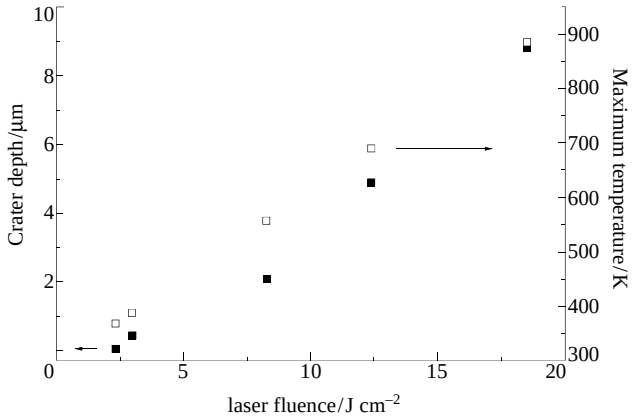

Figure 1 Dependence of mean crater depth during an irradiation pulse and maximum temperature on the surface of an amorphous carbon nitride target on irradiation fluence.

increase during a laser pulse with an increase in fluence, $\varepsilon(t)$, due to laser-induced heating (for a molar volume of V_m = 8 cm^3 mol^{-1} and a heat of C_p = 25 J mol^{-1} K^{-1}). Obviously, due to the high absorption depth in the material studied, the maximum evaporation temperature $T(\tau)$ is achieved at the end of the laser pulse (Figure 1).

Substituting equations (1) and (3) into (2), we obtained an expression for the heat of evaporation $\Delta\nu H(T)$ of amorphous carbon nitride in the form

$$\Delta\nu H(T) = RT^2\left(\frac{1}{V_{ev}}\frac{dV_{ev}}{dT} - \frac{1}{T}\right) \quad (4)$$

Taking into account the fact that the experimentally measured $X(\tau)$ is an integral value, V_{ev} was calculated through finite differences of X and ε for the average value $\varepsilon_{av} = (\varepsilon_{i+1} + \varepsilon_i)/2$ and temperature $T(\varepsilon_{av})$

$$V_{ev}(T_{av}) = \frac{X_{i+1} - X_i}{\tau[(\varepsilon_{i+1} - \varepsilon_i)/\varepsilon_{i+1}]} = \frac{\varepsilon_{i+1}}{\tau}\frac{dX(\varepsilon_{av})}{d\varepsilon} \quad (5)$$

where the physical meaning of the denominator in the middle part of the equation corresponds to a laser pulse duration with integral fluence ε_{i+1}, during which the crater deepens by $X_{i+1} - X_i$ as the fluence increases by $\varepsilon_{i+1} - \varepsilon_i$. The calculated magnitudes of T_{av}, $V_{ev}(T_{av})$ and $\Delta\nu H(T_{av})$ are presented in Table 1.

The heats of evaporation per atom of amorphous carbon nitride in the temperature range 400–700 K (Figure 2) correlate with the heats of formation of C_2N_2 molecules (300 kJ mol^{-1})[6]

Table 1 Experimental and calculated parameters of the laser evaporation of amorphous carbon nitride.

ε/J cm^{-2}	$T(\tau)$/K	ε_{av}/J cm^{-2}	T_{av}/K	$\Delta\nu H(T_{av})$/kJ mol^{-1}	vapour composition, Z/atoms per cluster	$P_s(T_{av})$/kbar
2.3±0.2	367±72	2.6±0.2	376±66	69±56	4	0.14±0.08
3.0±0.2	388±73	5.6±0.4	472±81	16±11	22	0.41±0.25
8.3±0.6	557±86	10.3±0.7	622±107	13±11	26	0.92±0.53
12.4±0.8	689±104	15.4±1.1	786±127			1.81±1.10
18.5±1.3	885±152					

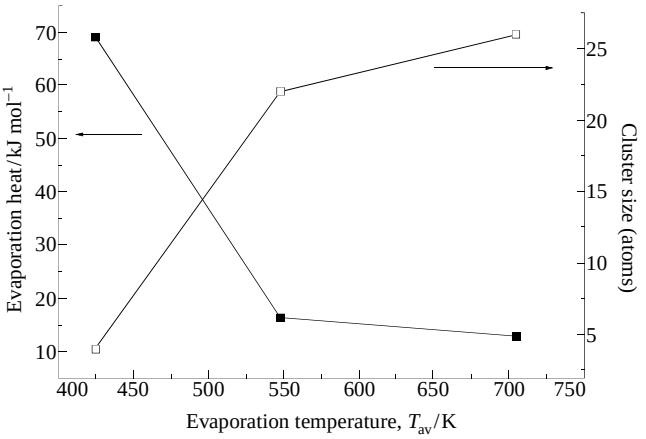

Figure 2 Dependence of evaporation heat and mean cluster size on temperature for amorphous carbon nitride.

and larger clusters, whose probable sizes $(CN)_{z/2}$ can be found approximately from equation (6)

$$Z(T) = \frac{E}{\Delta vH(T)} \quad (6),$$

where $E \approx 340$ kJ mol^{-1} is the mean energy of atom (carbon or nitrogen) removal from amorphous carbon nitride, as calculated from the known energies of CN bonds of various multiplicities for the monomeric amorphous carbon nitride moiety, *symm*-heptazine.

Due to a decrease in the evaporation heat of amorphous carbon nitride with increasing temperature, the dependence $Z(T)$ (Figure 2) displays a monotonic increase in the size of vaporised fragments from C_2N_2 (at 400 K) to clusters with monomer size $(CN)_6$ (*symm*-heptazine moiety) and larger sizes $[(CN)_{11–13}]$ at 600–700 K. This effect most likely indicates the cooperative character of cluster formation near the critical point of the phase studied ($C_3N_{4.25}$) rather than the usual thermal desorption of monomers of a compound, since the latter always takes place at temperatures below the start of thermal decomposition of the compound (yield of monomeric fragments), which does not occur in our case (Figure 2). In fact, the structure of a compound in the critical region is a 'gas' of droplets (density fluctuations) whose size grows as the critical point is approached. Because of anomalous growth and interaction (correlation) of fluctuations, evaporation is a cooperative process and occurs on the scale of the whole system, the properties of a new phase (vapour) appearing through fluctuations differing by an infinitely small amount from those of the original phase (liquid). Therefore, the appearance of the new phase does not involve surface energy changes and the thermal effect of the phase transition is close to zero.[7]

The anticipated yield of relatively large clusters $(CN)_{11–13}$ during laser evaporation of amorphous carbon nitride in the temperature range of 600–700 K is of significant interest for developing the technology of laser deposition of superhard crystalline carbon nitride of the composition β-C_3N_4 from precursors of similar composition, since in this case congruent transfer of material during the deposition ensures the necessary composition of the deposited film with a high degree of homogeneity. Unfortunately, the structure of mixed medium-size nitrogen–carbon clusters has scarcely been studied to date. Hence, no substantiated assumptions can be made whether the use of $(CN)_{11–13}$ molecular forms is the optimum solution for the deposition of the β-C_3N_4 phase with retention of their structure because of the 'memory' effect of clusters in the film.

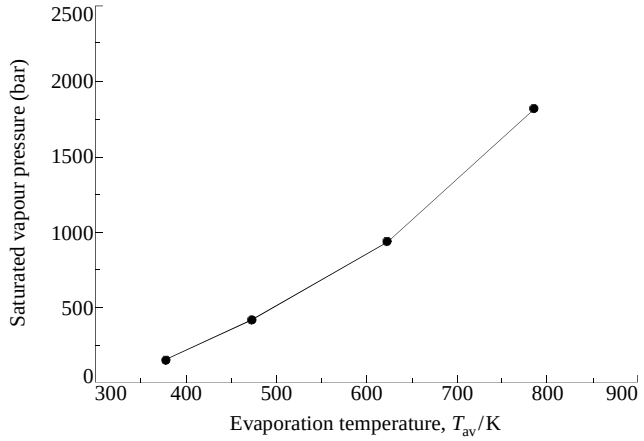

Figure 3 Dependence of saturated vapour pressure of amorphous carbon nitride on temperature.

An important issue in the deposition of films of nitrogen–carbon materials is the choice of deposition temperature.[4] If one assumes that the chemical composition and structure of an amorphous carbon nitride target heated by laser irradiation are similar to those of a carbon nitride film deposited on a heated substrate at high, near-critical evaporation and deposition temperatures, then model calculations of thermodynamic parameters of the evaporation of amorphous carbon nitride can be used for the prediction of optimum conditions for film deposition. For example, a calculation of the equilibrium saturated vapour pressure of the $C_3N_{4.25}$ phase in the range 400–800 K (Figure 3) by the formula[8]

$$P_s(T) = \rho_s V_{ev}(T) \sqrt{\frac{kT}{M_{(CN)_{z/2}}}} \quad (7)$$

showed that $P_s(T)$ increases rapidly in the range 700–900 K to reach 2000 atm, which is close to the characteristic critical pressures of the majority of materials, including carbon.[6] This fact makes it possible to assume that the substrate temperature during the deposition of nitrogen–carbon films should not exceed 600–700 K, otherwise the desorption rate may exceed the deposition rate,[4] which is determined by the evaporation temperature of the precursor material and by transfer efficiency. It is believed that from the viewpoint of deposition rate and composition of the film formed, the optimum mode is when the temperature of the precursor material (700–900 K) exceeds that of the deposition temperature (500–600 K).

It should be noted in conclusion that the assumptions regarding the optimum conditions for the deposition of crystalline films of superhard carbon nitride β-C_3N_4 have been made on the basis of processing the experimental data obtained. However, because of an interdependence of the thermodynamic parameters studied and the error accumulation in their computational determination, these assumptions acquire a character of prediction and direct confirmation is needed.

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