

Heat-induced polymerization of $a\text{-CN}_x$ films grown by Pulsed Laser Deposition.

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Abstract

A series of amorphous carbon nitride ($a\text{-CN}_x$) films have been prepared on silicon substrates by pulsed laser deposition. Films were heated from room temperature up to 900°C in 50°C steps. The chemical states and gas desorption were recorded simultaneously, as a function of temperature, by means of *in-situ* x-ray photoelectron spectroscopy (XPS) and quadrupole mass spectrometer. Nitrogen is incorporated to sp^2 -carbon structures in two-favored configuration: pyridinic and pyrrolic. The heat treatment induces a two-dimensioned polymerization that takes place upon rupture of the pyridinic and pyrrolic rings, followed by cycle-addition of nearby carbon rings and gasification of C_2N_2 and other species.

Introduction

Vast experimental efforts have been made to prepare carbon nitride materials. The impelling force of these works is the conjecture that a tetrahedral solid formed between carbon and nitrogen must have a high elastic bulk modulus. This prediction was made due to the high grade of covalence and short interatomic distance of the C-N bonds. A posteriori, this speculation was tested by several *ab initio* calculations using the $\beta\text{-Si}_3\text{N}_4$ as a prototype structure [1]. Results of these works suggest that a family of tetrahedral compounds exist that are feasible from a purely energetic point of view. Nevertheless, the experimental conclusion shows that crystalline compounds with the desired phases are difficult to prepare. The reason for this difficulty synthesis can be attributed to an opposing and energetically favorable process, which inhibits the formation of the four-coordinated carbon phases [2].

Experimental

The $a\text{-CN}_x$ films were grown on (111) *n*-doped silicon wafers at room temperature by ablating a high purity graphite target under different molecular nitrogen pressures. Target-substrate distance, laser energy, number of pulses, and pulse repetition rate were kept fixed at 10 cm, 800 mJ, 10,000 and 10 Hz, respectively. After completion of the deposition process, the growth chamber was evacuated to a

pressure of 10^{-8} Torr. At that point, the sample was translated to the adjacent analysis chamber.

Subsequently, the films were resistively heated with the aid of a programmable closed-loop controller, from room temperature up to 900°C in 50°C steps. The film evolution and outgases species were registered, simultaneously, in the thermal progression by means of XPS and quadrupole mass analyzer. XPS were collected after exciting the films with the Al K_α line (1486.6 eV). The instrumental resolution in the line C_{1s} is 1.1 eV, measured for highly oriented pyrolytic graphite. The experimental setup and sample preparation are thoroughly explained in ref 3.

Results

The core level binding energy (BE) of nitrogen basically consists of two well-resolved peaks centered at 398.1 eV, P_1 , and 400.1 eV, P_2 , with a width of ~ 1.8 eV, as it is shown in figure 1. In the same figure we can see the chemical state evolution as the temperature is raised, in this particular case, for a film deposited at 25 mTorr of N_2 . For the sake of clarity, only the curves at room, 400, 500, 750 and 900 °C temperatures are presented. The intensity normalization factor for this graph was taken from the integrated area under transition C_{1s} . Is obvious from this spectral progression that the nitrogen concentration in the film decreases. This effect is clearly seen in figure 2, where the ratio of the atomic concentrations N/C is plotted as a function of

temperature. However, the P_1 peak decreases faster than the P_2 peak. In effect, the P_1 peak is larger than the P_2 peak at room temperature, but the opposite occurs at 900°C .

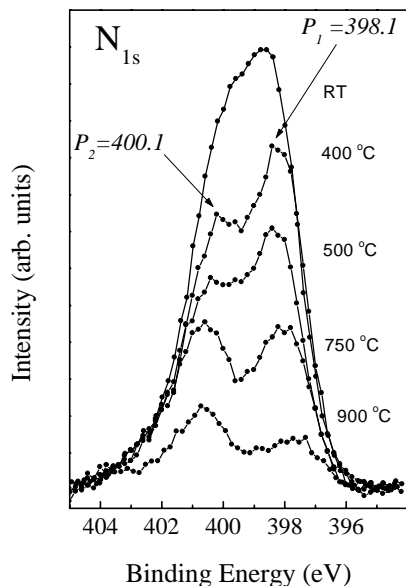


Figure 1. - XPS spectral evolution of transition N_{1s} . The normalization factor is the area under transition C_{1s} .

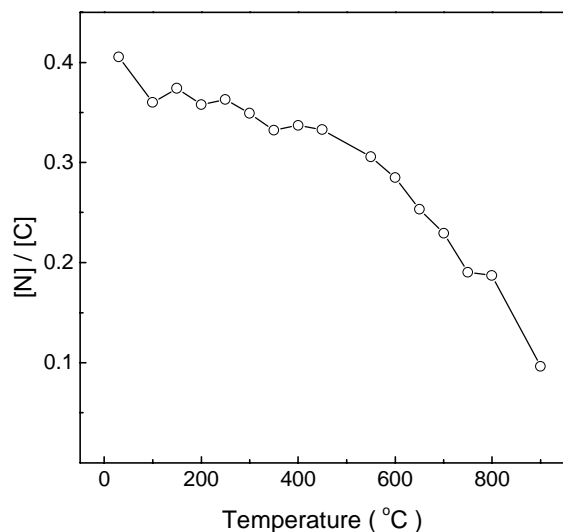


Figure 2. - Ratio of nitrogen to carbon as a function of the annealing temperature.

By means of the mass spectrometer, three different types of evolved gasses have been indexed: monomers and dimers of the elemental constituents (C , N , C_2 and N_2); compounds between C and N (CN , C_2N , CN_2 and C_2N_2); and compounds among C , N and hydrogen (CH_x , NH_x , H_xCN , H_xC_2N , H_xCN_2 , HC_2N_2). We detect that the most abundant species is the one assigned to cyanogen, 52 a.m.u.

Discussion

From the on-hand data several observations can be made: the atomic concentration of nitrogen in the films decreases as a function of temperature; the nitrogen is leaving the solid in gaseous species, where C_2N_2 is the most abundant; and P_1 decreases more rapidly than P_2 .

Even though in the films exist an important amount of chemical disorder, revealed by the broad XPS peaks, is helpful to simplify the analysis that the predominant nitrogen states, P_1 and P_2 , to be linked with two particular chemical environments. Given the lower BE of the P_1 peak, it must be associated with a site where there are more available electrons than in the P_2 site. In aromatic-rings the obtainable electrons are those that build up the π -system; then, the core-level-BE is an indirect measure of the aromatic extent in which the nitrogen atoms have been fixed. The BE for six-member-ring (pyridine-like) is in the 398.3 to 399.34 eV range, where the deviation is mainly due to the experimental uncertainty to chose an adequate reference level [4]. The energy difference between the pyridinic and pyrrolic nitrogen, as determined from the reported data available in literature and revised extensively by J. Lahaye *et al.* [4], is in the 1.35-2.00 eV range. Subsequently, is likely that P_1 and P_2 sites of this study to be related to nitrogen in six- and five-member-rings, respectively.

In figure 3 several heterocyclic configurations, pyrrolic- and pyridinic-like, are exposed. We can see that in the ‘top-sites’ the nitrogen atoms are prone to be removed. Figure 4 illustrates a proposed model of cycle-addition polymerization, where the top-nitrogen atoms are applied advantageous to sew up various contiguous carbon rings; C_2N_2 gas is generated in the course of actions. Given the chemical and structural disorder in the films, should exist quite a lot of equivalent process that result in the release of N_2 , $C\equiv N$, C_xN , CN_x , and every one of the indexed masses.

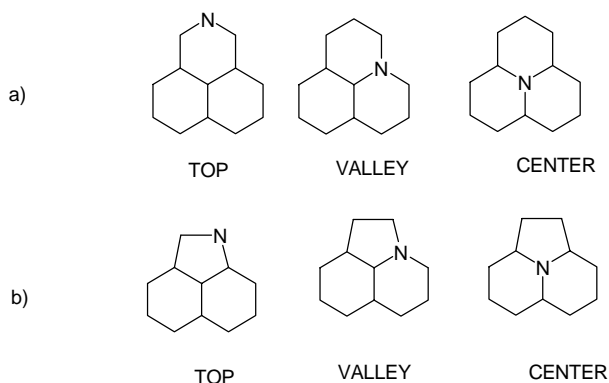


Figure 3. - Pyridinic-like (a) and pyrrolic-like (b) nitrogen configurations with two and three carbon neighbors.

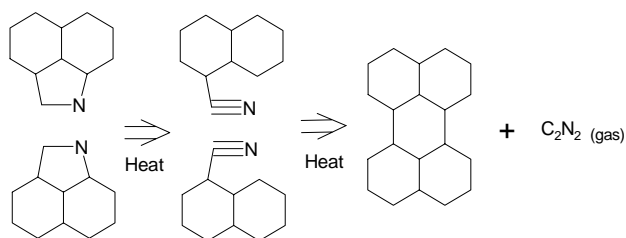


Figure 4. – Proposal where two ‘top position’ nitrogen in pyrrolic cycles are used to sew up a graphene layer. C_2N_2 is released in the process.

In contrast are the ternary varieties of nitrogen, valleys and centers sites, which lie in sheltered locations. In fact, the center-N is as stable as the surroundings are, remaining in carbon films heated up to $2200\text{ }^\circ\text{C}$ [5-7] and unavailable to generate polymerization reactions. As consequence, these nitrogen atoms are permanently stick in the carbon matrix.

Conclusions

In summary, we suggest a mechanism of polymerization that takes place upon rupture of pyridinic and pyrrolic rings, followed by cycle-addition of nearby carbon rings and gasification of C_2N_2 and other species. If our proposed model of cycle-addition is accurate, then the fact that P_1 is decaying faster than P_2 means that the polymerization is carried mostly at yield of pyridine-like rings. Accordingly, the nitrogen atoms that survive the thermal treatment are those in highly stable configurations, to be exact, those in center sites. Given that P_2 is the more persistent component, the largest part of nitrogen atoms that remain in the carbon matrix are the center sites linked to pyrrolic-like rings.

The inclusion of the five-member-pyrrolic ring within the layers is a way that could cause the bending and interweave between graphene planes [8,9].

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