

# Correlation between surface oxygen content and microstructure of carbon nitride films

T. Szörényi<sup>a,b,\*</sup>, A.L. Tóth<sup>c</sup>, I. Bertóti<sup>d</sup>, F. Antoni<sup>a</sup>, E. Fogarassy<sup>a</sup>

<sup>a</sup>CNRS-PHASE, BP 20, 67037 Strasbourg Cedex 2, France

<sup>b</sup>Research Group on Laser Physics, P.O. Box 406, H-6701 Szeged, Hungary

<sup>c</sup>Research Institute for Technical Physics and Materials Science, P.O. Box 49, H-1525 Budapest, Hungary

<sup>d</sup>Chemical Research Center of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

## Abstract

Carbon nitride films deposited by ArF excimer laser ablation of a graphite target in the 1–100-Pa N<sub>2</sub> pressure and 1.0–10-J cm<sup>-2</sup> fluence domains differ not only in their nitrogen but also in their oxygen content. The (surface) oxygen content correlates well with the compactness of the films. Oxygen contents below approximately 8 at.%, smooth surface, and mass densities above 2.2 g cm<sup>-3</sup> are typical of films deposited at low N<sub>2</sub> pressures (and high fluences) while deposition at/above 50 Pa results in films of oxygen contents exceeding 12 at.%, rough surface consisting of loosely connected cluster agglomerates, and density values at approximately 1.4 g cm<sup>-3</sup>. At medium pressures high fluence processing is advantageous in terms of both nitrogen content and film morphology. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Nitrides; X-Ray photoelectron spectroscopy; Scanning electron microscopy; Pulsed laser deposition

## 1. Introduction

In the majority of the papers on deposition and properties of carbon nitride films fabricated in intentionally hydrogen-free environment, *quantitative* composition analysis is restricted to the determination of carbon and nitrogen content. The message of the papers reporting complete chemical analysis is, that it is practically impossible to produce oxygen- (and hydrogen)-free films, and that the amount of oxygen sensitively depends on the preparation conditions ([1–9] and references therein). Since full listing and comparative analysis of these papers (actually less than one-quarter of the more than 100 relevant ones published in the last 5 years) should be the scope of a review, the references cited here should be considered as examples.

The results reported here prove that there exists a direct correlation between oxygen content and film microstructure. On the surface of compact, high-density

carbon nitride films max. 4–7 at.% oxygen can be measured, while the porous, low density ones (deposited at relatively high pressures) contain fairly high amounts of oxygen. The surface oxygen content of the carbon nitride films is, therefore, a sensitive indicator of the changes in film microstructure.

## 2. Experimental

The deposition chamber was pumped by a diffusion pump with a base pressure of <10<sup>-5</sup> Pa. During film deposition the chamber was backfilled with 1–100 Pa 99.999% nitrogen. The beam of the ArF excimer laser (193 nm, 22 ns, 10 Hz, max. 240 mJ per pulse) was focused to the surface of a nuclear grade graphite target, rotating with ≈1 rev. min<sup>-1</sup>, at approximately 45° of incidence through an UV grade quartz window. The energy density on the target surface was adjusted from 1 to 10 J cm<sup>-2</sup> by changing the pulse energy while keeping the dimensions of the ablated area constant at 1.2 mm<sup>2</sup>. Due to uncertainties in measuring the pulse energy and spot dimensions the experimental error in the absolute values of the energy densities is ±20% at best. Films of 50–500-nm thickness were deposited onto

\*Corresponding author. Research Group on Laser Physics, P.O. Box 406, H-6701 Szeged, Hungary. Tel.: +36-62-544274; fax: +36-62-544658.

E-mail address: t.szorenyi@physx.u-szeged.hu (T. Szörényi).

Si(100) wafers at a target–substrate distance of 30 mm, at room temperature.

The surface chemical composition of the films was determined by ex situ X-ray photoelectron spectroscopy (XPS). The spectra were recorded by a Kratos XSAM 800 spectrometer in fixed retarding ratio mode (FRR = 20) by using MgK<sub>α1,2</sub> (1253.6 eV) excitation. The overall experimental resolution was 0.75 eV.

Changes in surface morphology and inhomogeneity on sub-micrometer scale were followed by scanning electron microscopy (SEM), using a JEOL JSM-25SIII microscope (beam energy: 25 keV) in backscattered and secondary electron imaging modes (beam currents: BEI: 5 nA and SEI: 80 pA, respectively). Following digitizing, the images were contrast enhanced and gamma corrected by Adobe PhotoShop. The BE images showed no sign of atomic number contrast. While showing better contrast of roughness, because of the higher current used, the resolution of the BE images was lower than that of the SE ones, therefore, throughout this paper SE images are used for the characterization of surface morphology.

The density of the films was calculated from the areal density (number of atoms per unit area), as given by nuclear techniques (RBS and NRA), and film thickness, measured by a stylus profilometer.

### 3. Results and discussion

The results of XPS analysis of 25 carbon nitride films deposited in the 1–100-Pa N<sub>2</sub> pressure and 1.0–10-J cm<sup>-2</sup> laser fluence domains are compiled in Table 1. The nitrogen content of the films steeply rises between 1 and 5 Pa and levels off at approximately 10 Pa. The effect of the laser fluence in determining the N/C ratio is apparently more complicated. At 5 Pa an increase in the fluence from 1 to 3 J cm<sup>-2</sup> results in an increase in the N/C ratio from 0.25 to 0.32, while at 10 Pa it remains pinned to 0.40 ± 0.01 within the same fluence domain. A further increase in fluence results in a slight decrease in the nitrogen content, while approaching 10 J cm<sup>-2</sup> it starts to grow. This increase in nitrogen content at high fluences seems to be characteristic of the pressure domain at approximately 10 Pa [10,11]. At 50 Pa the N/C ratio remains practically constant at approximately 0.41, the film deposited at 10 J cm<sup>-2</sup> containing the smallest amount of nitrogen within the series.

Being motivated by the race for the synthesis of the C<sub>3</sub>N<sub>4</sub> phases, the authors usually stop at determining the dependence of nitrogen content on the process parameters. One novelty of our approach is that — besides recording the changes in both carbon and nitrogen content — the concomitant variation in the amount of surface oxygen has also been determined. As shown in Table 1 the oxygen content of the films systematically

Table 1

Surface chemical composition of carbon nitride films as determined by ex situ XPS

<i>P</i> (Pa)	Φ (J cm <sup>-2</sup> )	C (at.%)	N (at.%)	O (at.%)	N/C
1	1.00	86.9	6.1	7.1	0.07
5	10.0	70.8	24.5	4.7	0.35
5	5.00	71.0	22.3	6.7	0.31
5	3.00	71.3	22.6	6.1	0.32
5	2.00	72.0	20.9	7.1	0.29
5	1.58	71.9	20.8	7.3	0.29
5	1.26	72.0	20.5	7.5	0.28
5	1.00	72.9	18.3	8.8	0.25
10	10.0	63.7	28.4	7.9	0.45
10	7.50	67.8	23.7	8.5	0.35
10	5.00	65.7	23.8	10.5	0.36
10	3.00	64.3	25.1	10.6	0.39
10	2.00	64.7	26.0	9.3	0.40
10	1.58	63.4	25.6	11.0	0.40
10	1.26	64.3	25.0	10.7	0.39
10	1.00	63.2	25.5	11.3	0.40
50	10.0	63.8	24.2	12.0	0.38
50	7.50	62.8	25.2	12.0	0.40
50	5.00	62.3	25.6	12.1	0.41
50	3.00	61.5	25.5	13.0	0.41
50	2.00	61.6	26.3	12.1	0.43
50	1.58	62.0	25.6	12.4	0.41
50	1.26	62.2	25.6	12.2	0.41
50	1.00	62.0	26.1	11.9	0.42
100	7.50	61.9	24.1	14.0	0.39

varies both with N<sub>2</sub> pressure and laser fluence. The relative changes in the 5–10-Pa domain even exceed those of nitrogen. While an increase in N<sub>2</sub> pressure from 5 to 10 Pa results in an increase in the nitrogen content of the films from 18.3 to 28.4 at.% (extremes), i.e. with approximately 55%, the concomitant change in the oxygen content is more than twofold. At the surface of the films grown in 5 Pa of nitrogen the oxygen content varies between 4.7 and 8.8 at.%, and at 10 Pa the limits are 7.9 and 11.3 at.%. When depositing in a nitrogen atmosphere of 50 Pa the amount of oxygen measured on the film surface becomes independent of fluence and scatters between 11.9 and 13.0 at.%. The film deposited at 100 Pa contains the highest percentage of surface oxygen: 14.0 at.%.

As shown in Table 1 there is no correlation between the nitrogen and oxygen contents. Within the series deposited at 5 and 10 Pa the percentage of oxygen decreases while that of nitrogen increases with increasing fluence. Deposition at 10 J cm<sup>-2</sup> and 5 Pa results in films with N/C = 0.35 and 4.7 at.% oxygen, while nearly the same N/C ratio: 0.38 but 12 at.% oxygen characterizes the films deposited in 50 Pa N<sub>2</sub> at the same fluence.

On the other hand, parallel scanning electron and atomic force microscopy revealed that surface morphol-

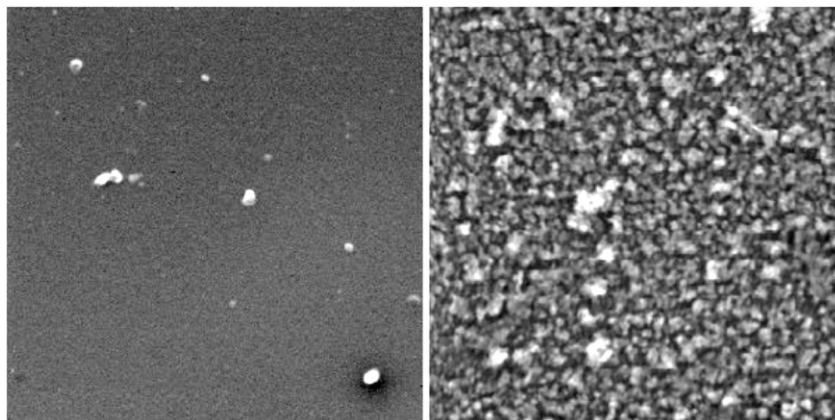


Fig. 1. Secondary electron images of carbon nitride films deposited by ablating a graphite target with ArF excimer laser pulses of 1.0 and 7.5 J cm<sup>-2</sup> of fluence in 1 and 100 Pa of nitrogen: left and right, respectively. Both pictures are 10×10 μm<sup>2</sup> in size.

ogy and oxygen content were correlated. Surface oxygen contents below approximately 8 at.% characterize the films possessing smooth, structureless surface (Fig. 1 left), while values at and above 12 at.% indicate films with extremely rough surface consisting of loosely connected, sub-micrometer dimension structures (Fig. 1 right). As a rule, low oxygen content and smooth surface are typical of films deposited at low N<sub>2</sub> pressures (and high fluences) while deposition at/above 50 Pa results in films of high oxygen content and rough surface. The films grown at pressures between these extremes show both characteristics, with abundances depending on the actual process parameters, revealing that in this domain both deposition of atomic species and cluster formation/deposition contribute to film growth. As exemplified in Fig. 2 an increase in the fluence leads to the improvement in surface quality in the 5–10-Pa pressure domain.

The results of parallel TEM and X-ray microanalysis [12] confirmed and complemented the picture sketched

above. The changes in the oxygen content measured within the whole film volume by EDS followed exactly the trend of XPS. The EDS figures were, however, systematically lower, the difference being less in the case of porous films. The difference between the surface and volume oxygen contents substantiates that oxygen uptake occurs when the films are exposed to the atmosphere.

The dependence of the mass density of the films on N<sub>2</sub> pressure gives independent evidence of the changes in the microstructure [13]. The decrease in mass density of the films deposited between 10<sup>-2</sup> and 5 Pa from 2.7±0.1 down to 2.2±0.2 g cm<sup>-3</sup> is a consequence of a nitrogen incorporation-driven structural transformation [14–16]. The sudden decrease down to a minimum value of 1.05 g cm<sup>-3</sup> (30 Pa and 10 J cm<sup>-2</sup>) and leveling at 1.4±0.2 g cm<sup>-3</sup> at and above 50 Pa, however, cannot be accounted for by changes in the chemical structure anymore. In this case the decrease in

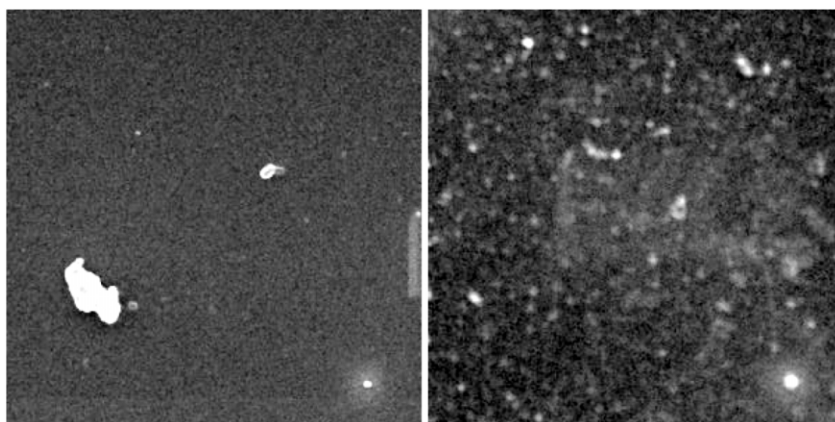


Fig. 2. Secondary electron images of carbon nitride films deposited by ablating a graphite target in 5 Pa nitrogen with ArF excimer laser pulses of 10 (left) and 1.0 J cm<sup>-2</sup> (right) fluence. Both pictures are 10×10 μm<sup>2</sup> in size.

density is a direct consequence of changes in the microstructure of the films resulting in increased porosity, which supports enhanced ex situ incorporation of oxygen into the network.

The fact that with increasing pressure the porosity of the films increases — practically independently of the technique applied — is well documented in the literature (e.g. [17–19] and references therein). In the particular case discussed here, in the 10–100-Pa pressure domain the carbon and nitrogen containing species undergo so many gas-phase collisions during their transport from the target to the substrate, that they become completely thermalized and, therefore, unable to build a dense, compact network when reaching the room temperature substrate. Comparative analysis of the pieces of information available in the literature [1–9] suggests that the results of this study are transferable to other deposition systems. The surface oxygen content of carbon nitride films can generally be used as a label of compactness, independently of the technique applied for film fabrication.

The message of this paper is that when analyzing the puzzling properties of amorphous carbon nitrides changes in both the chemical- and the microstructure of the material should be considered. A very recent paper by Papakonstantinou et al. [9] gives an example of such a comprehensive approach. In addition to 8 at.% N, they detected 8 at.% O in films deposited in 0.53 Pa nitrogen using a KrF excimer laser at  $10 \text{ J cm}^{-2}$ . The films grown in 5 and 10 Pa, contained 17 and 19 at.% N and 18 and 20 at.% O, respectively. The authors note that one explanation for the increased amount of oxygen is to be found on the porosity and low density of the film material. They explain the formation of structures with reduced three-dimensional cross-linking at high background nitrogen pressures with the thermalization of the laser ablated carbon species. Based on quantitative analysis of the Raman and XPS spectra they conclude, that the dramatic decrease in the hardness and Young's modulus with increasing  $\text{N}_2$  pressure is attributed to a transition from an amorphous structure consisting of predominately  $\text{sp}^3$  C bonds to a polymeric-like structure consisting predominately of double bonded C and N atoms.

#### 4. Conclusions

The microstructure of amorphous carbon nitride films deposited in the 1–100-Pa pressure and 1.0–10-J  $\text{cm}^{-2}$  laser fluence domains is controlled mainly by the  $\text{N}_2$  pressure, the effect of fluence being significant at medium pressures where high fluence processing is advantageous in terms of both nitrogen content and film morphology. When deposition parameters change from low nitrogen pressure (and high fluence) to high pres-

sure, the surface morphology of the films changes from a smooth one to a structured one consisting of cluster agglomerates, with a concomitant decrease in mass density. The (surface) oxygen content correlates well with the compactness. It is significantly higher in films, fabricated at higher pressures and composed of clusters, revealing that the oxygen content is a sensitive indicator of the changes in film microstructure, indeed.

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