

# Catalyst-free deposition of nanocolumnar carbon nitride films

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A possibility to obtain nanocolumnar carbon nitride films without a catalyst by the magnetron sputtering has been shown. The N/C ratio in the obtained nanocolumns attains 0.2. According to XPS analysis, the main fraction of nitrogen forms  $sp^2$ -hybridized bonds with carbon atoms and is included in the graphene layers as substitutional atoms. The rest of nitrogen atoms forms cross-linking between the graphene planes.

Показана возможность бескаталитического получения наноклоннарных пленок нитрида углерода методом магнетронного распыления графита. Соотношение N/C в полученных наноклоннах достигает 0,2. По данным XPS анализа, основная часть азота образует  $sp^2$ -гибридизированные связи с атомами углерода и входит в графеновые слои в замещающих положениях. Остальные азотные атомы образуют перекрестные связи между графеновыми слоями.

## 1. Introduction

Since the discovery of carbon (carbon-nitride) nanotubes/nanofibers (CNT/CNF) [1] numerous studies were aimed at their growth mechanisms [2, 3]. These researches were especially intense during the last decade, because such materials present both fundamental scientific interest and have promising technological applications. It is well known that the growth conditions, substrate type, and the catalyst used are of critical importance at the nanostructure synthesis [4]. As a rule, the use of catalytic metals (Ni, Co, Fe) is a decisive factor at growing of carbon nanomaterials (CNT/CNF). The catalyst is deposited on the substrate prior to the nanostructure preparation, and the nanotube/nanofiber diameter depends directly on the metal layer thickness [2]. At such growth mechanism, the substrate acts as a support for the carbon nanostructure and also interacts with the catalyst and environment near the growth surface. It has been discovered that when

obtaining the carbon nanotubes/nanofibers, it is necessary to maintain balance between the etching and growth processes to avoid damage of the growing nanofiber lateral surfaces, and at the same time to avoid a continuous carbon film formation [4, 5]. The important role of gas-phase etching at the growth of carbon nitride film  $CN_x$  materials has been demonstrated, too [6]. At present, the chemical vapor deposition (CVD) methods are mainly used for the synthesis of CNT/CNF materials. Another ways to nanostructures are under active development, too, in particular, magnetron sputtering which is compatible with the semiconductor technologies. In this work, we have obtained the carbon-nitride ( $CN_x$ ) nanocolumns by dc magnetron sputtering and it is shown that the nanocolumns can be grown without metal catalyst.

## 2. Experiment

The  $CN_x$  nanostructural films were grown by dc magnetron sputtering of graph-

ite target in pure nitrogen atmosphere onto quartz glass substrates. The plasma was generated by co-planar construction magnetron with a flat cathode and circular anode. The discharge power of magnetron did not exceed 20 W and discharge current, 40 mA. A graphite disk (special purity graphite for special analysis) of 40 mm diameter fixed on the cathode was used as the target. The target-to-substrate distance was 2.5–3.0 cm. The substrate temperature was 200°C. The substrates were preliminary cleaned in a solvent mixture. The gas pressure in the vacuum chamber was controlled by the instruments of a VUP-5M vacuum unit and was about 20 Pa. The film growth time was up to 120 minutes.

The surface morphology of films was analysed by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6330F instrument. The relative amounts of carbon and nitrogen in the material as well as the local chemical analysis of the film structure were obtained using the Mg K $\alpha$  high resolution X-ray photoemission spectroscopy (HR-XPS) on a KRATOS AXIS-165 spectrometer. The spectroscopic investigation of CN $_x$  films in the UV and visible range were carried out using a Shimadzu UV-2450 spectrophotometer ( $\lambda = 200$ –900 nm). The investigated electron spectra allow to estimate some important parameters of the material, in particular bandgap, and thus provide information on changes in the film electron structure. The film thickness was determined by the multibeam interference using a MII-4 microinterferometer.

### 3. Results and discussions

The absorption spectra of the obtained films are typical of those for conventional diamond-like amorphous carbon films. From here on, the results are presented for the K2 film with N/C ratio 0.18. In Fig. 1, shown is the absorption spectrum of the K2 film demonstrating the gradual smooth growth of absorption coefficient with increasing photon energy. The bandgap of the CN $_x$  film does not exceed 1.4 eV. In the short-wave area, there are absorption bands related to the  $\sigma$ -electron contribution to the electron structure of the obtained material.

The SEM shows a pronounced columnar structure of the material consisting of packed nanofibers (columns) of 60–80 nm average diameter (Fig. 2, K2 film). The column length corresponds to the film thickness, the nanofibers grow perpendicularly

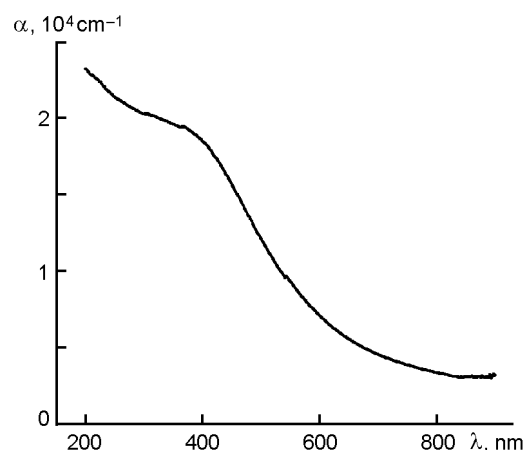


Fig. 1. Absorption spectrum of CN $_x$  film (K2 sample) in the UV and visible range.

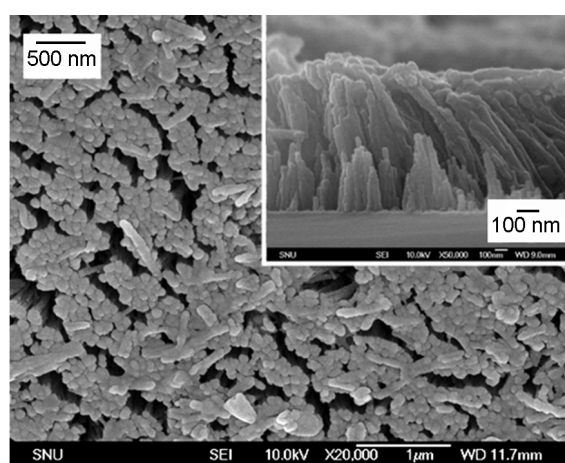


Fig. 2. Surface SEM-image of nanostructured CN $_x$  film K2 (inset: the cross-section view).

to substrate or at a small angle. The columns are packed in bundles, containing about 20–30 elements. The cross-section image demonstrates also the film columnar structure (see inset in Fig. 2). Thus, the obtained material can be attributed to the nanostructural class.

These structures were obtained without any special substrate preparation ("seeding" of catalytic metal particles). Any traces of metal were not found neither in the films nor in the graphite target by the XPS and FE-SEM chemical analysis. In our assumption, the use of magnetron sputtering plays a key role at such growth, providing coverage of the substrate surface at the initial sputtering moment with graphite particles, thus forming the nanocolumn growth centers (instead of metal nano-catalysts). Some oxygen (~3 %) was detected in the used target and obtained films. That is explained by the high porosity degree of the nanostruc-

tured films and used target. Nitrogen concentration in the films, as measured by quantitative XPS-analysis, reached up to 20 at.%.

The high-resolution XPS analysis of chemical structure has demonstrated the presence of C 1s and N 1s spectral lines. XPS spectrum of the K2 nanostructured film (nitrogen concentration N/C = 0.18) presented in Fig. 3. The broad asymmetrical lines are seen in the spectrum. This indicates that there are different types of chemical bonds between C and N atoms in the obtained samples. N 1s line approximated by a Gaussian function shows peaks of N1 = 397.8 eV and N2 = 399.3 eV (Fig. 3(a)). According to numerous HR-XPS analysis data [7–9], N1 and N2 lines correspond to nitrogen bound chemically with  $sp^3$  and  $sp^2$ -hybridized carbon, respectively. In other words, these lines correspond to nitrogen atoms forming the buckling bonds between the graphene layers and to atoms that entered into the graphene layers in substitutional positions. This is also confirmed by the ab initio calculations of binding energy in nitrogen-carbon alloys [10]. The relative integral intensity of N2/N1 lines shows thus ratio of substitutional nitrogen in layers (N2 line) to nitrogen forming the buckling bonds (N1 line). For the obtained films, N2/N1 ratio was 2.34, thus showing that majority of chemically bound nitrogen enters the graphene layers as substitutional atoms.

The C 1s band expanded into Gaussians demonstrates 3 lines: C1 = 284.4, C2 = 285.8, and C3 = 287.4 eV (Fig. 3(b)). The C1 line is identified usually as adventitious and surface carbon; the C2 and C3, as contributes from  $sp^2$ - and  $sp^3$ -hybridized carbon orbitals [8, 9]. The Raman and Fourier IR measurements confirm also that nitrogen atoms are predominantly bound with  $sp^2$ - and  $sp^3$ -coordinated carbon [7]. Sometimes, C 1s line was observed also at higher energies (~289.0 eV), and it is attributed to CO type bonds [8, 9]. Absence of such line in our spectra indicates for negligibly small amount of chemically bound oxygen in the films.

According to Ren et al. [2], carbon nitride nanotubes can be grown from the mixture of ammonia, but not from pure nitrogen. The "ordinary" (not nanocolumnar) films as well as closely packed nanofibers and fully isolated nanofibers can be obtained, depending on the  $C_2H_2$  to  $NH_3$  ratio in the gas mixture in the CVD chamber. Up

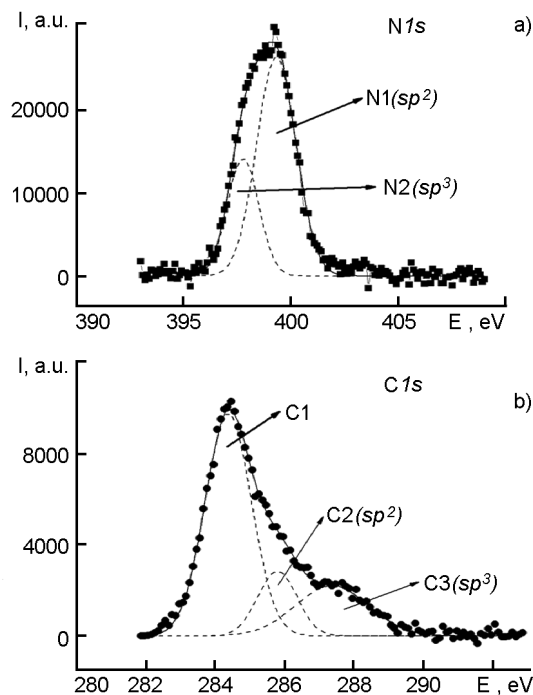


Fig. 3. HR-XPS spectra of N 1s (a) and C 1s (b) lines of nanostructured  $CN_x$  film K2.

to date, no films with nanofibers were obtained by magnetron sputtering. Such films have shown usually the fullerene-like [7, 11, 12], turbostratic [13], or tubular [14] structures, which was recognized using SEM, TEM, spectroscopy and nanoindentation. Such films were deposited at nitrogen pressures not exceeding 3 Pa [11, 12, 15]. At such rather low pressures, the N2/N1 ratio in the films is approximately 1.0 at nitrogen concentrations in  $CN_x$  films up to 15 % (thus being much lower than N2/N1 = 2.34 obtained for our nanocolumnar films). In such cases, nitrogen forms many buckling bonds between graphene layers, resulting in formation of fullerene-like structure [7]. We suppose that it is just a considerably higher nitrogen pressure in a gas chamber (~20 Pa) that causes formation of obtained nanofibers, even without using of any metal catalyst. It is possible that growth of carbon-nitride materials at pressures about 20 Pa hinders the bending of graphene planes and transformation thereof into fullerene structure, when the nitrogen concentration in the material reaches ~15 %.

#### 4. Conclusion

Thus, nanocolumnar film structures have been obtained by catalyst-free dc magnetron sputtering at low substrate temperatures.

The nanocolumns are packed in bundles containing 20–30 columns. The results show that catalyst-free nanocolumnar structure synthesis is possible at relatively high N<sub>2</sub> pressures (about 20 Pa).

### References

1. S.Iijima, *Nature*, **354**, 56 (1991).
2. Z.F.Ren, Z.P.Huang, J.W.Xu et al., *Science*, **282**, 1105 (1998).
3. J.C.Charlier, A.De Vita, X.Blase et al., *Science*, **275**, 647 (1997).
4. V.I.Merkulov, A.V.Melechko, M.A.Guillorn et al., *Appl. Phys. Lett.*, **80**, 476 (2002).
5. V.Melechko, V.I.Merkulov, T.E.McKnight et al., *J. Appl. Phys.*, **97**, 041301-39 (2005).
6. R.V.Shalaev, A.M.Prudnikov, V.N.Varyukhin et al., *Fiz. Tekhnol. Vysok. Davl.*, **16**, 88 (2006).
7. N.Hellgren, M.P.Johansson, E.Broitman et al., *Phys. Rev. B*, **59**, 5162 (1999).
8. D.Marton, K.J.Boyd, A.H.Al-Bayati et al., *Phys. Rev. Lett.*, **73**, 118 (1994).
9. Yun-Sik Jin, T.Shibata, Y.Matsuda et al., *Thin Solid Films*, **345**, 18 (1999).
10. S.Souto, M.Pickholz, M.C.dos Santos et al., *Phys. Rev. B*, **57**, 2536 (1998).
11. J.Neidhardt, Zs.Czigany, I.F.Brunell et al., *J. Appl. Phys.*, **93**, 3002 (2003).
12. H.Sjostrom, S.Stafstrom, M.Boman et al., *Phys. Rev. Lett.*, **75**, 1336 (1995).
13. H.Sjostrom, I.Ivanov, M.Johansson et al., *Thin Solid Films*, **246**, 103 (1994).
14. K.Suenaga, M.P.Johansson, N.Hellgren et al., *Chem. Phys. Lett.*, **300**, 695 (1999).
15. M.Terrones, N.Grobert, J.Olivares et al., *Nature*, **388**, 52 (1997).

## Безкаталітичне одержання наноколонарних плівок нітриду вуглецю

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Показано можливість безкаталітичного одержання наноколонарних плівок нітриду вуглецю методом магнетронного розпилювання графіту. Співвідношення N/C в отриманих наноколонах досягає 0,2. За даними XPS аналізу, основна частина азоту утворює sp<sup>2</sup>-гібридизовані зв'язки з атомами вуглецю і входить у графенові шари у заміщуючих положеннях. Решта азотних атомів утворює перехресні зв'язки між графеновими шарами.