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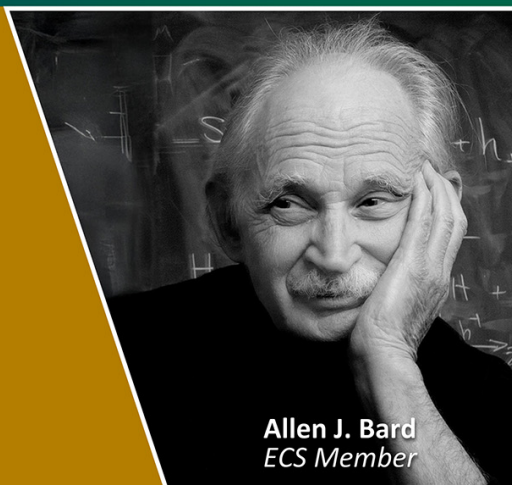


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XPS study of the structure of nitrogen doped a-C film

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Abstract. It was found change of phase composition and structure of the carbon coating, subjected to ion nitriding. It is shown that ion nitriding is in the surface layers of increasing the share of sp²-phase with a decrease in the size of the clusters. It was found that the ion nitriding of carbon coatings are formed CN_x connections to increase the number of the type of N-Csp² bonds.

1. Introduction

Amorphous diamond like films (a-C) have been arousing scientific interest for more than 30 years due to their unique properties. As it is known [1, 2] that the properties of a-C films are defined by the ratio of carbon atoms with sp³ and sp² of electronic hybridization. The efficient technological management method of structure and properties of such films is their doping by various chemical elements and compounds. The doping of a-C films is carried out by nitrogen for the purpose of synthesis of C₃N₄ carbon nitride which has theoretically been expected in the research possessing high hardness, wear resistance, and also good heat conductivity and optical transparency. As it is mentioned in [3], the introduction of nitrogen into the structure of a-C leads to the essential structural change and properties of a film. At the same time, the influence nature depends on the method and the mode of deposition. In order to produce nitrogen containing a-C, various methods of nitrogen introduction into the structure of a carbon matrix are applied, as follows:

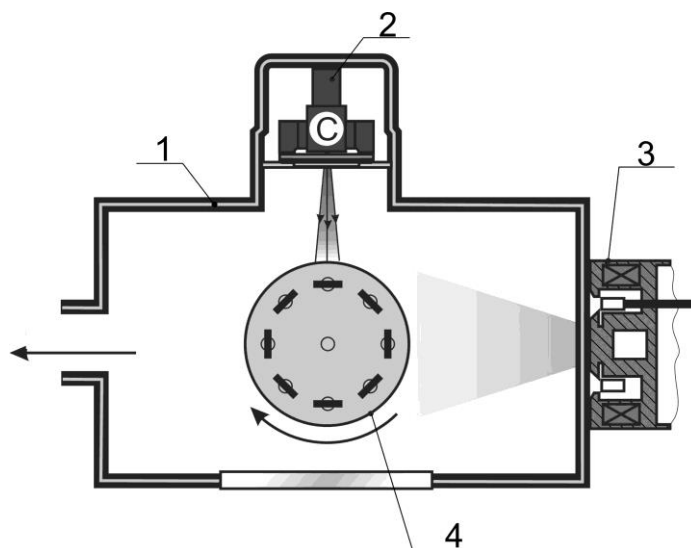
- 1) the deposition of carbonic films in the environment of molecular nitrogen (a-C:N_x);
- 2) the deposition of carbonic films with simultaneous treatment of the growing film by nitrogen ions with energy to 300 eV (a-C:N+low);
- 3) the subsequent ionic treatment of earlier formed carbonic films by nitrogen ions with energy to 1,5 keV (a-C:N+high).

We are studied how nitrogen ions with energy to 1,5 keV change the structure of carbon films.

2. Experimental

The deposition of a carbon film is produced by the evaporation of a graphite target with the influence of an impulse discharge. The carbon films formed with the frequency of impulse discharge of 20 Hz a-C:N+high are subjected to the subsequent treatment by nitrogen ions with energies up to 1,5 keV (Fig. 1). Voltage discharge is 350 V. The polished wafers of silicon monocrystal (100) and quartz serve as a substrate. In order to clean the substrate, the treatment of its surface is produced for 15 min by argon ions with energy 400 eV and with ionic current density of 25 A/m².





1 - vacuum chamber; 2 - pulse carbon plasma source; 3 - ion source; 4 - substrates
Figure 1. The scheme of the vacuum unit intended for the deposition of carbon films in conditions of ion bombing and the subsequent ion treatment of alloyed carbon films.

The microstructure of the carbon films is determined by Raman spectroscopy methods (the length of the exciting radiation wavelength is 532 nm and power is 5 mW) (Senterra, Bruker). The chemical composition and structure of the bonds are determined by X-ray photoelectron spectroscopy (XPS, PHI Quantera II) by initiating the substance by aluminum $K\alpha$ -radiation with photon energy 1486,6 eV and total power of 250 W. Before analyzing the carbon film is etched by the flow of argon ions with 5 keV energy. This energy is sufficient to remove the surface hydroxyl and hydrocarbon contaminants adsorbed while the films stay in the air. The scale of energy bonds in the XPS spectrum is calibrated by C1s (284,6 eV). XPS spectrum of C1s and N1s is estimated by XPSPEAK software. The spectrum of the background radiation is modeled with Shirley function.

3. The results and their analysis

It is stated that further treatment of an already formed carbon film a-C:N+high results in partial implantation of nitrogen ions, their content in the film does not exceed 2,5...3,5 at. % according to the energy dispersive analysis. It should be noted that the formation of carbon films in ion assisting conditions (regardless of assisting ion energy) exerts a significant influence on the phase composition. When assisting the ratio ID/IG increases from 0,5 to 0,9 and the G-peak width decreases to 174,6 cm^{-1} . After subsequent ion nitriding the ratio ID/IG equals 0,58 and the G-peak width is equal to 189,2 cm^{-1} . These changes are explained by different mechanisms of phase transitions $\text{sp}^3 \rightarrow \text{sp}^2$ of carbon films. At ion assisting the main cause of phase composition change are inelastic collisions of nitrogen ions and carbon in a plasma, while ion nitriding is superficial, and etching processes and local heating of the upper film layers predominate [3–5].

The further treatment with nitrogen ions causes significant phase transitions in single-component films of carbon, which is proved by XPS. The presence of N1s peak in XPS spectra indicates the process of implantation of nitrogen ions into the surface layers during subsequent processing [6, 7].

Table 1 shows that the subsequent processing of single-component ionic carbon a-C:N+high films leads to an increase in the content of the sp^2 -hybridized carbon atoms, which is partly confirmed by Raman spectroscopy, introducing a slight increase in ID/IG ratio. The changes in the content of sp^3 -phases are difficult to judge, because with the decomposition of a component with a binding energy of 285,4 eV ~ we mean Csp3 and C – N, C = N bonds.

However, even with the contribution to the intensity of the component of compounds such as C and C = N–N type, it is seen that the proportion of integral area slightly decreases in all cases. It is clear from the analysis of N1s that at the ion treatment the bonds of CNx type are formed with predominant content of N– Csp2N- type bonds. It is found that the subsequent ion nitriding increases the microhardness, regardless of the type of carbon film.

Ion nitriding of carbon films leads to the formation of compounds of nitrogen and carbon with a predominant content of N–Csp2 bonds. In addition, there is a slight increase of sp^2 -hybridized carbon

atoms, which is confirmed by XPS and Raman spectroscopy. On the basis of what can be assumed that during the bombing occurs the implantation of nitrogen ions into the surface layers, followed by the formation of chemical compounds of carbon and nitrogen.

Table 1 - Analysis of XPS of carbon films after ion nitriding

Film	Peaks of XPS spectrum	Bond type	Peak, eV $\pm 0,2$ eV	Width, eV	Area share, %
<i>a</i> -C	C1s	Csp ²	284,4	1,21	34
		Csp ³	285,3	1,34	65
		C–O	286,5	0,59	1
	O1s	O–C	531,9	3,42	–
		Csp ²	284,5	1,07	50
<i>a</i> -C:N ^{+high}	C1s	Csp ³ , C=N, C–N	285,4	1,65	48
		C–O	286,7	1,02	2
	N1s	N–sp ³ C	398,2	1,37	38
		N–sp ² C	399,9	1,96	57
		N–O	401,7	0,78	3
	O1s	O–C	531,9	2,39	–

It is stated that at ion nitriding (1,5 keV) of carbon films the relative content of N–Csp³ bonds 3,5...3,7 times higher than in carbon films formed in the presence of molecular nitrogen or in assisting with energy nitrogen ions to 0,3 keV. This fact can be explained by a higher energy of implanted nitrogen ions as well as lower content of sp²-clusters in the initial film [7, 8].

In practice for improvement of physical and chemical properties of materials of the electronic equipment, the creation of the set superficial nanostructures by etching and thermal annealing, the ion-beam and thermal methods of activation and modification of materials are widely used [9–12].

4. Conclusion

In conclusion, as a result of analysis of the microstructure of film *a*-C:N^{+high} films the mechanism of influence of ion nitriding on the structure, processes of chemical interactions and properties of carbon films are defined. Increased nitrogen activity and decrease in the kinetic energy of carbon ions in the plasma are favorable for the formation of chemically related structures in N-alloyed carbon films. It is defined that at ion nitriding (up to 1,5 keV) the relative content of carbon films of N- Csp³ bonds is 3,5...3,7 times higher than in carbon films formed in the presence of molecular nitrogen or in the assisting conditions with energy nitrogen ions to 0,3 keV. This fact can be explained both by a higher energy of implant nitrogen ions and lower content of sp²-clusters in the initial film.

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References

- [1] Majumdar A, Das S C, Bogdanowicz R, Shripathi T, Langel W. Rainer Hippler Role of nitrogen in evolution of sp²/sp³ bonding and optical band gap in hydrogenated carbon nitride 2013 *Vibrational Spectroscopy* **66** 63–68
- [2] Aleutdinov A D, Ghygazov S A, Mylnikova T S, Luchnikov P A Thermal shock removal of defective glass-enamel coating from cast-iron products 2015 *IOP Conf. Ser.: Mater. Sci. Eng.* **81** 012069
- [3] Liu D G, Tu J P, Zhang H, Chen R, Gu C D Microstructure and mechanical properties of carbon nitride multilayer films deposited by DC magnetron sputtering 2011 *Surf. Coat. Technol.* **205** 3080–3086
- [4] Chen R, Tu J P, Liu D G, Yu Y L, Qu S X, Gu C D Structural and mechanical properties of TaN/*a*-CN_x multilayer films 2012 *Surf. Coat. Technol.* **206** 2242–2248

- [5] Voevodin A A Comparative study of wear-resistant DLC and fullerene-like CN_x films produced by pulsed laser and filtered cathodic arc depositions 2005 *Surface & Films Technology* **197** 116–125
- [6] Broitman E Mechanical and tribological properties of CN_x films deposited by reactive magnetron sputtering 2001 *Wear.* **248** 55–64
- [7] Cohen M L Structural, electronic and optical properties of carbon nitride 1995 *Material Science Engineering* **209** 1–4
- [8] Gammon W J Experimental comparison of N(1s) X-ray photoelectron spectroscopy binding energies of hard and elastic amorphous carbon nitride films with reference organic compounds 2003 *Carbon* **41** 1917–1923
- [9] Luchnikov P A, Rogachev A V, Yarmolenko M A, Rogachev A A, Besspal'ko A A Dynamics of combined electron beam and laser dispersion of polymers in vacuum 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **110** 012081
- [10] Luchnikov P A Structure Formation Mechanisms and Electrical Properties of PVD Fluoropolymer Films 2015 *Russian Physics Journal* **57** 9 1239–1245
- [11] Rogachev A A, Yarmolenko M A Xiaohong Jiang, Shen Ruiqi, Luchnikov P A, Rogachev A V Molecular structure, optical, electrical and sensing properties of PANI-based coatings with silver nanoparticles deposited from the active gas phase 2015 *Applied Surface Science* **351** 811–818
- [12] Surzhikov A P, Frangulyan T S, Ghyngazov S A, Lisenko E N, Galtseva O V 2006 *Russian Physics Journal* **49** 5 506–10