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The Effect of Gas Phase Composition on the Structural Characteristics and Resistivity of Nitrogen-doped Nanostructured Diamond Coatings

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The experimental results of the effect of the gas phase composition on nitrogen-doped nanostructured diamond coatings synthesized in the glow discharge plasma on their structure and resistance have been presented. It was shown that changes in the electrical conductivity of the nitrogen doped nanostructured diamond coatings are primarily related to changes in the electrical conductivity of the grain boundaries and did not to changes in the grain size of the diamond phase.

Keywords: Diamond coating, Doping by nitrogen, Nanostructure, Resistivity, Composition of the gas phase.

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1. INTRODUCTION

Nanocrystalline diamond film is considered as a new material with great potential use in the techniques, medicine and other fields [1]. It has been found that deposition of nanostructured diamond coatings by CVD-method in the presence of nitrogen resulted in appearing of significant electrical conductivity, which expands the fields of diamond nanocrystalline films possible application. Detail studies of such coatings have shown that electrical conductivity of nitrogen-doped nanostructured diamond films related to the effects of nitrogen on the conductivity of grain boundaries consisting mainly of sp^2-hybridized carbon atoms or other non-diamond forms of carbon, whose percentage in the volume of nanostructured diamond films can be up to 10%. Accordingly, the conductivity of diamond coatings must depend on the proportion of grain boundaries per unit volume of the diamond film, i.e. the grain size and the value of electrical conductivity of grain boundary layers themselves.

In this connection it is of interest to perform studies of the effect of the gas phase composition at synthesis of nanostructured nitrogen doped diamond films on their structural characteristics and the value of their resistivity. This was the aim of this work.

2. EXPERIMENTAL

Diamond coatings synthesized from a gas mixture of hydrogen, methane, argon and nitrogen in DC glow discharge plasma stabilized by magnetic field. The concentration of nitrogen in the gas mixture can vary from 0 vol. % up to 38 vol. %, argon from 50 vol. % up to 75 vol.%, hydrogen from 0 vol. % up to 38 vol. %. The concentration of methane in the gas phase remained unchanged and was of 2 vol. %. The equipment used for synthesis of nitrogen doped nanocrystalline diamond coatings did not differ from those given in [2].

According to X-ray phase analysis in all coatings synthesized within this study, regardless of the composition of the gas phase used for the coating deposition, it was formed the polycrystalline diamond (cubic Fm3m space group symmetry). Due to the relatively small thickness of the films (4-10 microns) in the most part of X-ray spectra have been registered only the first two of the most intense reflection of diamond – (111) and (220) whose intensity increases with increasing film thickness. The typical X-ray spectra of the films shown in Fig. 1.

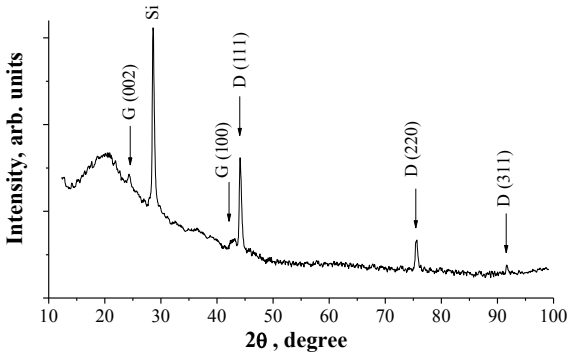

Fig. 1 – X-ray diffraction pattern of the nanocrystalline diamond film on a silicon substrate, arrows indicate the position of the diffraction peaks of diamond (D) and graphite (G)

In addition to the diamond peaks on some diffraction patterns revealed very weak lines at the angles 2θ close to 25 and 42 degrees that may belong to the non-diamond forms of carbon most likely to graphite [3]. In addition, the halo was present at angle approximately of 20 degrees due to the presence of X-ray amorphous phase which we could not identified. By the angular positions of the diffraction peaks it was calculated the lattice parameter of diamond films. The values obtained were in the range (0,3545-0,3557) nm, which is slightly smaller than the tabular values for natural diamond ($a = 0.3567$ nm). The size of the coherent scattering region (CSR) for the studied films did not exceed 40 nm and depended on the deposition

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parameters of diamond coatings.

On Fig. 2a it was shown the data on size of CSR value for nanocrystalline diamond coatings synthesized in gas mixtures containing argon of 60 vol. %, methane of 2 vol. %, and different concentrations of nitrogen C_N and hydrogen. On Fig. 3 it was shown the scanned electron images of the samples surface.

From these figures it can be seen that increasing the nitrogen concentration in the gas mixture generally leads to reduction the size of structural elements in electron microscopic images and decreasing the CSR value in comparison with the film which was deposited without nitrogen (0 % N_2). Such behaviour with increasing the nitrogen concentration is non-monotonic. In the range of nitrogen concentration of 6-19 vol. % the structural elements rather increased, the size of the CSR increased from 20 to 25 nm. With further increase of the nitrogen concentration in the gas mixture the structural elements take the form of an elongate needle, and the average CSR value reduced to 10 nm. In Fig. 2b it has been shown the data on resistivity of diamond coatings ρ_n synthesized from a gas mixture with different nitrogen concentrations.

It can be seen that at decrease of CSR size in several times the resistance of diamond coatings decreased by more than three orders of magnitude with an increase of the nitrogen concentration in the gas phase.

It is known that the grain size and structure of the diamond coatings are very dependent on the concentration of argon in the gas mixture [4]. In this regard, the experiments were performed at constant concentration of nitrogen in the gas mixture that was of 19 vol. % and different argon and hydrogen concentration, respectively. In Fig. 4a it was shown the dependence of CSR size of diamond coatings and on Fig. 4b the dependence of the diamond coatings resistivity on the concentration of argon C_{Ar} for the same series of samples.

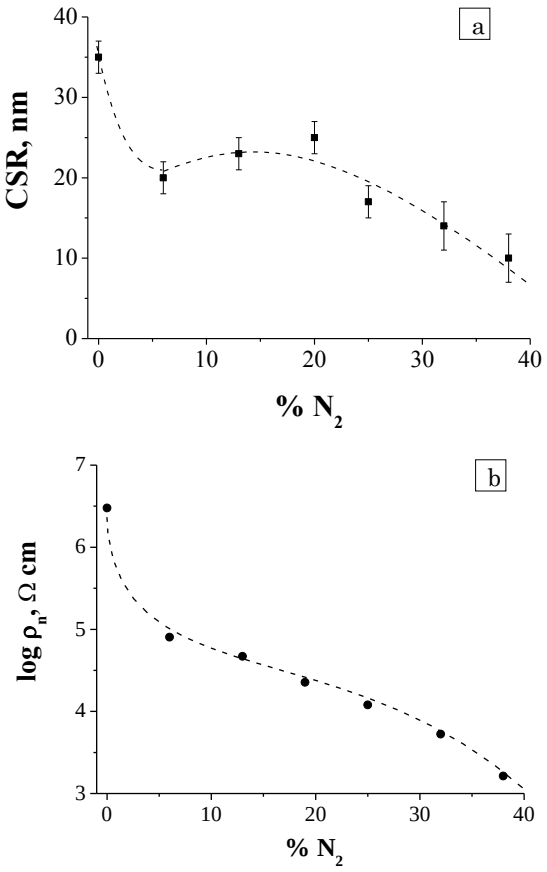

Fig. 2 – The dependence of CSR size and resistivity ρ_n for nanocrystalline diamond films on the concentration of nitrogen in the gas mixture containing argon of 60 vol. %, methane of 2 vol. % and hydrogen (38 % – C_N %) vol. %: a – CSR size; b – resistivity

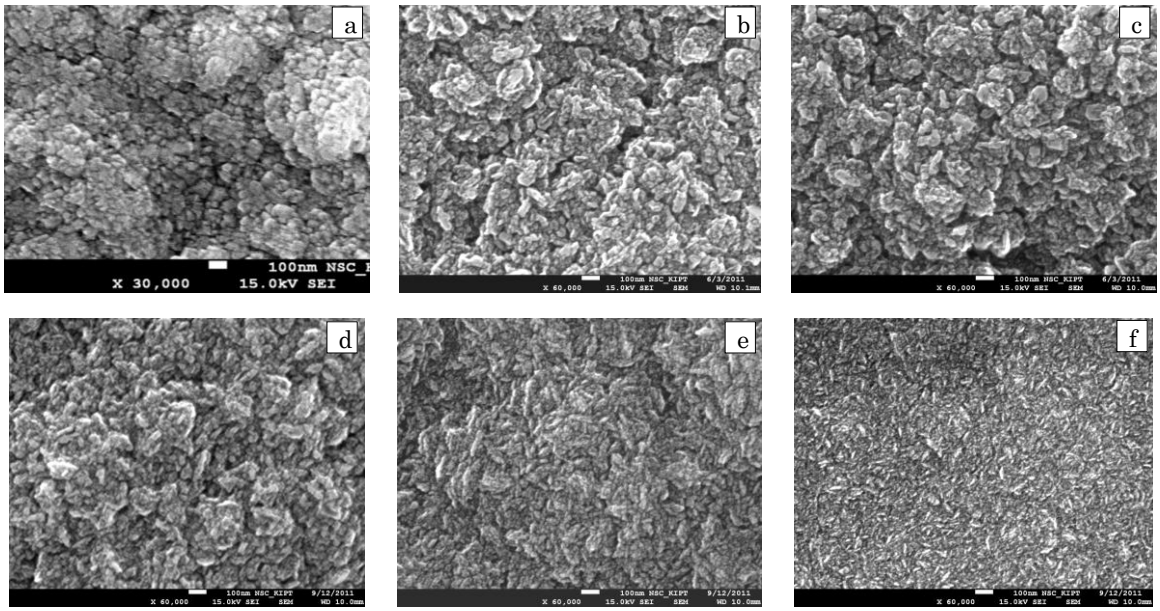

Fig. 3 – The microstructure of the diamond coatings surface deposited in a gas mixture of argon of 60 vol. %, methane of 2 vol/ %, hydrogen of (38 %-C_N %) vol/ % and nitrogen: a – 0 vol. %; b – 13 vol. %; c – 19 vol. %; d – 25 vol. %; e – 32 vol. %; f – 38 vol. %

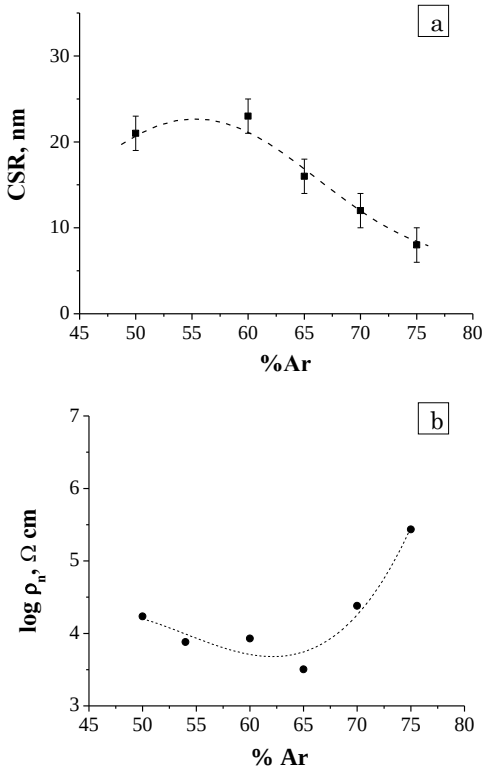

Fig. 4 – The dependence of CSR size and resistivity ρ_n for nanocrystalline diamond films on the concentration of argon in the gas mixture containing nitrogen of 19 vol. %, methane of 2 vol % and hydrogen (79 % – C_{Ar} %) vol. %: a – CSR size; b – resistivity

Comparison of the data in Fig. 4a and Fig. 4b shows that in this case the change of the resistance and CSR size in investigated diamond films generally occurred in opposite directions

3. CONCLUSIONS

The data obtained on the value of the nanostructured diamond coatings resistance and the value of their CSR size indicates that changes in the electrical conductivity of nanostructured diamond films doped with nitrogen are related primarily to changes in the electrical conductivity of the grain boundaries, but not with the size of the diamond phase grains.

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