

Electrochemical Properties of Nitrogen Doped Nanostructured Diamond Coatings Synthesized in the Plasma of Direct Current Glow Discharge

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The work is devoted to the study of electrochemical properties of nanostructured diamond electrodes doped with nitrogen which are deposited using gas phase chemical synthesis on the molybdenum substrates. The essential influence of gas mixture composition and substrate temperature on the morphology, electrical and electrochemical properties of the electrodes was demonstrated. The best samples of diamond electrodes have a number of advantages over the electrodes made of traditional materials for the electrochemical analysis of aqueous media.

Keywords: Diamond, Doping, Nitrogen, Electrode, Electrochemical assay.

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1. INTRODUCTION

Diamond has an extremely high chemical resistance, stability of the electrochemical properties, a wide window of available potentials in aqueous media (a window of ideal polarizability) and a very low value of the background current. Due to a combination of these properties it exceeds such materials as gold, platinum, glassy carbon and other electrode materials which are widely used in electrochemistry [1]. The development of methods for obtaining the doped electrically conducting diamond materials, especially gas-phase chemical synthesis of diamond (CVD-methods) in the form of the coatings of an area of tens of square centimeters, has opened the possibility of practical use of the unique properties of diamond as the electrode material in different fields [2].

The CVD synthesis method of nitrogen doped diamond coatings in the nanostructured state is widely used currently in the production of electrically conducting diamond coatings. Conductivity in such materials is conditioned by the conductivity, first of all, of the grain boundaries, which depends on the degree of doping with nitrogen [3]. In general, the properties of such coatings will depend on the coatings structure and nitrogen doping level, i.e. on the synthesis conditions and method implementation. Therefore, on the one hand, there is a possibility to obtain coatings with a very wide spectrum of properties, and, on the other hand, comparison and interpretation of the investigation results of the coatings obtained by different authors and various methods is complicated. This concerns, in particular, the results of the study of electrochemical properties of such coatings.

Synthesis in the plasma of microwave discharge is the most widespread synthesis method of diamond coatings including nitrogen doped nanostructured coatings. Correspondingly, most of the results on the electrochemical properties of nitrogen doped nanostructured coatings are obtained in the study of the coatings synthesized by this method. It is shown in [4, 5] that formation of nanostructured diamond coatings during synthesis in the plasma of glow discharge in the crossed E/H fields occurs at the

concentration ratios of the gas phase components which significantly differ from the composition in the case of synthesis in the plasma of microwave discharge. Moreover, equipment for the synthesis of diamond coatings in the plasma of glow discharge is substantially simpler in comparison with that in which microwave discharge is used. The latter is important if consider prospects for practical use of the method for obtaining electrodes on the basis of diamond coatings.

Therefore, it was of interest to perform studies aimed at determination of the electrochemical characteristics of nitrogen doped nanostructured diamond coatings obtained in the plasma of glow discharge and the effect on them of the structure and specific conductivity as well as the conditions for obtaining coatings.

2. EXPERIMENTAL

Production of nanostructured diamond coatings was carried out by the equipment with the key features represented in the work [4]. Molybdenum plates of sizes of 7×7 mm² and thickness of 0.4 mm were used as the substrates in the preparation of diamond coatings. Before coating deposition, substrate surface was treated by the powder of ultradispersed diamond to create the primary crystallization centers of the diamond phase on the substrate surface. Synthesis of nitrogen doped nanostructured diamond coatings was performed from the gaseous phase with the content of argon of 60 %-65 %, nitrogen of 19 %-25 % and methane from 1.8 % to 2.1 % at the total pressure of 8×10^3 Pa. Change in the composition of the gaseous phase in the specified range during synthesis of nitrogen doped nanostructured diamond coatings as well as the temperature of their synthesis, as shown in [6, 7], allowed to obtain coatings with different structure and value of the electrical resistivity in the range from units of Ohm \times cm to 10^5 Ohm \times cm. In Table 1 we present the data with characteristics of the obtained samples studied in the work.

Coating deposition time was chosen from the conditions of achievement of thickness not less than 4 μ m.

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Table 1 – Characteristics of the samples

Sample number	Composition of Ar/H ₂ /N ₂ /CH ₄ gaseous phase	Substrate temperature, °K	Coating thickness, μm	Coating resistivity, Ohm × cm
1	60 / 18.9 / 19 / 2.1	1185	4.7	2.8×10^4
2	60 / 19.2 / 19 / 1.8	1270	5.8	8×10^2
3	65 / 14.2 / 19 / 1.8	1195	6.3	2×10^1
4	65 / 14.2 / 19 / 1.8	1160	5.4	1.3×10^3
5	65 / 7.9 / 25 / 2.1	1160	6.9	0.9

As the preliminary investigation of the structure of these diamond coatings has shown, at such thickness coatings do not have through pores that excludes involvement of the substrate into electrochemical processes and its influence on the electrochemical properties of the coating.

In Fig. 1 we show the surface structure of diamond coatings obtained in different conditions.

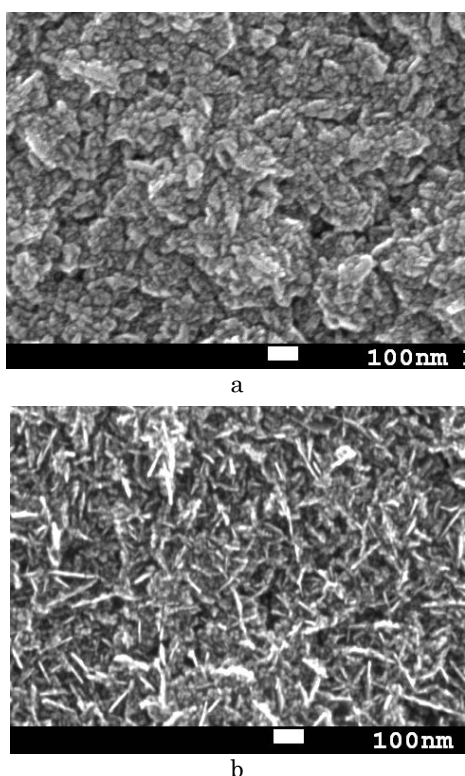


Fig. 1 – Scanning electron microscopy of the surface of diamond coatings obtained in different conditions: a) sample No1 and b) sample No5

Investigation of the electrochemical characteristics of diamond coatings was carried out by cyclic voltammetry method [8] in three-electrode electrochemical cell with Ag/AgCl reference electrode and counter electrode of platinum foil. 0.1 M solution of NaClO₄ in H₂O was used as the supporting electrolyte. The well-studied redox system 1 mM K₃Fe(CN)₆ + 1 mM K₄Fe(CN)₆ with high reversibility of oxidation and reduction reactions and often used as the test one in the study of electrodes was applied for estimation of the electrochemical activity of the obtained diamond coatings [9].

As the study showed, the region of potentials of ideal polarizability and electrochemical activity of nitrogen doped nanostructured diamond coatings obtained in various conditions are markedly different. The analysis of the obtained results showed that these differences corre-

late heavily with the change in the nitrogen concentration in the gas phase composition or any other its component during synthesis of diamond coatings. Connection between the changes in the working potential window and resistivity of the investigated coatings was more clearly distinguishable. Coatings with the electrical resistivity at the level of (10^4 – 10^5) Ohm × cm had the maximum values of the potential window (about 4 V) (Fig. 2).

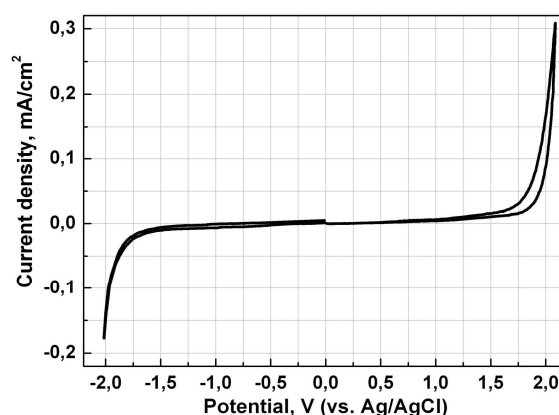


Fig. 2 – Background cyclic voltammogram in aqueous medium at the diamond electrode (sample No1). Potential scan rate is 100 mV/s

With decreasing resistivity of diamond coatings, the working potential window also decreased to the value of about 3 V for the coatings with resistance at the level of 10^3 Ohm × cm and less. In Fig. 3 we illustrate the background voltammogram of the sample with resistivity at the level of 20 Ohm × cm (sample No3). The background voltammogram for the glassy carbon electrode is also shown for the comparison. The working potential window for the considered sample belongs to the range from -1.65 V – 1.45 V and is equal to 3.1 V. The boundaries of the window are determined at the level of the background current of 0.1 mA/cm² that approximately corresponds to the value of the oxidation current peak of the investigated redox couple in the concentration of 1 mM at the scan rate of 100 mV/s.

The greatest interest to diamond electrodes for the electrochemical analysis is associated with low level of the capacitive current compared with other electrode materials that allows to significantly decrease the detection limit of analytes. As seen from the voltammograms in Fig. 3, the recharge current of the double electrical layer capacity on the glassy carbon electrode substantially exceeds the same for the nitrogen doped diamond coating. The average value of the capacitive current in the potential range near zero is approximately equal to 76 μA/cm² for glassy carbon and 5.3 μA/cm² for diamond, i.e. the latter is approximately 14 times less.

The study of the electrochemical activity of nitrogen doped nanostructured coatings with electrical resistivity more than $10^4 \text{ Ohm} \times \text{cm}$ has shown that such samples manifest an extremely low electrochemical activity; and a significant broadening of the redox process waves and a strong relative shift of the potentials of the forward and backward wave peaks by the value of the order of 1.4 V are observed (see Fig. 4).

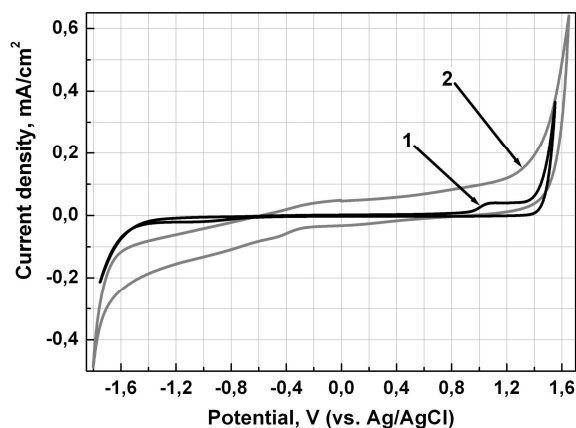


Fig. 3 – Background cyclic voltammograms in aqueous medium on the diamond (1) (sample No3) and glassy carbon (2) electrodes. Potential scan rate is 100 mV/s

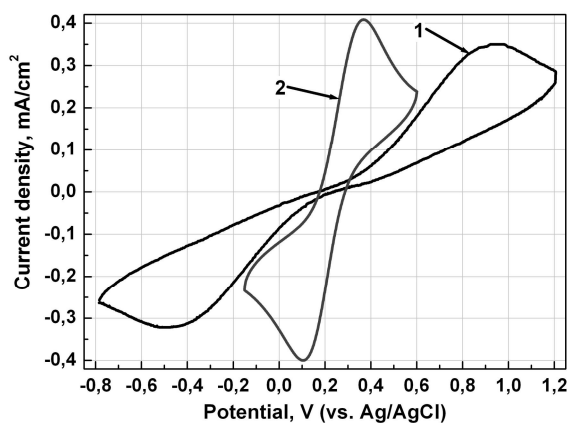


Fig. 4 – Cyclic voltammograms of the 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ aqueous solution on the diamond (1) (sample No1) and glassy carbon (2) electrodes. Potential scan rate is 100 mV/s

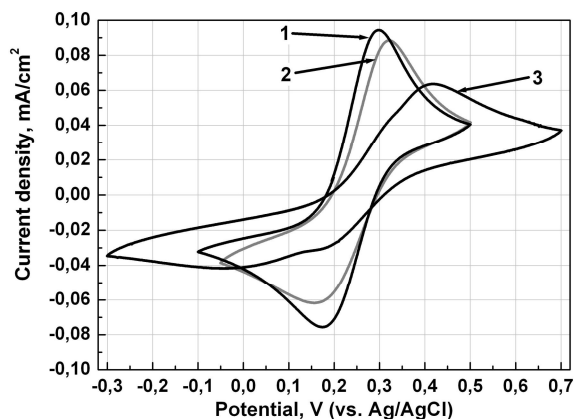


Fig. 5 – Cyclic voltammograms of the 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ aqueous solution on diamond electrodes: 1 – sample No2; 2 – No3; 3 – No4. Potential scan rate is 10 mV/s

With decreasing resistivity of diamond coatings, the potential difference between the peaks of the forward and backward wave currents of the redox process decreases on the voltammograms.

Investigations of the samples with resistivity at the level of 10^3 and less show that the substrate (on which deposition occurs) temperature has a significant impact on the electrochemical properties of the obtained diamond films. In Fig. 5 we illustrate the cyclic voltammograms of the redox couple on diamond electrodes No2, No3 and No4 at the potential scan rate of 10 mV/s obtained at the identical gas mixture composition, but at different substrate temperatures (1270 K, 1195 K and 1160 K, respectively). As seen from the figure, decrease in the currents of the oxidation and reduction peak of the redox couple is observed with decreasing substrate temperature. At the same time, shift of the potentials between the forward and backward waves increases and one can observe the increase in asymmetry of the redox process. The asymmetry lies in the disproportionate decrease in the reduction wave peak compared with the oxidation wave. For the considered samples this correlation is equal to: No2 – 1.15, No3 – 1.43, No4 – 1.48. For comparison, this correlation on the glassy carbon sample is equal to 1.11. This may indicate a slowdown of the electron transfer from the surface of the diamond-modified samples to its acceptor in the solution in comparison with the inverse process, i.e. the presence of the valve effect typical for semiconductor electrodes takes place.

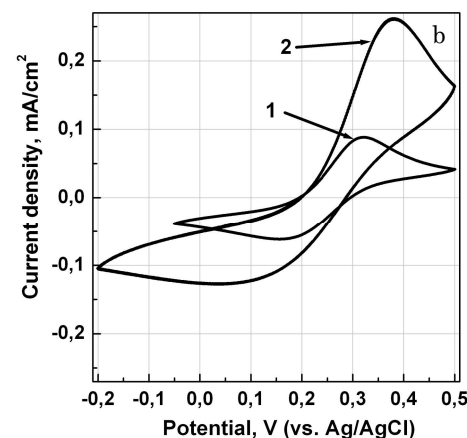
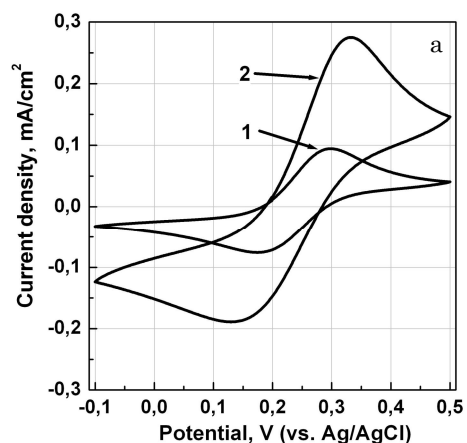


Fig. 6 – Cyclic voltammograms of the 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ aqueous solution on diamond electrodes: No2 (a) and No3 (b) at the potential scan rates of 10 mV/s (1) and 100 mV/s (2)

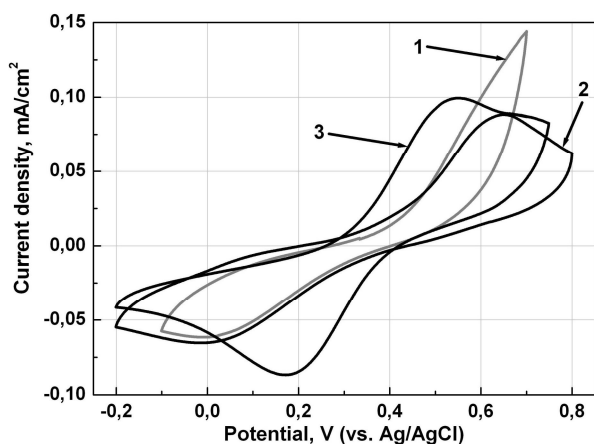


Fig. 7 – Cyclic voltammograms of the 1 mM $K_3Fe(CN)_6$ + 1 mM $K_4Fe(CN)_6$ aqueous solution on the diamond electrode No5 at the potential scan rate of 10 mV/s; 1 – the first cycle; 2 – after one cycle in the range of $-1 - 1$ V; 3 – after three cycles in the range of $-1.5 - +1.5$ V

One should also pay attention to the fact that oxidation and reduction peaks, which precede the main waves of the oxidation and reduction processes, are observed in Fig. 5 (curve 3, sample with the worst electrochemical activity). Seemingly, they are associated with the presence of the adsorbed form of electroactive composition at the surface or inside of the porous structure of nitrogen doped diamond electrodes [10].

Further increase in asymmetry of the redox processes for the studied electroactive composition at diamond electrodes is observed with increasing potential scan rate of the working electrode to 100 mV/s (Fig. 6). As seen, the degree of asymmetry with increasing scan rate increases stronger for the electrode which initially possessed the worst electrochemical activity (see Fig. 6b, sample No3). Thus, peak current ratio for the sample No2 is changed from 1.15 to 1.45, while for the sample No3 – from 1.43 to 2.04. For comparison, increase in the asymmetry of the redox process of the $K_3Fe(CN)_6$ + $K_4Fe(CN)_6$ couple on the glassy carbon electrode occurs from the value of 1.11 at the rate of 10 mV/s to the value of 1.22 at 100 mV/s.

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It was revealed during the electrochemical study of the obtained samples that scanning of the electrode potential in a wide range in the solution of supporting electrolyte has a positive impact on the electrochemical activity of some of them. In Fig. 7 we illustrate the cyclic voltammograms of 1 mM $K_3Fe(CN)_6$ + 1 mM $K_4Fe(CN)_6$ redox-active composition for the diamond electrode with a low electrochemical activity (sample No5) immediately after being placed in the cell (1) and also after one scanning cycle of the electrode potential in the range of $-1 - 1$ V (2) and after three scanning cycles of the electrode potential in the range of $-1.5 - 1.5$ V (3). A significant improvement in the course of the redox processes is observed in this case, as well as the appearance of distinct oxidation and reduction waves and also convergence of the oxidation and reduction peak potentials of the studied redox couple.

3. CONCLUSIONS

Thus, by the gas phase chemical synthesis method we prepared the samples of electrodes representing the molybdenum substrate on which a nitrogen doped nano-diamond film is deposited. Investigation of the electrochemical properties of the obtained samples showed that the decrease in the resistivity of nanostructured diamond coatings increases their electrochemical activity, thus making them closer to the ideal electrode materials. An important role of the substrate temperature, on which deposition of a diamond film occurs, is also shown. The best of the obtained samples possess electrochemical activity not inferior to the samples of glassy carbon; in this case, the value of the capacitive currents is lower than of glassy carbon by more than one order of magnitude that is substantial when using electrodes for the electrochemical analysis. On the other hand, decrease in the resistivity of diamond coatings is accompanied by the decrease in the working potential window and its value is no less important characteristic for the electrode material. Therefore, in the practical use of nitrogen doped nanostructured diamond coatings as the electrodes, one should take into account such dependence of the characteristics on the resistance and choose the optimal variant of their resistivity depending on the assignment.