

Electrochemical Behavior of Semiconductive Diamond Single Crystals in Aqueous Solutions

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The majority of the electrochemical investigations of diamond electrodes were made using film diamond (doped polycrystalline, single-crystalline) and diamond-like (a-C, a-C-H, modified diamond-like carbon) materials [1,2,3]. The study of semiconductive diamond single crystals is devoted several works of Y.V. Pleskov's school of electrochemists [4,5]. The peculiarities of this type of diamond electrodes are large data scattering of electrophysical and electrochemical characteristics depending from crystallographic orientation of crystal faces under investigation. Nevertheless, the study of electrochemical behavior of semiconductive diamond single crystals is actual scientific and applied problem though of its high fabrication cost. Thanks to their unique corrosive inertness, these electrodes can be successfully applied in the electrochemical monitoring of extraordinarily aggressive environments.

The goal of this paper is electrochemical study of semiconductive diamond single crystals of p-type and correlation of its behavior with crystal structure and electrophysical parameters.

Experimental.

The subjects of the investigations are diamond single crystals (of IIb type) grown from the iron-aluminous solvent-alloy using a seed by the temperature gradient method in the apparatus of high pressure of anvil type with crater-toroid. Procedure, conditions of synthesis, impurities-defects composition and electrophysical characteristics of diamonds under investigation are described in [6]. Doping of diamonds was made by introduction of boron containing compound in to the carbon source. The concentrations of boron in the solvent alloy are in the range of 0,12 ÷ 0,13 mass % for blue diamond (# 4) and 0,5 mass % for dark diamonds (#12, #13, #14). All grown crystals have cubooctahedron habitus with octahedron faces surface is about 65-70 % and sizes are about 4-6 mm. Different individual faces of the crystals and gang of faces (vertex of pyramid) sequentially exposed to the electrolytes were studied. Ohmic contacts to the rear side of the crystal faces were realized by silver clay, the cleared paraffin insulated an inoperative surface of electrode. Potencidynamic voltampere curves of Redox systems of $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $\text{Ce}^{3+/4+}$ and $\text{Fe}^{2+/3+}$ in the background electrolyte solutions 1 M KCl; 0,5 M H_2SO_4 were obtained by potentiostat Pi-50-1.1 with the linear scanning of potential rate $V=5\div 500$ mV/s. The concentrations of the Red-Ox forms of depolarizators were changed within the limits of 10^{-4} – 10^{-1} mol/l. For the impedance measuring in range 0,1÷20 kHz and for the cyclic voltametry at the rapid potential rates the computerized measuring system Unilab was used.

Results and Discussion

We investigated 4 semiconductive diamond single crystals of different sizes, forms and boron concentration. It was found that potential window (background currents < 10 mkA/cm²) of diamond electrodes is in the limit {-2,0

÷ + 1,2 V} for 0,5 M solution of H_2SO_4 and {-1,0 - +0,8 V} for 1 M solution of KCl and did not depend from boron concentration and crystallographic orientation of crystal faces. Electrochemical response to various forms of depolarizator, on the contrary, essentially depends from crystallographic orientation of crystal faces under investigation and preliminary surface treatment. It was found that that the most electrochemical active are lateral faces {100} and {111}, but not central grown face {100}. These conclusions are in agreement with results of work [6], where was established, that boron concentration is higher in faces grown pyramids {111} than in {100}. Kinetic characteristics (transfer coefficients and rate constants) were determined for the individual crystal faces from dependencies of current peak potentials on the potential-scan rates. The rate and reversibility of studied redox systems also depended from surface polishing of the faces and from consequence of electrode polarization direction. Freshly polished electrochemical active faces in due course became inactive and for its activation it needed new polishing or electrochemical oxidation. The resistance of studied crystals was estimated by impedance and direct current methods, its values are in the range 50 ÷ 0,5 Ohm cm.

Conclusions.

Thus, the results of electrochemical researches confirmed zonal-sectorial nature of distributing of boron acceptor impurity in the explored diamonds, set in [6] by other physical methods. This fact together with passivation of working surface in the process of the electrochemical measuring are causes of unstable work of such type of diamond electrodes. Overcoming these difficulties will be the aim of further researches.

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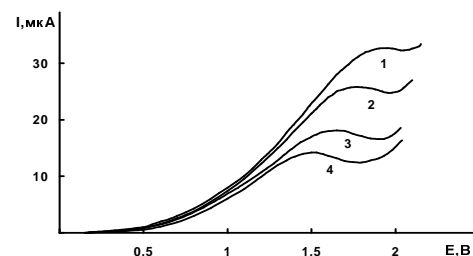


Fig.1 I-V scan of diamond # 13 at lateral face {111} in solution 10^{-2} M of $[\text{Fe}(\text{CN})_6]^{4-}$ in 0,5 M H_2SO_4 , $V, \text{mV/s}$: (1)- 100; (2) – 50; (3) – 20; (4) – 10. ($S=0,05 \text{ cm}^2$).