Vacuum-Annealed Undoped Polycrystalline CVD Diamond: a New Electrode Material

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Vacuum-annealing imparts conductivity to initially insulating undoped polycrystalline chemical-vapor-deposited diamond, thus turning it to a possible electrode material. Using the HREM analysis [1], formation of amorphous, turbostratic, and/or well crystallized graphite layers up to 20 nm thick along the grain boundaries was visualized. These amorphous carbon and/or graphite-like layers compose a continuous conducting network making the primarily insulating material conductive.

In the present work we studied the electrochemical behavior of a free-standing vacuum-annealed undoped polycrystalline CVD diamond film [in particular, of its outer (growth) side and an inner (nucleation) side] in indifferent electrolyte (2.5 M H_2SO_4) and 0.01 M $Fe(CN)_6^{3-/4-}$ redox system.

A 400 μm-thick diamond film was grown in a methane/hydrogen/oxygen mixture on a polished silicon substrate using a 5 kW microwave plasma-enhanced CVD system. Typically the resistivity of the film was in the range of 10^{11} to 10^{12} Ω cm. The samples were annealed at temperatures T_{ann} between 1725 and 1925 K for 1 hour in vacuum of 10^{-5} Torr. The diamond film annealed at 1775 K appeared to be practically not conducting. With further increase in the annealing temperature above T_{ann} = 1825 K,

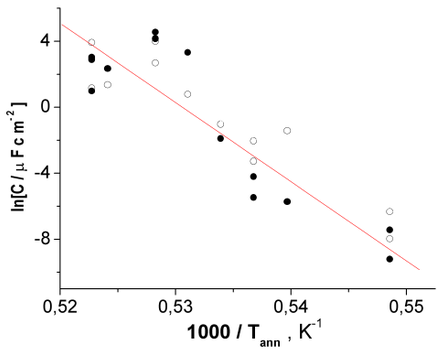

Fig. 1. Arrhenius plots for logarithm of differential capacitance C (**o** - growth side, ● - nucleation side).

the film effective resistivity decreased from initial value of 10^{11} – 10^{12} Ω cm down to less than 0.1 Ω cm.

Upon the annealing, the differential capacitance (measured in 2.5 M H_2SO_4 at steady-state potential) increased from ~ 10^{-3} to ~ 50 μF per 1 cm^2 of geometrical surface (Fig. 1); the transfer coefficients for electrochemical reactions in the $[Fe(CN)_6]^{3-/4-}$ redox solution increased from ~ 0.2 to 0.5 (Fig. 2); and the degree of reversibility of the electrochemical reaction increased.

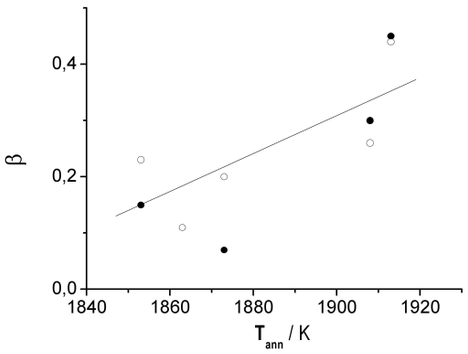

Fig. 2. Dependence of transfer coefficient β for $Fe(CN)_6^{4-}$ oxidation on T_{ann} (**o** - growth side, ● - nucleation side).

The observed changes in the electrode properties are attributed to gradual change in the thickness and/or properties (first and foremost, conductivity) of the nondiamond carbon phase formed along the intercrystallite boundaries upon the annealing. The conductive phase is outcropping at the film surface as an array of microelectrodes ("active sites").

The sort of composite diamond--«graphite» films can be of interest for electrochemical applications as an alternative both to semiconductor diamond and other carbonaceous-material electrodes.

[1] L. Nistor, V. Ralchenko, I. Vlasov, A. Khomich, R. Khmelnitskii, P. Potapov, J. Van Landuyt, Phys. Stat. Sol. (a) **186** (2001) 207.

This work was carried out financed in part by NEDO International Joint Research Grant Program (Project 01MB9) and Russian Foundation for Basic Research (Projects 01-02-16826 and 01-03-32045).

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