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The regularities of high-fluence ion-induced graphitization of diamond

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ABSTRACT

The process of high-fluence ion-induced graphitization and the influence of irradiation by 10–30 keV Ar^+, Ne^+, N^+, N_2^+ and C^+ ions at temperatures from 30 to 720 °C on the conductivity and microstructure of polycrystalline diamond surface layer were experimentally studied. The increase of diamond temperature during irradiation leads to the ion-induced graphitization at $T_{ir} > T_{gr} \approx 200$ °C. It has been found that T_{gr} practically coincides with the corresponding temperatures of dynamic annealing of radiation damage in graphite. The Raman spectra indicate that irradiation with neon and argon ions at temperatures of the diamond more than $T_{ir} > 500$ °C leads to the formation of nanocrystalline graphite layer that increases resistivity of the irradiated layer. This effect is not observed under irradiation by nitrogen ions. As for C^+ ion irradiation the synthesis of diamond with a thin graphite-like layer formation on the surface has been observed.

1. Introduction

Studies of ion-beam modification of diamonds and diamond-like materials have been made for more than 40 years [1–11]. The main feature of ion irradiation of diamond in comparison with, for example, silicon, is associated with metastability and with the ion-induced transition of diamond to stable graphite-like forms. High-fluence irradiation ($>10^{16}$ ion/cm^2) leads to formation of a conductive graphite-like layer [4–11]. The value and nature of the conductivity of graphite-like materials depend on the degree of sp^2 hybridized carbon atom ordering [12]. Graphites with the three-dimensional ordered graphene packs in the form of allotropic hexagonal lattices of graphite have the highest conductivity. Less-ordered two-dimensional sp^2 carbon in various turbostratic forms such as glassy carbons has a lower conductivity. The lowest conductivity characteristic for semiconductors has amorphous sp^2 carbon. In the latter case, conductivity is described by a hopping mechanism, whereas, for two and three-dimensional ordered sp^2 carbon materials, it has close to metallic conductivity.

At irradiation fluences somewhat higher than the diamond graphitization fluence Φ_{gr} ~10^{16} ion/cm^2, the resistivity ρ of a modified diamond layer is very large and corresponds to amorphous semiconductors with a hopping conductivity. Resistivity decreases by several orders of magnitude with increase in the irradiation fluence and usually at sufficiently high fluences ($\geq 10^{17}$ ion/cm^2) goes to a stationary level which depends on the irradiation temperature T_{ir}. The high-fluence irradiation of monocrystalline and polycrystalline diamonds by argon and neon ions with 30 keV energy observed in our previous studies, showed that the steady-state conductivity of a modified diamond layer can correspond to conductivity of all three sp^2 carbon forms depending on the irradiated temperature [10,11]. The layer resistivity corresponding to hexagonal graphites is observed at elevated temperatures of irradiated diamond $T_{ir} \geq 200$ °C. At temperatures $T_{ir} < 200$ °C the resistivity of a formed layer increases exponentially. Apparently it was connected with abrupt decrease in the proportion of graphite phase in a heterogeneous structure of the diamond modified layer [11].

At temperatures $T_{ir} < 200$ °C the graphite-like layer is not thermally stable. Heat treatment in vacuum leads to an exponential drop of the resistivity at temperatures of about 600–700 °C to the values of graphites. Note that the thermal graphitization of

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diamond in vacuum begins at temperatures above 1770 °C [13]. In this connection, ion-induced graphitization at $T \geq 200^{0}$C can be characterized as ion-stimulated thermal graphitization of diamond with decreasing graphitization temperature of order several hundred degrees [11].

Studies in Refs. [10,11] were carried out at irradiation temperature up to 400 °C. At the same time, there are reasons to assume that the ion-induced graphite layer is not in dynamic equilibrium at large (T > 400 °C) temperatures of ion irradiation. Carbon ion irradiation in Ref. [14] showed that the increased resistances of the irradiated layer are observed not only at temperatures close to room temperature, but also, at elevated temperatures T_{ir} > 400 °C. Authors have assumed that the latter is due to the dynamic annealing of radiation damage in diamond. In a well-known paper [1], devoted to the invention of the method of diamond synthesis *via* high-fluence carbon ion implantation with energies 5–100 keV, it was possible to increase the thickness of diamond crystals to 10 μm. It was found that the synthesis of diamond occurs at elevated temperatures of more than 350 °C. At lower temperatures graphite-like structures were formed. In the present paper the high-fluence ion-induced conductivity of polycrystalline diamond is studied at irradiation temperatures from RT to 720 °C for Ar and Ne noble gases, nitrogen and carbon ions. The structure of the modified layer is analyzed by reflected high-energy electron diffraction (RHEED) and Raman spectroscopy.

2. Experimental

Polycrystalline diamond samples have been used as the targets, as well as a synthetic single crystal of diamond. Plasma-chemical synthesis of polycrystalline diamond was performed on an ARDIS-100 installation [15] at microwave power of 3.8 kW, frequency of 2.45 GHz and H_2/CH_4 mixture pressure of 91 mbar. Methane content of the mixture was 5%. Synthesis temperature was 940 °C. A polycrystalline diamond plate with a thickness of 450 μm and grained structure (crystallite sizes up to 100 μm) has been obtained on a silicon wafer. The Raman spectrum has only one narrow diamond line at 1333 cm^{-1}.

Ion irradiation was carried out along the normal to the surface of diamond samples on the mass-monochromator of the Skobel'tsyn Research Institute of Nuclear Physics, Moscow State University [16] using the procedure similar to [10,11]. The diamond samples were irradiated with 10, 20 and 30 keV Ar^+ ions, 30 keV Ne^+ ions, 30 keV molecular and atomic nitrogen, and 30 keV C^+ ions. The ion current density was about 0.2–0.3 mA/cm^2 for the beam cross-section of 0.3 cm^2, and the irradiation fluence was $\geq 10^{18}$ ion/cm^2. A special holder with the possibility of cooling the target with running water was used to prevent heating during irradiation. The flat resistive furnace in the target holder allowed the target to be heated up to 720 °C. The target temperature has been measured with a chromel-alumel thermocouple fixed on the irradiated side of the sample outside of the irradiation area. The modified targets have been analysed by a Horiba JobinYvon T64000 Raman spectrometer with the laser excitation wavelength 514 nm. The crystalline structure of the surface layers has been analyzed by the method of reflection high energy electron diffraction (RHEED). The RHEED was performed in EMR-102 (Russian model) operated at 50 kV and electron beam current 50 mA. Electrical measurements of the sheet resistance R_s were used by a four point probe method at room temperature.

3. Characterization of high-fluence ion irradiation

To compare the results of the studies of the modified diamond layer after irradiation with different ions and energies the depth distributions $\nu(x)$ of the number of displacement per atom (*dpa*) (damage depth profiles) were calculated. The profiles $\nu(x)$ are determined by the depth distributions $\Sigma(x)$ of the average number of vacancies formed by one ion per path length, which can be derived by computer simulation of the ion interactions with solids using the SRIM code [17]. At not too high fluences $\nu(x) \approx \Phi \cdot \Sigma(x)/n_0$ where the fluence $\Phi = \varphi \cdot \tau$ is equal to the product of ion beam flux φ and irradiation time τ, n_0 is the atomic target concentration [18]. At high fluences, a factor limiting the concentration of implanted particles and radiation damage is surface erosion. Because of movement of the surface boundary due to sputtering, dynamically equilibrium conditions are established in many cases, in which the profiles of concentration of implanted particles and radiation damage become stationary [16,18–24]. In the dynamically equilibrium irradiation conditions the damage depth profile $\nu_{st}(x)$ is attained at $\Phi > R_d n_0/Y$, where Y is the sputtering yield, R_d - the depth of defect production, cf [24].

$$\nu_{st}(x) = \frac{1}{Y} \int_{X}^{Rd} \sum(x') \cdot dx'. \quad (1)$$

In present study the $\nu_{st}(x)$ profiles were performed using sputtering simulation based on SRIM 2013. To take into account sputtering in the calculations of the $\nu_{st}(x)$ profiles numerical integration was used using shifting the profiles $\Sigma(x)$ by a distance δ. The fluence Φ_δ was determined from the relation $\delta = Y\,\Phi_\delta/n_0$.

Fig. 1a shows the calculated profiles $\Sigma(x)$. The parameters of the irradiated target in the simulation corresponded to graphite because, for high-fluence irradiation, $\Phi > \Phi_{gr}$. According to [25] for displacement energy E_d = 60 eV, surface binding energy E_c = 7.41 eV and bulk binding energy E_b = 2 eV, the target density corresponds to the theoretical graphite density of 2.2 g/cm^3. Simulation of irradiation with 30 keV N_2^+ molecular ions was carried out in the approximation of independent interaction of two 15 keV N^+ ions with the target, see Ref. [26].

From Fig. 1a one can see that, with ion mass increase at the same energy, the maximum of the $\Sigma(x)$ profile increases, and the depth of defect production decreases in the order C-N-Ne-Ar. The stationary profiles $\nu_{st}(x)$ calculated from the computer simulation data for these ions are shown in Fig. 1b. The initial $\Sigma(x)$ dependences are transformed into decreasing curves $\nu_{st}(x)$ with a maximum ν_0 on the surface. It is also seen that the dependence of ν_0 on the ion mass becomes inverse compared with the maximum of the dependences $\Sigma(x)$. Values ν_0 grow with an increase in the ion penetration depth [23].

Based on the calculated profiles of $\nu_{st}(x)$, the thickness t of the modified surface layer which is necessary for calculations of resistivity $\rho = R_s \cdot t$, was estimated. The value of t was determined from the level of 10 *dpa*. This value of ν is attained over the depths $x \leq R_d$ at ions fluences of about 10^{17} ion/cm^2 when the steady-state conductivity of the irradiated diamonds is observed (see Introduction). Unlike irradiation by gas ions for C^+ ion irradiation the thickness of the modified layer increases due to the implanted carbon ions, since self-sputtering yield (0.21) is less than 1 [27]. For this reason, in the $\nu_{st}(x)$ profile calculations for irradiation of diamond with carbon ions, the denominator of formula (1) was (1-Y). For estimating the thickness t, the thickness of the deposited carbon to the modified layer thickness obtained from $\nu_{st}(x)$ was added.

4. Results and discussion

Fig. 2 shows the experimental values of the resistivity ρ of the modified diamond layer as a function of the irradiated target temperature T_{ir}. The table values of the graphite-like materials