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Structural transformation of implanted diamond layers during high temperature annealing

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ABSTRACT

In the recent years graphitization of ion-beam induced amorphous layers became the basic tool for device fabrication in diamond. The etchable graphitic layers can be removed to form free-standing membranes into which the desired structures can be sculpted using FIB milling. The optical properties of the devices fabricated using this method are assumed on the model of sharp diamond–air interface. The real quality of this interface could depend on degree of graphitization of the amorphous damage layers after annealing. In the present work the graphitization process was studied using conventional and analytical TEM. It was found that annealing at 550 °C results in a partial graphitization of the implanted volume with formation of the nano-crystalline graphitic phase sandwiched between layers of tetrahedral amorphous carbon. Annealing at 1400 °C resulted in complete graphitization of the amorphous layers. The average size of graphite nano-crystals did not exceed 5 nm with predominant orientation of *c*-planes normal to the sample surface.

1. Introduction

The progress in the fabrication of synthetic diamond has resulted in increasing number of its potential applications. Single crystal diamond has also attracted enormous interest as a solid state platform for quantum information processing. Nitrogen-vacancy (N-V) color centers in diamond show remarkable quantum properties such as long coherence times and single spin readout, and can be used as qubits in a quantum computer architecture [1–3]. In order to take advantage of these properties, it is highly desirable to fabricate photonic components in diamond at the micro and even nano-scale level. In a previous work we demonstrated the ability of fabricating three-dimensional structures in diamond at the micro-scale level using lift-out method [4]. MeV ion implantation was used to create a buried damage layer which transformed into a graphite-like layer upon high temperature thermal annealing. The graphitic layer can be selectively etched to form a free-standing membrane into which the desired structures can be sculpted using focused ion beam (FIB) milling. Ion implantation with tens of keV ion energy [5] or multiple energy implantation techniques [6] when combined with FIB milling allows device fabrication in diamond at the micro- and nano-scale. The modeling of the optical properties of the devices fabricated using this method [4–8] are based on the assumption of a sharp diamond–air interface. The real quality of this interface could depend on many factors, for example, on the degree of graphitization of the amorphous damage layers after annealing. Kalish et al. [9] reported complete graphitization of the implanted layer in diamond after a 20 min annealing at 600 °C. However, a recent study [10] using high-resolution electron microscopy (HREM) revealed the presence of a transition area with pockets of crystalline diamond in the graphite matrix near surface, after high temperature vacuum annealing of implanted layer in diamond. Thus, the real quality of the diamond surface after chemical removal of graphitic layer can be far from ideal. In the present work the processes of the ion-beam-induced amorphisation and graphitisation in diamond were studied using cross-sectional conventional and analytical TEM. The graphitisation of the amorphized layers was carried out at annealing temperatures of 550 °C and 1400 °C.

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2. Experimental

Synthetic (001) diamond samples produced by Sumitomo Inc. were implanted at room temperature with He^+ ions to a fluence range of 3×10^{16}–10×10^{16} cm^{-2}. The energy of the He^+ ions was 0.5 MeV or 2 MeV. The ion implantation with ion energy of 0.5 MeV was performed through a mask, (a copper TEM mesh grid). Thus, the latter sample contains implanted areas separated by unimplanted areas screened during implantation by grid bars. The 0.5 MeV implantation was chosen to create the damage layer in diamond much closer to the specimen surface for TEM imaging of the cross-section of implanted and unimplanted regions at the same time.

The samples were annealed for 1 h in forming gas (4% hydrogen in argon) atmosphere at 550 °C and in vacuum at 1400 °C. Cross sectional TEM samples were prepared using the lift-out method [11,12] after ion implantation and after thermal annealing. Prior to TEM specimen preparation, all implanted diamond samples were coated with thin carbon films and 300 nm thick Pt protection layers were deposited using electron-beam deposition facility of the FEI Nova Nanolab dual-beam FIB system in order to mask the TEM cross section from the Ga beam. Cross-sectional TEM samples were prepared in [110] and [100] orientations. Also, a cross-sectional TEM sample was prepared from the sample after annealing at 550 °C and chemical etching of graphitic layer in boiling acid (1:1:1 H_2SO_4/$HClO_4$/HNO_3). This TEM lamella contains the bottom interface of the diamond cap layer (i.e. the layer comprised between the surface and the buried heavily damaged layer). Conventional TEM imaging was done using a Tecnai TF 20 electron microscope operated at 200 kV. Energy-filtered TEM (EFTEM) imaging was conducted at 200 kV (JEOL, JEM-2100). Electron energy loss spectroscopy (EELS) was conducted at 300 kV (JEOL 3000F).

The vacancy density profiles for 0.5 MeV and 2 MeV He^+ ions in diamond were calculated using the SRIM 2008 Monte Carlo code [13] with the diamond density 3.52 g/cm^{-3} and the atom displacement energy 52 eV. The simulation gives peak positions of defect density 0.98 μm and 3.5 μm from the diamond surface correspondingly for 0.5 MeV and 2 MeV He^+ ions.

3. Results and discussions

The interaction of the energetic ions with the diamond substrate initiates a sequence of displacement events that leads to the production of lattice defects (vacancies and interstitials) and, at sufficiently high fluences, to the crystalline-to-amorphous (c–a) transformation of the irradiated volume [4,6]. The amorphous damage layer after 0.5 MeV He^+ ion implantation is clearly visible in the bright-field TEM image in Fig. 1a due to absence of the diffraction contrast or long-range order in this area. The vertical amorphous–crystalline interface at the edge of the implanted area reflects the defect density profile at the end of the ion range for the 0.5 MeV He ions and has peak position at 1 ± 0.05 μm which correlates well with SRIM simulations. With the exception of the area in the vicinity to the right edge, the amorphized damage layer has uniform thickness (200 ± 10) nm. The surface height step (75 ± 4 nm) between unimplanted (masked by TEM grid bar) and implanted regions is evident and is indicated by the white line and the arrow in Fig. 1a. The conducted EELS measurements have shown the presence of both sp^2 and sp^3 bonding in the implanted region. The swelling of the implanted layer has been attributed to the conversion of the diamond's sp^3 bonds to graphite-like sp^2 bonds with significant decrease in density. The positive step height between unimplanted and implanted regions could be a result of a Poisson ratio effect arising from the biaxial compressive stress in the plane of the implanted layer [14].

Fig. 1b shows the damage layer in diamond after 2 MeV He^+ implantation. The thickness of this amorphous layer was measured to be ~210 nm, with leading edge at ~3.45 μm from diamond surface. Thus, the position of implanted layer was found in good agreement with SRIM simulated data. Dark strain contours can be noticed along both amorphous–crystal interfaces in Fig. 1a and b. These contours represent strain field in the implanted region. Fig. 1b and c shows magnified bright field and **g**-3**g** weak beam dark field (WBDF) images with diffraction vector **g** = [2 −2 0] from an area implanted with 2 MeV He^+. WBDF is a powerful method for imaging crystal defects like dislocations with a high spatial resolution. Only near the core of the lattice defects the strain is large enough to bend the crystal planes back to the Bragg condition. The contrast in the WBDF image is very strong and sharp in the regions where the crystal lattice is distorted and this area is visible as a band of small white spots in Fig. 1c. However, it is worth noting that despite of the large number of the lattice defects diamond remains crystalline in this region. The distorted region is thicker for the leading edge of the implanted area and thinner for tailing edge, which correlates with damage profile as simulated by SRIM. Simulated damage profiles have asymmetrical shape with broad leading edge and sharp trailing edge [4,6]. The concentration of point defects here is below the critical value which is known as the amorphisation threshold (D_c) but high enough to cause local crystal lattice distortion. Depending on the fabrication technique, amorphous carbon films can have a wide range of diamond-like, sp^3 bonded carbon content, ranging from pure sp^2 to approximately 80% sp^3 (tetrahedral amorphous carbon) [15]. EELS measurements of the carbon K-edge in the amorphous damaged region showed a prominent feature at 285 eV, i.e. the π^* peak associated with the presence of sp^2 bonding [16]. This, together with swelling, indicates the conversion of the diamond sp^3 bonds to sp^2 in the amorphous damage area. Using a mass-balance calculation with the values of height step and amorphous layer thickness (Fig. 1), the average density of the amorphous damage layer after ion implantation in diamond was calculated to be ~2.2 g cm^{-3} (~20% sp^3 fraction), a value which is close to the density of graphite (2.09–2.23 g cm^{-3}).

Fig. 2a shows the damage layer in diamond implanted with 2 MeV He^+ ions after 1 h annealing at 550 °C. A new phase is visible with brighter contrast in the middle of the damage layer. Selected-area diffraction patterns taken from the area containing this damage layer from the specimens prepared in [100] and [110] orientations are shown in Fig. 2b and c. The diameter of the selected area aperture was slightly bigger than the width of the damaged layer covering interfaces with diamond and diffraction spots from the diamond are also present (some are identified in these pictures).

Two arcs in the diffraction pattern are also visible (Fig. 2b and c), which correspond to graphite (002) atomic planes. These arcs indicate the presence of the graphite nano-crystals which are oriented semi-randomly with some preferred orientation. Such preferential orientation has graphite (002) planes parallel to diamond (040) atomic planes for diffraction into [100] direction (Fig. 2b) and parallel to diamond (220) atomic planes for diffraction into [110] direction (Fig. 2c). This means that graphite crystals in the damaged layer after annealing are oriented semi-randomly with (002) atomic planes arranged predominantly vertical to the diamond surface. The dark field image of the damage layer with diffraction vector [002] of graphite is shown in Fig. 2d. Graphite nano-crystals are now visible as the bright spots. The average size of the graphite nano-crystals does not exceed 5 nm. These nano-crystals are only visible in the central part of the damage layer. This means that at the given annealing conditions the