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Direct fabrication of three-dimensional buried conductive channels in single crystal diamond with ion microbeam induced graphitization

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ABSTRACT

We report on a novel method for the fabrication of three-dimensional buried graphitic micropaths in single crystal diamond with the employment of focused MeV ions. The use of implantation masks with graded thickness at the sub-micrometer scale allows the formation of conductive channels which are embedded in the insulating matrix at controllable depths. In particular, the modulation of the channels depth at their endpoints allows the surface contacting of the channel terminations with no need of further fabrication stages.

In the present work we describe the sample masking, which includes the deposition of semi-spherical gold contacts on the sample surface, followed by MeV ion implantation. Because of the significant difference between the densities of pristine and amorphous or graphitized diamond, the formation of buried channels has a relevant mechanical effect on the diamond structure, causing localized surface swelling, which has been measured both with interferometric profilometry and atomic force microscopy. The electrical properties of the buried channels are then measured with a two point probe station: clear evidence is given that only the terminal points of the channels are electrically connected with the surface, while the rest of the channels extends below the surface. IV measurements are employed also to qualitatively investigate the electrical properties of the channels as a function of implantation fluence and annealing.

1. Introduction

The process of graphitization induced in diamond by ion implantation was first investigated by Vavilov et al. in the 70s [1]. This pioneering work triggered a series of studies on the effects of ion induced damage on the electrical transport properties of diamond. Hauser et al. demonstrated that the electrical properties of ion-implanted diamond layers were similar to those of amorphous carbon produced by sputtering graphite [2,3]. The hopping conduction in diamond implanted with carbon ions at different energies and fluences was investigated by Prins [4,5], who interpreted the onset for this process with mechanisms of vacancy–interstitial interaction, focusing on the different mobility of vacancy and interstitial defects in the crystal. In a series of Ar and C implantation experiments carried at different temperatures, Sato et al. demonstrated that target temperature during implantation has a strong influence on the ion damage processes that determine the increase in conductivity, as confirmed by Raman characterization [6,7]. The effect of C and Xe ion induced graphitization in polycrystalline samples grown by chemical vapor deposition was studied by S. Prawer et al., demonstrating that the fluence dependence of the electrical conductivity of the implanted area is similar to what measured in single crystal diamond [8]. Selective Co ion implantation on self-supporting diamond films was employed by B. Miller et al. to pattern conductive areas on which subsequent redox electron transfer and metal deposition were demonstrated [9]. S. Prawer et al. performed IV measurements *in-situ* during C and Xe implantation at different temperatures, showing complex non-monotonic dependencies of the electrical conductivity from the ion fluence. These trends confirm that the critical fluence at which a sharp decrease in conductivity (due to the formation of a continuous conducting pathway) is observed strongly depends from the implantation temperature [10,11]. B implantation studies carried by F. Fontaine et al. on polycrystalline diamond [12] confirmed the basic interpretation of the process, while introducing two different critical fluences. In their interpretation, when a "percolative threshold" fluence is reached, a continuous conductive path of sp^3-like defects is established in the implanted material and variable range

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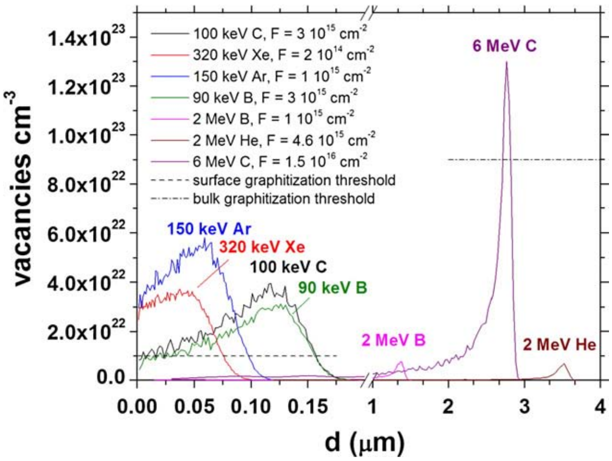

Fig. 1. TRIM Monte Carlo simulations of the damage density profile induced in diamond by 100 keV C at a fluence $F = 3 \cdot 10^{15}$ cm^{-2} [PRB_51_15711], 320 keV Xe at $F = 3 \cdot 10^{15}$ cm^{-2} [PRB_51_15711], 150 keV Ar at $F = 1 \cdot 10^{15}$ cm^{-2} [NIMB_32_145], 90 keV B at $F = 3 \cdot 10^{15}$ cm^{-2} [DRM_5_752], 2 MeV B at $F = 3 \cdot 10^{15}$ cm^{-2} [APL_71_1492], 2 MeV He at $F = 4.6 \cdot 10^{15}$ cm^{-2} [DRM_15_1714] and 6 MeV C at $F = 1.5 \cdot 10^{16}$ cm^{-2} (present work). The graphitization thresholds for shallow and deep implantations are also reported in dashed and dot-dashed lines, respectively.

hopping conduction appears, while at fluences above a slightly higher "amorphization threshold" a network of sp^2-bonded defects is formed, which leads to the permanent graphitization of the implanted areas upon thermal annealing. F. Prins carried further theoretical calculations on the data reported in [11] to interpret the onset for variable-range-hopping in a model that does not include the formation of displacement spikes in diamond crystal [13]. An extensive IV characterization in temperature of diamond implanted with Xe ions at low temperature was carried by A. Reznik et al. [14,15], allowing the extraction of a number of characteristic energies for hopping sites from the temperature dependence of the resistivity [16].

While the interpretation of the onset of hopping-related conduction mechanisms at low damage densities has been debated in detail in the above mentioned works, the formation of ohmic conductive paths in diamond at high damage densities has a more straightforward interpretation based on the formation of a stable graphite-like sp^2 network, and also found several interesting applications. S. Prawer et al. demonstrated that electrically heated resistive paths created with carbon implantation can act as infrared radiation emitters, in which IR emission is confined to the conductive damaged areas [17]. A. V. Karabutov et al. employed nitrogen implantation followed by thermal annealing to provide surface electrical conductivity to diamond microtips and improve their performance as field emitters [18,19a]. A. I. Sharkov et al. employed buried graphitized layers as integrated light absorbers in a diamond-based high speed bolometer [19b]. Moreover, the possibility of creating effective ohmic contacts on doped or intrinsic diamond by high fluence implantation has been explored in several works [20–24a].

Interestingly, while this research topic can be considered mature in terms of fundamental studies and technological applications, the possibility of fabricating buried graphitic channels, i.e. conductive paths extending below the diamond surface, has not been fully explored, with the exception of the works reported by A. A. Gippius et al. [24b], R. Walker et al. [25,26] and by E. Trajkov et al. [27]. In the former work, the fabrication of buried graphitic layers with good electrical conduction properties by means of MeV ion implantation was demonstrated for the first time. In the second work, buried conductive layers were created with 2 MeV B implantation; the implantation fluence was kept below the graphitization threshold in order to achieve doping-related p-type conduction, although the buried channels were contacted with the sample surface with laser-induced graphitization. In the latter work, 2 MeV He ions were implanted in order to measure defect-related conductivity in the sub-graphitization range.

It is worth stressing that, with the exception of the above mentioned works, the implantation of relatively heavy ions (C, Ar, Xe, Co, B, N) at energies of few hundreds of keV has been employed so far, thus leading to the formation of conductive paths and contacts at the sample surface. In the present work we report for the first time, to our knowledge, on the formation and electrical characterization of buried graphitic microchannels formed in diamond with MeV ion microbeam implantation.

2. Ion implantation in diamond

The process of damage induced by energetic ions in matter occurs mainly at the end of ion range, where the cross section for nuclear collisions is strongly enhanced, after the ion energy is progressively reduced by electronic collisions occurring in the initial stages of the ion path [28]. The permanent conversion of ion-implanted diamond to a graphite-like phase upon thermal annealing occurs when a critical damage density (usually referred as "graphitization threshold") is reached. Such threshold value has been estimated as $1 \cdot 10^{22}$ vacancies cm^{-3} for shallow implantations by C. Uzan-Saguy et al. [29] and as $9 \cdot 10^{22}$ vacancies cm^{-3} for deep implantations by P. Olivero et al. [30]. The discrepancy between the two values has been attributed in [30] to the higher internal pressure for deep implantations which could effectively increase the graphitization threshold, as already suggested in previous works [31,32].

In the range of keV ion implantation conditions applied in the above mentioned works, when the critical fluence is reached for the onset of the graphitization process, the damaged layer extends from the end of range of ions to the surface of the sample. On the other hand, MeV implantation reported in the above mentioned works do not reach the graphitization threshold. This is shown in the TRIM [33] Monte Carlo simulation in Fig. 1 for the implantation conditions reported in [6,11,12,25,27]. The curves were calculated by setting a value of 50 eV for the atom displacement energy in the diamond lattice [34,35]. In Fig. 1 the damage profile of 6 MeV carbon ions in diamond is also shown; for an implantation fluence of $1.5 \cdot 10^{16}$ cm^{-2}, the higher value of the graphitization threshold in the bulk material determines the formation of a narrow damaged layer at a depth of ~2.75 μm below the surface, which can permanently convert to a graphite-like phase upon thermal annealing. On this basic concept the "diamond lift-off" process was developed by N. P. Parikh et al. [36].

In order to connect the endpoints of the channels to the sample surface, a three-dimensional masking technique was developed to

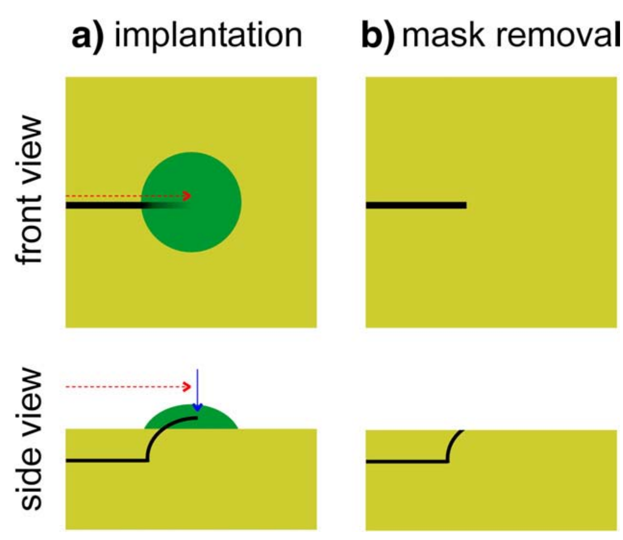

Fig. 2. Schematics of the three-dimensional masking technique adopted to control the penetration depth of implanted ions. A semi-circular mask (in green) is positioned on the diamond surface, so that the depth at which the heavily damaged layer (in black) is formed is modulated at the end of the ion beam scan (Fig. 2a). After the removal of the mask, the damaged layer is connected with the sample surface at its endpoint (Fig. 2b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)