Surface & Coatings Technology 307 (2016) 236–242

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Lithium implanted into diamond: Regular trends and anomalies

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ARTICLE INFO

Article history:
Received 20 January 2016
Revised 12 August 2016
Accepted in revised form 16 August 2016
Available online 17 August 2016

Keywords:
Diamond
Ion implantation
Lithium
Diffusion
SIMS
Swelling

ABSTRACT

Diamond single crystals implanted with $^{7}Li^{+}$ ions within broad range of fluences including those higher graphitization threshold were studied by secondary ion mass spectrometry (SIMS) and optical interference profilometry. It has been shown that sputtering coefficient of diamond does not depend on the level of radiation damage and on the microstructure of the material, which may be due to the formation of an amorphous layer on the surface during the ion bombardment. Graphitization domains were observed immediately after high-fluence ion implantation, prior to annealing. No diffusion of implanted lithium (at any fluences) was observed in diamond both at high-temperature treatment and under strong photothermal excitation near the ablation threshold. SIMS measurements have shown sharp decrease of lithium ion yield in strongly damaged diamond, particularly in graphitized region, which has not yet been satisfactorily explained.

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1. Introduction

In silicon electronics, doping with lithium is used in fabrication of ionizing radiation detectors [1]. The atom of lithium in an interstitial position in the silicon lattice acts as a donor with ionization energy of 0.033 eV [2]. By analogy with silicon, in the crystal lattice of diamond a single interstitial Li atom, according to theoretical calculations, should be a donor with activation energy of about 0.1 eV [3]. Such an impurity is much needed for diamond applications in electronics. Until now, unfortunately, only a very high-resistivity *n*-type diamond, hardly suitable for electronic devices, is produced by doping with phosphorus, whose activation energy is 0.6 eV [4,5]. Another application of lithium in combination with diamond is the development of thermal neutrons converters for diamond neutron detectors based on ^{6}Li [6]. It would be tempting to incorporate ^{6}Li atoms directly into the body of a diamond detector so as to avoid problems of coupling the external converter of thermal neutrons to the diamond detector [7]. Diamond can be doped with lithium during growth, but good material of *n*-type has not been obtained [8,9]. Possibly, due to their high chemical activity, lithium atoms do not occupy single interstitial positions but aggregate [10] or couple with other impurities [8,11] and defects [12]. Although theoretical calculations predict a low activation energy of Li diffusion in the crystal lattice of diamond (as of silicon) [3,10,13], attempts of diffusion (including electrodiffusion) of Li into the bulk of diamond proved to be unsuccessful [10,11]. In graphite, Li (as other alkaline metals – K, Na etc.) dissolves very well, which enables fabrication of the so called intercalated graphite [14]. Alkaline metal atoms are located in gaps between graphite's basal planes and readily diffuse along these planes.

Attempts have been made to produce the *n*-type conductivity in diamond by Li ion implantation [15], including ion channelling regime [16]. Deceleration of ions is accompanied by the formation of a large number of lattice defects (vacancies, interstitial atoms etc.) and is of statistical character [17]. For this reason, atoms incorporated in this manner are present at different depths with Gaussian-like concentration profile (Fig. 1). Generally, attempts to produce the *n*-type conductivity in diamond by ion implantation of Li proved unsuccessful [16]. A thin *n*-type layer of low-conductivity was found only at the very "tail" of the concentration profile of implanted Li after a high-temperature annealing [15]. The failure was explained by the coupling of Li atoms with radiation-induced defects, considered that according to the Monte-Carlo simulation data, about a hundred of knocked-off atoms are produced during the deceleration of one Li ion with initial energy of several tens of keV (Fig. 1). Experiments with implantation of radioactive ^{8}Li into diamond showed that about 40% of ^{8}Li atoms are located in tetrahedral interstitial positions; about the same number in random

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http://dx.doi.org/10.1016/j.surfcoat.2016.08.047
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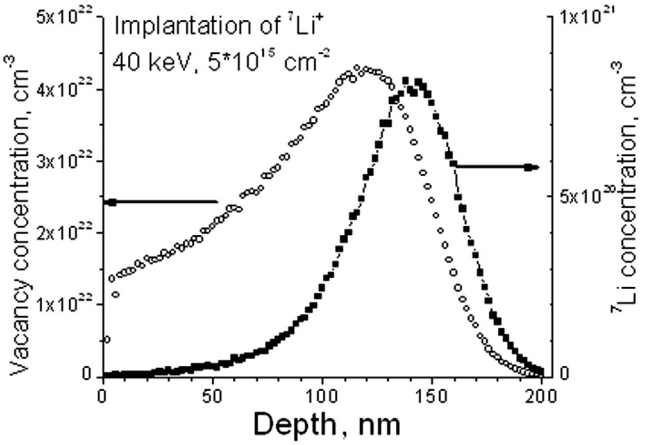

Fig. 1. Profiles of implanted ^{7}Li (filled squares) and vacancies of radiation origin (empty circles) obtained by the modelling by means of the SRIM code for an implantation fluence of 5×10^{15} cm^{-2}.

positions; and 17% in substitutional positions (where they can act as acceptors [13]) and this ratio does not change up to implantation temperature of 900 K [18]. Generally doping of diamond by lithium is still poorly understood (for a detailed review, see [19]).

The goal of the work was to study the behaviour of lithium implanted into diamond mainly by secondary ion mass spectrometry (SIMS) [20]. The method is highly sensitive but not quantitative. Quantitative data can be obtained by normalization per implantation fluence under the assumption that the implanted impurity does not leave the implanted layer and the ion yield of this impurity in the SIMS procedure does not change during etching. At typical implantation energies the depth of ion penetration into solids ranges from several tens of nanometres up to several micrometres. These thicknesses are convenient for SIMS analyses, so the two methods match well. The sensitivity of SIMS to lithium in diamond is particularly high. Based on the signal to noise ratio in our experiments we estimate the minimal detectable concentration of Li as ~10^{14} cm^{-3}. This high sensitivity is due to the fact that a significant fraction of lithium in sputtered material is in an ionized state. It is important that this fraction can depend on the electronic structure and electron affinity of material [21–24]. That is, the yield of lithium is sensitive to the microstructure of material. Chemically active atoms of lithium can form various compounds with carbon, including lithium carbides [25], the most stable of which is lithium acetylenide Li_2C_2, and intercalated graphite structures [14]. Investigation of implanted lithium in diamond could hopefully clarify the nature of radiation damage of diamond, still mysterious in many ways (especially at high radiation damage level) [26,30,31] and help to understand the behaviour of lithium in diamond and graphitized material. Besides, the following tasks are set: a) to investigate the dependence of the ion sputtering rate on the level of radiation damage in diamond; b) to try to stimulate the diffusion of implanted lithium into the depth by thermal and photothermal treatments.

To calculate the profiles of both ^{7}Li implanted into diamond and of radiation defects produced by implantation (represented by vacancies), we used the well-known SRIM code [27] based on the modelling of ion paths in a solid by the Monte Carlo method (Fig. 1). Detailed damage calculation with displacement energy of 30 eV was performed by using SRIM2013 version. This simulation takes into account the inelastic energy loss of ions due to interaction with electronic subsystem; elastic losses in collisions with atoms of matter actually lead to the generation of radiation-induced defects. It does not take into account the crystalline nature of the bombarded substance, the interaction between defects, their diffusion and the formation of amorphous pockets, that is, it gives a "frozen" picture of the primary point defects. Furthermore, it does not consider the effects of "ballistic annealing", when knocked out atoms may occupy the previously formed vacancies. The result of SRIM simulation is the linear density of vacancies per ion. We estimated the volumetric density of vacancies by multiplying the linear density of vacancies with the experimentally determined implantation fluence. A peculiar feature of diamond is its metastability at room temperature and pressure conditions. Strong radiation damage at high implantation fluences leads to transformation of diamond into graphitized material [28]. Due to the metastability of diamond, there exists a critical ion-implantation fluence (**Dgr**) such that, for fluences below this critical value, subsequent annealing restores the diamond lattice structure, whereas, for fluences above this critical value, annealing converts diamond to graphitized material [29–32]. The calculated vacancy concentration is usually taken as a criterion of the radiation damage level (Fig. 1). At monoenergetic implantation, the graphitization threshold is reached at the calculated vacancy concentration of $(7 \pm 2) \times 10^{22}$ cm^{-3} [30–33]. The implantation fluence of 1×10^{16} cm^{-2} slightly exceeds **Dgr**, that is why at a depth of ~120 nm near the radiation damage concentration maximum a graphitized layer is formed after annealing. With the further increase of the implantation fluence the graphitized layer expands mainly in the direction of the surface, as it is seen in Fig. 1. Annealing of diamond with radiation damage lower than the graphitization threshold restores the diamond structure. Naturally, **Dgr** depends on the energy and type of ions, as well as on the temperature of the sample during the implantation [33,34].

2. Experiment

$^7Li^+$ ions of energy 40 keV were implanted into diamond at room temperature with a broad range of fluences: 0.01, 0.1, 0.3, 0.5, 1, 2, 3, 5, 7, 10, 11, 15 and 18×10^{16} cm^{-2}. We used 14 polished plates cut in the crystallographic plane (110) from natural diamond crystals of type IaA with intrinsic concentration of nitrogen in A-form no more than 5×10^{18} cm^{-3}. Used implantation fluences create high concentrations of defects and lithium, much higher than concentrations of native defects and impurities in diamonds. Some plates were implanted through removable masks with 0.7×0.7 mm windows. Implantation was performed at a heavy ion accelerator produced by High Voltage Engineering Europa B.V. (Netherlands). The implanted Li profiles were measured at a CAMECA IMS-4F unit (France), which is a secondary ion mass spectrometry with the magnetic mass analyzer and double focusing. For sputtering, O_2^+ ions of energy 8.5 keV and Cs^+ ions of energies 5.5 keV and 14.5 keV were used. In sputtering of diamond with O_2^+ ions, the chemical interaction of oxygen with carbon has its effect [35]. In the SIMS technique the measured variation of the ion yield versus sputtering time can be transformed into the profile of chemical element along the depth using the value of the depth of the etched crater measured upon the completion of the sputtering process. The surface topography of diamond plates, including that of the etched craters, was measured by optical interference profilometry (Zygo NewView 5000 profiler (USA)). The vertical resolution of the technique is 1 nm; the resolution in the sample plane is about 500 nm. Thermal annealing of implanted diamonds was done in a graphite vacuum furnace for 1 h at a temperature of 1600 °C. Annealing of some samples shows that at the implantation of $^7Li^+$ ions of energy 40 keV into diamond the value of **Dgr** is within the range of $(0.5–1) \times 10^{16}$ cm^{-2}. The onset of graphitization was fixed by appearance in diamond of optically opaque layer.

The photothermal treatment of implanted diamonds was carried out under normal conditions by multishot irradiation with femtosecond laser pulses (duration, $\tau_{FWHM} \approx 200$ fs; wavelength, $\lambda \approx 515$ nm). Laser radiation was focused on the sample surface by an objective of numerical aperture NA = 0.1 into a spot 3.5 μm in radius by the intensity level of 1/e. The pulse recurrence frequency varied within the range of 1 kHz up to 100 kHz, which corresponds to the range of values of the effective number of absorbed pulses per each spot, from 5 up to 500. Pulse energy was 1 μJ, which corresponds to the peak intensity of about 1×10^{13} W/cm^2. This mode of exposure is slightly lower than the

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