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Surface Brillouin scattering on annealed ion-implanted CVD diamond

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ABSTRACT

Single crystal <100> diamond samples were implanted with a total fluence of 1.5×10^{16} ions/cm^2 at single energy of 150 keV using carbon ions. This implantation fluence created a damage density that would not restore the diamond structure after annealing. Surface Brillouin scattering studies show that the elastic properties of the highly damaged diamond layer starts to transit from diamond-like to amorphous carbon state at an annealing temperature of 500 °C. The amorphous carbon layer is shown to have a sound velocity (elastic properties) similar to those reported for tetrahedral amorphous carbon (ta-C). Raman spectroscopy, EELS and HRTEM has been used in conjunction with the SBS data to monitor the changes in the carbon implanted diamond at different annealing temperatures.

1. Introduction

Unlike the other group IV semiconductors, i.e., Si and Ge, ion implantation in diamond is challenging for application in semiconductor device construction. The tight bonding of the carbon atoms in the sp^3 hybridization, metastability of diamond and its vast difference in temperature with regards to the mobility of vacancies and interstitials act as stumbling blocks when using ion implantation and annealing to trap impurity atoms for *n* and *p* type doping [1].

Ion implantation causes structural changes in the sub-surface region in a material. The damage in diamond due to ion implantation and subsequent thermal treatment has been extensively studied [2–5]. It has been shown that ion implanted diamond with ion energies >10 keV to fluences above a damage threshold of $4–6 \times 10^{22}$ vac/cm^3, which is a simulated damage using TRIM irrespective of the implanted ion [6], will result in the collapse of the implanted region to an amorphous carbon. Subsequently annealing to temperature above 600 °C results in the damaged region evolving to a moderately graphitic layer. This region can be etched by boiling the diamond in an oxidizing acid solution or in an O_2 plasma environment. This approach has been used to lift off thin diamond layers and can be useful in ion beam patterning and machining of diamond [7]. The damaged layer after implantation and annealing apart from having graphitic carbon, also has amorphous carbon in the sp^n form where $n = 1, 2, 3$. This is in contrast with other group four elements (Si, Ge and Sn) single crystals which are isovalent with respect to carbon where ion implantation above the damage threshold results in amorphous sp^3 region [8,9].

This study investigates and reports changes in carbon ion implanted diamonds from observations made primarily using surface Brillouin spectroscopy (SBS). The observed results in SBS are compared with results obtained using Raman spectroscopy. Raman spectroscopy is a well established technique for studying structural changes of carbonaceous materials [10,11]. Furthermore, this information is correlated with electron energy loss spectroscopy (EELS) and high resolution transmission electron spectroscopy (HRTEM) measurements.

The extent of the damage induced by the carbon ions was theoretically estimated using the quantum Monte Carlo simulation program, SRIM2008 [12] using a displacement energy of 45 eV for the carbon in the diamond lattice (Fig. 1). The simulated damage density lies close to the damage threshold near the surface for the implanted fluence of 1.5×10^{16} ions/cm^2. It is observed that the damage profile gradually rises from the surface and reaches a maximum towards the tail end of the implanted range then abruptly falls off.

2. Experimental

The samples used were CVD single crystal diamond plate purchased from Element Six, of dimensions $3.0 \times 3.0 \times 0.5$ mm^3 with the 3.0×3.0 mm^2 polished faces oriented in {100}. The surface roughness of the polished faces was <30 nm as specified by the supplier. The implants were performed using a Varian 200-20A2F ion implanter at iThemba LABS, Gauteng, South Africa. The implantations were performed on one polished face at room temperature on samples tilted at about 7°. The ion beam was uniformly scanned over the sample surface with a beam current of $\approx 1.0\ \mu$A/cm^2. The low current minimized the effect of beam heating during implantation. The samples were implanted with single energy of 150 keV to a total fluence of 1.5×10^{16}

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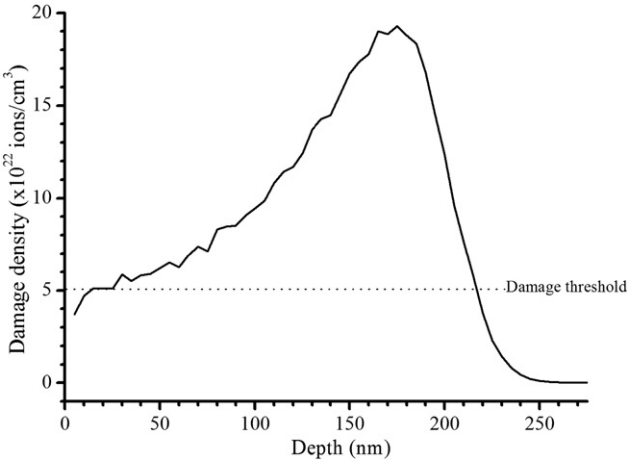

Fig. 1. Ion implantation scheme as implemented in SRIM2008. Carbon ions of fluence 1.5×10^{15} ions/cm^2 and displacement energy of 45 eV were used in the simulation.

ions/cm^2. Ion implantation caused visible optical changes in the samples observed as variation in transmission discussed in Section 3.1.

Isochronal annealing was done using the Carbolite Eurotherm 2416 furnace. Annealing temperatures were 200 °C, 400 °C, 500 °C, 600 °C, 800 °C, 1000 °C and 1200 °C in an inert Ar environment. A quartz glass tube that was held horizontally in the usual ceramic furnace tube (see Fig. 2) allowed for horizontal 'shoot in' of sample after pre-heating the furnace to a desired temperature. The quartz glass tube was purged for 15 min while the furnace temperature was ramping up to the desired annealing temperature. Once the dwell point was reached, the furnace was left to stabilize for at least 10 min. The sample was then introduced and annealed for 30 min. At the end of annealing time, the sample was quickly withdrawn from the heating zone by pulling away the quartz glass tube. It was then cooled in the continuous Ar gas flow until the temperature at point C was less than 100 °C. This was measured using thermocouple probe placed in such a way that it was in contact with the quartz tube at section C.

The sample was introduced by dropping it through funnel B then suddenly increasing the flow rate of the gas, "shooting it in" into the annealing section C, by an impulsive force. It was prevented from flying past this region by the perforated tube at D. The perforations also enable the exiting of the Ar gas from the annealing chamber. The gas flow rate is then gently reduced while monitoring the rotameter at A to ensure that the supply is never completely cut off. Gas flow is kept continuous throughout the purging, annealing and cooling processes. During this annealing process, the temperature of the sample is raised to a predefined set point in a small time interval of less than a second. The changes measured are therefore due to that particular temperature.

SBS and Raman measurements were taken after every anneal process. One such set of measurements were called a cycle. The same sample was annealed at a higher temperature and the cycle repeated. Raman measurements were done in backscattering using the 514.5 nm single laser mode. Like for Raman measurements, the SBS probing beam source was from an Ar^+ laser tuned on a 514.5 nm single mode line. SBS is the inelastic scattering of light by thermally excited phonons by dynamical modulation of the dielectric function of the medium (the elasto-optic effect) and/or dynamic corrugation of the surface (the surface ripple). A Brillouin scattering measurement involves illumination of the specimen by monochromatic laser light and analyzing the spectrum of the scattered light. In this study, a plane polarized light of ≈ 400 mW was produced at the source. The travel distance, reflections at mirrors and presence of an acousto-optic modulator (AOM) reduces the beam intensity to <100 mW on the sample. This is good enough to ensure minimal heating that does not affect the sample in any significant way. A scattered solid cone of light from the sample was collimated and focused onto the analyzer by means of mirrors and lenses. The scattered light was analyzed by a 3 + 3 pass Sandercock type tandem Fabry–Pérot interferometer described in [13]. The Krüger geometry [14] in backscattering mode was used to interpret the SBS data as both direct and indirect scattering mechanisms can be observed when the ion damaged diamond is still relatively transparent and the free polished surface at the opposite side of the implanted layer was held in position against a flat reflective aluminum plate. When the damaged region becomes semi-opaque after annealing at temperatures above 500 °C, then it can be interpreted that both the surface ripple mechanism and direct scattering from the bulk occur in the ion damaged and annealed layer.

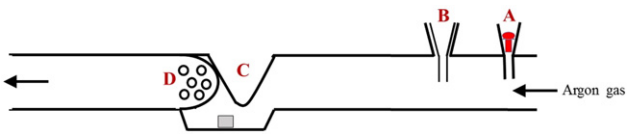

Fig. 2. A longitudinal cross-section of the modified glass tube used for annealing.

3. Results and discussions

3.1. SBS results

In Fig. 3, a consideration of the observed modes for both pristine diamond and C^+ implanted sample measured under the same scattering geometry shows no observable difference in frequency shift position of the implanted sample with respect to the pristine diamond. From Fig. 3, and subsequently in Fig. 4, the annealed diamond spectra up to 400 °C do not show any significant new features when compared to the pristine diamond. As shown in Section 3.3, the implanted region of width ≈240 nm sits on pristine diamond. Transmission measurements showed that pristine diamond transmits 69.3% of the 514.5 nm light. The transmission reduced to 15.8% for the as-implanted and anneal temperatures of up to 500 °C. In relation to SBS data, it is our view that the implanted region at the annealing cycles below 500 °C is not optically distinct from the pristine diamond below, and thus the elasto-optic scattering mechanism is unable to yield information specific to the implanted region at these lower annealing temperatures for the

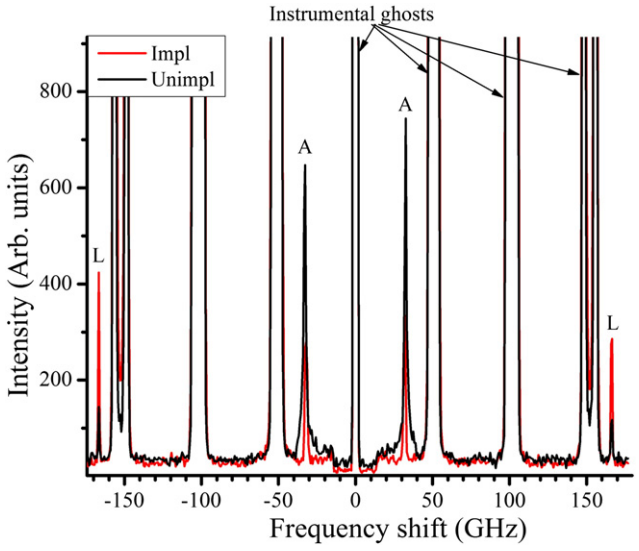

Fig. 3. SBS spectra recorded at 45° incidence for both the as-implanted and pristine diamond. The peaks labeled L (167 GHz) are bulk longitudinal modes due to direct elasto-optic scattering and the peaks labeled A (33 GHz) are due to indirect scattering via the Krüger scattering geometry [14] corresponding to transverse modes of the two samples. Instrumental ghosts are transmission peaks that are a function of the instrument and are useful in calibrating the spectrometer.