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Amorphization and graphitization of single-crystal diamond — A transmission electron microscopy study

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ABSTRACT

The amorphization and graphitization of single-crystal diamond by ion implantation were explored using transmission electron microscopy (TEM). The effect of ion implantation and annealing on the microstructure was studied in (100) diamond substrates Si^+ implanted at 1 MeV. At a dose of 1×10^{15} $cm^{-2,}$ implants done at 77 K showed a damage layer that evolves into amorphous pockets upon annealing at 1350 °C for 24 h whereas room temperature implants (303 K) recovered to the original defect free state upon annealing. Increasing the dose to 7×10^{15} Si^+/cm^2 at 303 K created an amorphous-carbon layer 570 ± 20 nm thick. Using a buried marker layer, it was possible to determine that the swelling associated with the amorphization process was 150 nm. From this it was calculated that the layer while obviously less dense than crystalline diamond was still 15% more dense than graphite. Electron diffraction is consistent with the as-implanted structure consisting of amorphous carbon. Upon annealing, further swelling occurs, and full graphitization is achieved between 1 and 24 h at 1350 °C as determined by both the density and electron diffraction analysis. No solid phase epitaxial recrystallization of diamond is observed. The graphite showed a preferred crystal orientation with the (002)g//(022)d. Comparison with Monte Carlo simulations suggests the critical displacement threshold for amorphization of diamond is approximately $6\pm2\times10^{22}$ vacancies/cm^3.

1. Introduction

Diamond, in many crystallographic forms but especially single-crystal diamond, is gaining academic and industrial interest [1–3]. Relative to silicon (Si), diamond exhibits a significantly higher thermal conductivity (~1000× greater), a higher hole and electron mobility (3800 cm^2/Vs vs 450 for holes and 4500 vs 1500 for electrons), and diamond holds great promise for high frequency and MEMS devices. Ion implantation of single-crystal diamond is of great interest to the micro-electrical-mechanical systems (MEMS) community for creating new single-crystal diamond devices [4,5]. Amorphization and/or graphitization of diamond via implantation is used to enable etching of sacrificial layers for diamond MEMS processing [6,7]. Even though ion implantation into single-crystal diamond has been studied for decades, [8,9] cross-sectional transmission electron microscopy (XTEM) studies of the effect of ion implantation exist [10] but are rare, due to the difficulty in making XTEM samples [11]. There are key questions surrounding the evolution of ion-implantation damage in single-crystal diamond including (1) the threshold value for amorphization of the diamond lattice, (2) whether amorphization or graphitization occurs immediately following the implant, and (3) whether any solid phase epitaxial regrowth (SPER) occurs during annealing. The critical implantation dose to surpass the 'graphitization' threshold for room temperature implants has been estimated in the past by a combination of secondary ion mass spectroscopy, chemical etching and TRIM [12] simulations to be 1×10^{22} vacancies (vac)/cm^3 by Uzan-Saguy et al. in 1995 [13]. However, recent studies using a FIB-assisted lift-off technique and TRIM analysis and, in a separate study, Raman spectroscopy have put this threshold as high as 9×10^{22} vac/cm^3 [5,13]. Above this threshold the diamond is believed to be either in the graphitic state (hence the term 'graphitization' threshold) or in a form of amorphous carbon. Above 430 °C it has been suggested that the amorphous carbon begins to graphitize by forming sp^2 bonded nanoclusters [15]. However, it has also been suggested that the amorphous region was not truly amorphous, but is actually a vacancy rich diamond crystal lattice, [16] and that relaxation to the graphite state might occur before a real amorphization (such as in silicon) takes place [17].

In 1999, Kalish et al. reported that complete "graphitization" is reached at 600 °C (after a 20 min annealing) when conductivity becomes metallic, due to an overlapping of the localized states [15]. However, the density of the amorphous layer does not equal to that of graphite until approximately 800 °C with a sharp drop in density occurring near 500 °C [15]. This process has been simulated by computational methods; molecular dynamic images of the evolution

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from damaged diamond to graphitic planes were demonstrated by Kalish et al. [14,17,18]. Additionally, in Si and Ge, annealing after amorphization is accompanied by solid phase epitaxial regrowth (SPER) and can produce characteristic extended defects in the crystal lattice. It is unknown whether any SPER occurs in diamond during annealing and whether end-of-range defects are observed [19]. The stable defect in diamond is a point defect known as the split interstitial, [5] and no extended defects, such as seen in Si after ion implantation, have been reported.

This TEM study investigates the amorphization and graphitic phase formation process upon ion implantation and annealing of a single-crystal diamond substrate. It also determines the amount of SPER that occurs upon annealing and if any extended defects nucleate during the process.

2. Experimental details

Single-crystal diamonds, produced through a University of Florida optimized process and commercialized by The Gemesis Corporation, were used for this study. High-pressure, high-temperature single-crystal diamonds, approximately $5\times5\times1$ mm^3 each, were Si^+ implanted in a tandem accelerator implanter, with a dose rate of 0.44 μA/cm^2 and dose accuracy of ±5%, and were tilted 7° relative to the incident ions to minimize ion channeling. The original nitrogen (N_2) impurity concentration of the diamonds, obvious from the visible light-orange color, is on the order of 10^{18}–10^{20} cm^{-3}, [20] and was uniform throughout the crystals. Annealing was performed in a graphite chamber furnace at diffusion pump vacuum pressures ($\leq10^{-4}$Torr) [21] with a residual helium environment. During annealing, the samples were placed in tantalum (Ta) foil envelopes to assist the prevention of oxidation of the diamond surface. Cross-sectional TEM (XTEM) samples were prepared according to the procedure previously published by Hickey [22], which demonstrated preservation of the diamond surface during the sample extraction. TEM analysis was performed on JEOL 200CX and JEOL 2010 microscopes. Both weak beam dark field (WBDF) and bright field TEM modalities were employed in this study. WBDF is less sensitive to strain contrast from dislocation cores, and therefore this modality was employed to define the transition regions at the amorphous/crystalline interfaces where significant strain contrast may be present. The g_{220} vector is parallel to the surface in all presented TEM images.

Three experiments will be presented. For the first experiment, (001)-oriented diamond substrates were Si^+ implanted at 1 MeV to a dose of 1×10^{15} cm^{-2} at both 77 K and 303 K. In the second experiment, to create a buried marker layer, (001)-oriented diamond was Si^+ implanted at 2 MeV to a dose of 1×10^{15} cm^{-2} at 77 K. This sample was additionally Si^+ implanted at 1 MeV to a dose of 7×10^{15} cm^{-2} at 303 K. For the third experiment, (001)-oriented diamond was Si^+ implanted with 1 MeV to a dose of 3×10^{15} cm^{-2} at 303 K. According to SRIM simulations, [12] the damage peak (R_d) and projected range (R_p) for 1 MeV Si^+ implantation is 540 nm and 570 nm, respectively, and for 2 MeV Si^+ implantation, 840 nm and 900 nm respectively. These three experiments were chosen to both bracket the amorphization threshold and study the effects of annealing; a summary of the experiment implants is presented in Table 1.

Table 1
Experimental implants.

Energy (MeV)	Dose (cm^{-2})	Temperature, T_i (K)	Ion	R_d (nm)	R_p (nm)
Implants below amorphization threshold					
1	1×10^{15}	**77**	Si^+	540	570
1	1×10^{15}	303	Si^+	540	570
Implant exceeding amorphization threshold; investigate swelling effect					
1 (exceeds threshold)	7×10^{15}	303	Si^+	540	570
2 (buried marker layer)	1×10^{15}	77	Si^+	840	900
Implant exceeding amorphization threshold; investigate graphitization and SPEG upon annealing					
1	3×10^{15}	303	Si^+	540	570

3. Results and discussion

3.1. Low dose implants

Fig. 1 shows XTEM images of diamond implanted with 1 MeV, 1×10^{15} Si^+/cm^2 at 77 K (Fig. 1(a)) and 303 K (Fig. 1(c)). The temperatures chosen are in the range that 'freezes in' point defects in diamond [23]. However, it is known that a room temperature (303 K) implant can, due to dynamic annealing, achieve significantly different results than at liquid nitrogen temperature (77 K). As-implanted, the range of damage for the 77 K implant is larger than that of the 303 K implant. Additionally, the 77 K implant seems to have a band of severe damage in the midst of the larger damage band at approximately the projected range (R_p), designated on Fig. 1(a) by a gray arrow. Upon initial imaging, this was thought to be a continuous amorphous layer of material, but upon high-resolution imaging, was shown to be severely damaged diamond but the single-crystal lattice was still intact. After annealing at 1350 °C for 24 h, the sample implanted at 303 K, shown in Fig. 1(d), completely recrystallized to diamond. However, for implantation at 77 K the damage layer was much more obvious. This suggested that there is some dynamic annealing occurring upon room temperature implantation. Upon annealing the 77 K implant at 1350 °C (Fig. 1(b)), the damaged region collapsed into small amorphous or possibly graphitic pockets (Fig. 2). HRTEM imaging shown in Fig. 3, was used to confirm that this layer of contrast consists of small (<100 Å) pockets are no longer crystalline diamond. Contrary to what is seen in Si, no extended defects were observed either in the damage range of the specimens implanted at 303 K implant or around the amorphous pockets of material in specimens implanted at 77 K. The lack of extended defects agrees with molecular dynamics simulations [24] that predict that the stable defect in diamond is the <110> split interstitial, also referred to as a dumbbell structure. This point defect would not observable in TEM. The most likely explanation that extended defects (such as the {311} defect and dislocation loops common in the Si lattice) are not forming in the diamond lattice is the strong covalent bond between the carbon atoms may make formation of extended defect configurations thermodynamically unstable.

3.2. Exceeding the amorphization threshold

To study the phase change of the amorphization of diamond after ion implantation, a buried marker layer, 2 MeV, 1×10^{15} Si^+/cm^2 implant, is used (Fig. 4(a)). The damage is centered at 900 nm which is consistent with the projected range from TRIM simulations (Fig. 4(b)) [12]. Although significant damage to the lattice is apparent, high-resolution (HR) TEM and selected area diffraction pattern (SADP) analysis confirmed the crystalline nature of the damaged region. Fig. 4(b) presents the simulation of ion implantation induced damage from the marker implant and the planned secondary 1 MeV implant. Although the second implant occurs into pre-damaged material, Fig. 4(b) shows that the level of damage from the previous 2 MeV is an order of magnitude less in the area of interest, specifically from the surface to approximately 600 nm in depth. Fig. 4(c) shows the sample after addition of the 1 MeV, 7×10^{15} Si^+/cm^2 implant at 303 K. The TEM image shows the formation of an amorphous layer. The amorphous-carbon layer (designated by α-carbon in the figure) exists from approximately 300 nm below the surface to approximately 850 nm deep. When the marker layers are aligned, it is apparent that approximately 150 nm of swelling occurred during amorphization. Using a mass balance calculation, the density of the amorphous layer was