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Ion implantation of diamond: damage, doping, and lift-off

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Over the past decade considerable progress has been made in diamond research. Much of the effort has been concentrated in obtaining high quality epitaxial films by different deposition techniques. Unfortunately heteroepitaxial film growth has not yet been observed. In order to make good quality economical diamond electronic devices, it is essential to grow such films and to dope these films to obtain n- and p- type conductivity. In this review talk we discuss first doping by ion implantation plus annealing of the implantation damage, and second how to make large area single crystal diamonds.

We found that C implantation damage below an estimated Frenkel defect concentration of 7% could be recovered almost completely by annealing at 950^o C. For a defect concentration between ~ 7 % and 10 %, a stable damaged form of diamond ("green diamond") was formed by annealing. At still higher damage levels, the diamond graphitized.

To introduce p-type doping, we have co-implanted B and C into natural diamond at 77K, followed by annealing up to 1100^o C. The resulting semiconducting material has electrical properties similar to those of natural B-doped diamond. To create n-type diamond, we have implanted Na⁺, P⁺ and As⁺ ions and have observed semiconducting behavior in the temperature dependent conductivity with activation energies between 0.3 and 0.5 eV. These results have been compared with carbon or noble element implantation, in an attempt to isolate the effect of radiation damage.

Recently, in order to obtain large area single crystals, we have developed a novel technique for removing thin layers of diamond from bulk or homoepitaxial films. This method consists of an ion implantation step, followed by a selective etching procedure. High energy (4-5 MeV) implantation of carbon or oxygen ions creates a well-defined layer of damaged diamond that is buried at a controlled depth. This layer is graphitized and selectively etched either by heating at 550^o C in an oxygen ambient or by electrolysis. This process successfully lifts off the diamond plate above the graphite layer. The lift-off method, combined with well-established homoepitaxial growth processes, has considerable potential for the fabrication of large area single-crystal diamond sheets

1. INTRODUCTION

Many interesting electronic and thermal properties of diamond, such as large band gap ($E_g = 5.4$ eV), high thermal conductivity (20 W/cm-C), etc. suggest the possibility of its use in the field of semiconductor devices. This has created a large interest in diamond research. The major effort is to understand the nucleation and growth of diamond films by various techniques, particularly the growth of heteroepitaxial films. Two major hurdles to be overcome before economically feasible diamond devices can be realized are (i) the fabrication of large area single crystal substrates and (ii) the doping of diamond substrates both to create n-type and p-type materials.

In this paper we have addressed these two issues by applying ion beam techniques. This paper is divided into three parts (i) implantation damage and recovery (ii) p- and n-type doping and (iii) lift off to obtain large area single crystal diamond. The first two topics are well covered in recent reviews by Prins [1] and Dresselhaus & Kalish [2].

2. RESULTS AND DISCUSSION

2.1 Implantation Damage and Recovery

The implantation process is accompanied by lattice damage; even after high temperature annealing some active defects may yet be present which could adversely affect the electrical conduction. To understand the effects and extent of implantation

damage as well as the potential for recovery, a detailed study was carried out by implanting 100 - 350 keV C^+ ions into natural diamond at 77 K and annealing the samples in a vacuum furnace (10^{-6} Torr) or in a rapid thermal annealing furnace [3,4]. The effects of annealing were analyzed by Rutherford backscattering spectroscopy/channeling (RBS) and Raman spectroscopy. Figure 1 shows the RBS/channeling spectra from a sample implanted with $1.5 \times 10^{15} C/cm^2$. This damage is completely recovered after annealing at $950^\circ C$ for 1 hr. and the annealed spectrum looks very much like that of the virgin diamond crystal. This suggests that most of the implantation damage was recovered by thermal annealing. Optical absorption measurements also show that most of the damage has been recovered, though some damage complexes yet remain.

When the implantation dose was raised to $3 \times 10^{15} C/cm^2$ followed by a series of thermal anneals at $950^\circ C$ for 30 min., three distinct regions were apparent in the annealed spectra (Fig. 2). The near surface regions (500 - 700 keV) showed a full recovery as shown in fig. 1. The center region, where the damage density was the greatest, showed no recovery of the lattice structure after annealing. The region behind the damaged layer also channels like a virgin crystal with an increased yield due to dispersion of the analyzing

beam passing through the damaged region. The sharp drop from the random to the near virgin level on either side of this layer suggests a well defined cut-off for the degree of damage from which the original crystal structure can be recovered by thermal annealing. In addition to the formation of a non-channeling layer, there was a dramatic change in color from brown to a striking golden green. This "green phase" was thermally stable to at least $1100^\circ C$ and was formed by slow annealing to $800^\circ C$ as well as by RTA to $1000^\circ C$. Raman and micro-Raman analyses were performed on a sample with a green layer that transmitted $<5\%$ at the analyzing wavelength of 514.5 nm. The diamond material in the 150 nm layer above the green phase gave the expected $1332 cm^{-1}$ line. No other lines were observed including those known to exist for amorphous carbon or graphite.

High dose implantation shows that there exists a critical damage density above which the green phase is no longer formed. At this damage density the diamond is sufficiently amorphized to form a graphite layer after thermal annealing. This layer is many orders of magnitude more conductive than diamond and etches readily in chromic acid.

An estimation of ion damage (no. of vacancies produced/ion) was calculated by a Monte-Carlo simulation (TRIM) [5]. Approximately 65.4 Frenkel vacancy/interstitial pairs are created by each incoming

Fig. 1. RBS/channeling of a diamond implanted with $1.5 \times 10^{15} C^+/cm^2$ at 100 keV, and annealing at $950^\circ C$ for 30 min.

Fig. 2. RBS/channeling of a diamond implanted with $3 \times 10^{15} C^+/cm^2$ at 200 keV and annealed at $950^\circ C$ for 30 min.

C⁺ ion of 100 keV, assuming the displacement energy to be 80 eV and the binding energy to be 3.26 eV. By comparing the simulated vacancy density profile to the RBS channelled spectra we estimate a Frenkel defect density of 7-10% is necessary for the formation of the "green phase."

2.2 Doping by ion implantation

Natural type IIb diamonds exhibit p-type conduction with an activation energy between 0.32 and 0.37 eV which is attributed to boron contamination in the diamond. Natural type Ib diamonds contain nitrogen, a potential n-type donor. However the donor level is too deep (~ 1.7 eV) to be useful. The common way to introduce dopants in semiconductor devices is by ion implantation or during growth.

For the use of electrical conductivity measurements to study implantation doping, we caution that in the early work a major problem was discovered [6]; namely, that some edges of the diamond substrates were conductive. This conductivity was a result of damage caused by laser cutting of the diamond substrates. The conductivity mechanism of the damaged edges in some cases dominated the total conduction, leading to an activation energy around 0.1 eV. In order to overcome this problem of edge conduction, a 0.5 mm unimplanted border was left around the circumference of the implanted region. This border acted to isolate the implanted region from the window edge.

p-type doping:

p-type doping of diamond has been done successfully by several groups [7, 8, 9, 10] using boron ion implantation, or by doping during diamond growth [11]. Braunstein and Kalish [12] reported unambiguous proof for p-type doping by boron implantation. They bombarded their samples to such a high dose that the surface turned to graphite. After removing the graphite surface layer they found that a residual layer of p-type conduction was left behind. They identified the existence of boron in this layer by $^{11}\text{B}(p-\alpha)^8\text{Be}$ nuclear reaction analysis. This effect was further contrasted by comparison to implantation of carbon under identical conditions where no residual p-type layer was formed. Prins [8] introduced a recipe of p-type doping by co-implanting carbon and boron at low temperature such that the damage from the carbon implantation overlaps the implanted boron profile. The idea behind this method is to increase the likelihood of boron going into a substitutional site by

increasing the density of vacancies in the neighborhood. During implantation at 77 K, the interstitials and vacancies are frozen-in, but during annealing at high temperature the boron ions start filling in the vacancies. We have carried out a detailed investigation of p-type doping at various boron doses and at different substrate temperatures [6]. As mentioned earlier, implantation damage in the crystal lattice acts to compensate the electrical properties of the implanted dopants. To minimize the implantation damage a multiple energy implantation scheme (using TRIM calculation [5]) was implemented. In addition to maintaining low damage density with this scheme, it produces a broader doped layer which helps in reducing contact resistance and forms a uniform doping profile. Fig. 3 shows one of these $\ln(R)$ vs. $1000/T$ measurements for a sample implanted with 12 - 65 keV B⁺ ions to give B concentration of 0.05 nm^{-3} [6]. An activation energy of 0.30 eV was observed from room temperature up to 400° C which is similar to the activation observed in type IIb diamond (0.32 eV). At higher temperature the conductivity was dominated by second mechanism (1.42 eV). This conductivity mechanism was observed prior to implantation (1.6 eV) and is suspected to be due to substitutional nitrogen which introduces a donor level at ~ 1.7 eV. SIMS analysis showed a Nitrogen content of $10^{18}/\text{cm}^3$ in type "IIa" diamond [6].

Fig. 3. $R(T)$ for a diamond implanted with multiple energy 12 - 65 keV to give B concentration of 0.05 nm^{-3} .

n-type doping:

We have implanted Na^+ , P^+ and As^+ into type IIa diamonds as possible n-type dopants [13]. Particular emphasis was placed on the implantation of Na at different temperatures and doses. Combined implantation energies of 55, 80 and 120 keV were used to provide a uniform doped layer concentration over a depth of ~ 100 nm. The implanted layer exhibited an activation energy between 0.40 to 0.48 eV, as determined by temperature dependent resistance measurements shown in Fig. 4. In addition, implantation of $^{22}\text{Ne}^+$ was used to introduce damage equivalent to the $^{23}\text{Na}^+$ implant, while not introducing an electrically active species. The activation energy and the electrical resistance were similar but higher than those produced by implantation with Na. We concluded that the electrical properties of the Na implanted samples were at least partially due to electrically active Na but that residual damage was still important.

Fig. 4. $R(T)$ for Ia diamond implanted with multiple energies of 55, 80 and 120 keV to a uniform concentration of 0.045 Na^+ or Ne^+/nm^3 at 77 K

2.3 LIFT - OFF

The need for large area, single crystal diamond films for electronic applications has been made apparent [14]. Recently Stoner, et.al.[15] have grown highly oriented diamond crystallites by biasing the substrate on single crystals of Si and SiC. At present, those attempting to synthesize diamond thin films are a long way from being able to grow large area single crystals heteroepitaxially. However, some groups [16] have successfully grown homoepitaxial films.

In order to achieve high-quality thin films of diamond, we have developed a novel technique [17] utilizing a completely different approach than the ones used in typical diamond growth. In this technique, a well defined, thin buried graphitic layer was created by ion implantation (4-5 MeV C^{++} or O^{++}) followed by annealing (950°C for 30 min. in vacuum), and this layer was then etched preferentially by heating it in an oxygen ambient at 550°C, thus removing the top $\sim 2\mu\text{m}$ thick plate from the diamond template. This introduces great potential for the growth of large-area thin films of diamond; since homoepitaxial growth has been shown to be possible, one could obtain several "lifted" diamond film substrates from a single master diamond, and arrange them as tiles to form a large surface area template.

Recently Marchywka, et al. [18] demonstrated that damaged, graphitized diamond and non-diamond carbon on diamond surfaces can be etched away by electrolysis. Applying this technique, we evaluated the use of electrolysis for etching away the buried graphitic layer, as opposed to using a heated oxygen ambient. The preservation of high crystal quality near the surface is the major criterion for determining which lift-off method is the best, as high crystalline quality is desirable for successful homoepitaxial diamond growth. To find the optimum method of implantation/annealing which minimized the near surface damage, yet still introduced a buried graphitic layer to allow for the etching/lift-off, we conducted a study using various combinations of implantation fluences and annealing conditions [19]. The results were characterized with Raman spectroscopy and RBS/Channeling techniques.

The physical details of electrochemical etching of graphite is studied by R. Murray's group [20]. Diamond is one of the best insulators known, while graphite is a good conductor-- relative to diamond and deionized water. Therefore, when a diamond which has

Fig. 5 Schematic of equipotential contours and E field lines for lift off via electrolysis.

a buried graphitized layer is placed in the electric field created by parallel plate electrodes, the E field lines and the equipotential lines would look like those shown in Figure 5. Because graphite is a conductor, charges are free to move within it, and the E field within it is zero. By superposition the E field induced in the plane of the conductor by the charge distribution built up on either end of the conductor must oppose the E field which would be induced by the two parallel plate electrodes alone. The consequence of this is analogous to slurry electrolysis [21] positive charges accumulate at the edge of the graphite closest to the cathodic electrode, while negative charges accumulate at the edge of the graphite closest to the anodic electrode. The result is that a "virtual-anode" is created where the positive charges have built up, and anodic oxidations occur [20, 22].

The lowest dose which allowed for liftoff via the furnace etching in an oxygen ambient was $3 \times 10^{17} \text{ O}^{++}/\text{cm}^2$, whereas using etching by electrolysis, the surface layer of a diamond implanted with $1 \times 10^{17} \text{ O}^{++}/\text{cm}^2$ was lifted off in under an hour.

We studied diamonds which were implanted at 850°C , where dynamic annealing takes place, as compared to those implanted at 77 K , where the damage is frozen in. We also made a study of step implantation/annealing, where the substrate was

Fig. 6 Lifted diamond piece after 12 hr. of electrolytic etching in deionized water. The sample was lifted from a diamond substrate implanted with $8 \times 10^{15} \text{ O}^{++}/\text{cm}^2$ at 5 MeV.

implanted in three distinct steps, with vacuum anneals for 1 hr. at 950°C between each step-implant.

From this study it was realized that whatever method we used for implanting a fluence of $1 \times 10^{17} \text{ O}^{++}/\text{cm}^2$, the near surface damage was still too high to affect the good quality homoepitaxial growth. A series of diamonds were implanted, to determine the lowest dose which yet allowed for liftoff to be performed in a reasonable amount of time. A diamond implanted at $8 \times 10^{15} \text{ O}/\text{cm}^2$ after annealing at 950°C , was lifted in 12 hr. as shown in Figure 6. This was very encouraging, since at this dose virtually all the near-surface damage was annealed out as seen from RBS/channeling spectra of annealed and virgin diamond (Fig. 7).

3. SUMMARY

Using ion beams, progress has been made in two distinct areas in diamond technology: the chemical doping of diamond and the liftoff of thin films from a diamond substrate. Reasonable p-type doping has been achieved, while controlled n-type doping has yet to be realized. "Lift-off," the novel technique

Fig. 7 RBS/channeling of the diamond of Fig. 6 before and after the annealing at 950°C for 30 min. in vacuum.

combining ion implantation with electrochemical etching gives new possibilities for development of large area single crystal diamonds.

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