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Investigation of the magnetic properties of proton irradiated type Ib HPHT diamond

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ABSTRACT

Nitrogen rich type Ib HPHT grown synthetic diamonds were investigated following large area irradiation of the samples using 2.2 MeV protons. Studies on possible magnetic properties induced after the irradiation were performed using a SQUID magnetometer. Magnetisation measurements of pristine (unirradiated) control samples revealed a superparamagnetic-like signal at 300 K. After the proton irradiation, a Curie-like paramagnetic curve was observed for thermal cycles at an applied magnetic field of 2 kOe which exhibits a transition at temperatures around 50–55 K, with hysteretic behaviour below these temperatures.

1. Introduction

The magnetic properties of carbon have gained significant attention over the recent years with extensive experimental and theoretical research continuously been performed on this challenging topic. Magnetic ordering in this class of carbon-based materials at room temperatures could lead to revolutionary new technologies in nanotechnology, biomedicine and many other fields [1] since they are light weight and inexpensive to produce [2]. Such materials present unique prospects in terms of spin-based electronics due to the fact that the weak spin–orbit coupling in carbon results in the critically desired long diffusion lengths and coherence times.

However, ferromagnetism in carbon allotropes is rather unanticipated as their electronic structure calls for electrons to pair up to form covalent bonds which results to a zero net magnetic moment, in contrast to natural ferromagnetic elements with unpaired electrons. Nevertheless, recent reports of magnetic ordering observed at room temperature for a number of different carbon allotropes such as highly oriented pyrolytic graphite (HOPG) [3] as well as graphene [4] have motivated new research studies in order to understand the intriguing mechanism(s) which can induce ferromagnetism in pure carbon systems.

Research conducted by P. Esquinazi et al., has revealed ferromagnetism in proton irradiated highly oriented pyrolytic graphite (HOPG) with a Curie temperature above room temperature [3]. X-ray magnetic circular dichroism (XMCD) studies [5] performed by the same group on proton irradiated thin carbon films showed indisputably the ferromagnetic character of the irradiated regions and its relation to the carbon element. Since then, a number of experimental studies of magnetic carbon systems have confirmed similar observations. Consequently, a number of theoretical studies have been undertaken in order to explain the origin of carbon magnetism with respect to the presence and type of different defects in the graphene plane and in the graphite structure such as vacancies, edges and cracks which could nucleate magnetic moments and produce the observable effects with respect to magnetization and the associated Curie temperature [6,7].

We extend this research effort to the investigation of possible defect induced magnetic ordering in diamond (another allotrope of the carbon family) after proton irradiation. Diamond is a unique carbon allotrope which possesses exceptional and extreme properties such as hardness, electrical insulation, thermal conductivity, high charge carrier mobility and radiation hardness. As such diamond could find applications in microelectronics, spintronics, quantum cryptography, ultraviolet light-emitting diodes and optics, and high-power microwave electronics [8]. Ideal conditions for coherent spin manipulation can be found in diamond due to its long diffusion lengths and coherent times. We investigate proton irradiated nitrogen rich type Ib diamonds. The presence of nitrogen vacancy (NV) centres in diamond has sparked

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much interest. The negatively charged NV centre has been shown to have weak spin–orbit coupling in the diamond matrix resulting in long spin coherence times at room temperature and long diffusion lengths. This allows for fast resonant spin manipulation. Coherent manipulation of individual electron spins associated with the NV colour centre using optical and microwave frequencies have already been demonstrated [9,10]. Numerous possibilities of the uses of magnetic carbon have been envisioned within this spintronics context and several technical challenges need to be overcome in order for these applications to be realised. One of the primary challenges is to induce magnetic ordering in these materials as a prerequisite for them being used as spin valves.

In this work, we investigate the possibility of inducing magnetic ordering in nitrogen rich diamond type Ib through proton irradiation. This is the second generation of experiments performed for this purpose in diamond within our research group. In the first experiments ultrapure CVD grown type IIa diamonds were used [11]. The absence of π-electrons in the sp^3 configuration of diamond could act as a test for theoretical calculations which have suggested that vacancy induced ferromagnetism is based on interaction between local magnetic moments and conduction π-electrons. In the present work, the emphasis lies on the theoretical suggestion that nitrogen resident nearby a vacancy can generate a larger magnetic signal as compared to a standalone carbon vacancy [7].

2. Experimental details

Two nitrogen rich type Ib diamond samples were investigated for their magnetic properties. These diamonds were synthesised using high pressure, high temperature (HPHT) methods by the DeBeers Research laboratory (DRL) in South Africa and have a nitrogen content of approximately ~200 ppm. A mixed metal seed is used as a catalyst during the synthesis process which leads to magnetic impurities being contained within the samples. These magnetic impurities were quantified using Particle Induced X-Ray Emission (PIXE) at iThemba Labs Gauteng in South Africa and revealed a total magnetic impurity content of approximately 92.4 ppm.

The two samples B1 and B2 have masses of 14.4 mg and 12.7 mg respectively, and dimensions ~$3.3 \times 1.9 \times 0.66$ mm^3. Large area irradiations of the samples were conducted with 2.2 MeV protons using the 5 MV tandem accelerator at the Centre of Micro-Analysis of Materials (CMAM) at the Universidad Autónoma de Madrid. The proton beam was at normal incidence with respect to the diamond samples and parallel to the <001> axis. Sample B1 was irradiated with a total dose of approximately 1120 μC and a total fluence of 1.9×10^{17} H^+/cm^2. Sample B2 was irradiated with a total dose of approximately 4480 μC and a total fluence of 6.3×10^{17} H^+/cm^2 (See Table 1). Monte Carlo Simulations performed using the Stopping and Range of Ions in Matter (SRIM) [12] showed that protons with 2.2 MeV kinetic energy have a longitudinal range of approximately 28.5 μm in diamond and a longitudinal straggle of approximately 0.55 μm, with the displacement energy set to 45 eV [13] in order to account for the radiation hardness of diamond. Nuclear stopping is dominant near the range (~28.5 μm) of the protons and this is where the maximum defect density of 11 vacancies/ion on average are created according to SRIM calculations.

Table 1
Summary of the irradiation details for samples B1 and B2.

	Sample B1	Sample B2
E (MeV)	2.2	2.2
Q_{total} (μC)	1120	4480
F_{total} (H^+/cm^2)	1.9×10^{17}	6.3×10^{17}
Beam area (mm^2)	3.7	4.5

In order to investigate a change in the magnetic properties of the diamond samples, in terms of the proton induced defects and their associated magnetic moments, magnetisation measurements were conducted using a super conducting quantum interference device (SQUID) at the ICMM-CSIC in Madrid, Spain. These measurements were conducted on the pristine (before irradiation) samples as well as after the irradiation. Special care was taken in order to avoid magnetic contamination and in that respect the samples were mounted on specifically made gold-coated quartz sample holders using a small amount of diluted cryogenic varnish. The sample holders fit into the irradiation target chamber as well as the SQUID magnetometer [14]. This minimised the sample handling and allowed for the direct effects of the irradiation to be obtained, thus ensuring a high reproducibility of the observed results.

The samples were further characterised using Raman Spectroscopy at the University of the Witwatersrand in South Africa. A 514.5 nm green emission line from an argon laser was utilised in conjunction with a Horiba Jobin-Yvon LabRAM HR Raman spectrometer. The laser beam was focused onto the samples using a microscope attachment with a 100× objective lens. The backscattered light was dispersed via a 600 line/mm grating onto a liquid nitrogen-cooled charge coupled device (CCD) detector.

3. Results and discussion

Magnetisation measurements of the pristine samples at 300 K show that samples B1 and B2 exhibit a diamagnetic susceptibility of $\chi \approx -6.98 \times 10^{-9}$ emu/Oe and $\chi \approx -6.42 \times 10^{-9}$ emu/Oe respectively. Hence, a diamagnetic susceptibility of the diamond samples of $\chi \approx -4.85 \times 10^{-7}$ emu/g and $\chi \approx -5.05 \times 10^{-7}$ emu/g is obtained respectively which correlates well with previous studies [15,16]. SQUID measurements of the magnetic moment (μemu) of samples B1 and B2 as a function of the applied magnetic field (kOe) cycled between ±50 kOe at 300 K are shown in Fig. 1. The linear diamagnetic background measured before the irradiations for the two samples has been subtracted respectively and an overall superparamagnetic behaviour can be conjectured. This superparamagnetic behaviour could be due to magnetic inclusions [17]. It should be recalled here that the growth of the studied crystals requires the use of iron as a catalyst and therefore, this can be the origin of the magnetic inclusions already detected in the pristine samples However, a closer look reveals a finite value for the coercive field (around 40 Oe) and a small non-zero remanence (around 2×10^{-7} emu) confirming an additional contribution of some blocked moments. It can therefore be concluded that there is a broad distribution of sizes in the magnetic inclusions; most of them are in a few nanometer length-scale and, consequently, they are

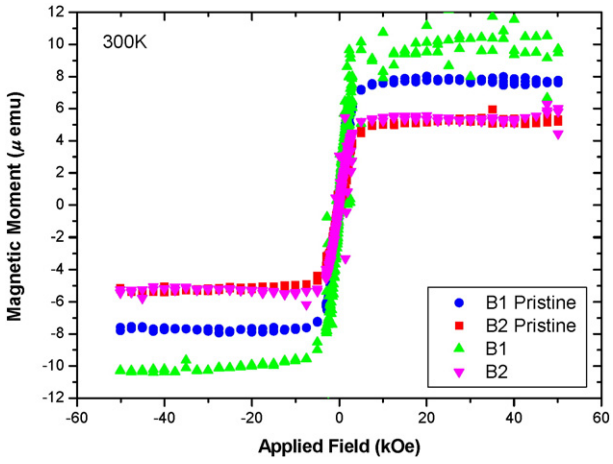

Fig. 1. Magnetic moments as a function of applied magnetic field at 300 K showing the superparamagnetic behaviour of samples B1 and B2.