LATTICE SITES OF ION IMPLANTED Cu ATOMS IN DIAMOND

K. Bharuth-Ram¹, U. Wahl², J.G. Correia^{2,3}, and the ISOLDE collaboration³

¹ School of Physics, University of Natal, Durban 4041, South Africa

² Instituto Tecnológico e Nuclear, Sacavém, Portugal

³ CERN, CH-1211 Geneva, Switzerland

Radioactive ^{67}Cu atoms were accelerated to 60 keV at the online isotope separator ISOLDE at CERN, and implanted into a type IIa natural diamond sample to a dose of $2 \times 10^{12} \text{ cm}^{-2}$. The channeling of β^- particles and conversion electrons emitted in the decay of ^{67}Cu and $^{67}\text{Zn}^*$, respectively, were monitored about the three major axial directions with a two dimensional position-sensitive detector. The electron emission channeling data were collected from the room temperature implanted sample and after annealing at 1200 K. The observed channelling patterns were fitted with simulations based on the many beam formalism of electron motion through a crystal lattice. In the as-implanted sample, 25% of the Cu atoms were located a mean, isotropic displacement of 0.25(5) Å from substitutional sites, and the remainder, $f_R = 75\%$, at sites that gave an isotropic emission yield. Annealing at 1200 K results in enhanced axial and planar channeling effects. The fits to the data yield either a fraction $f_1 = 43(5)\%$ of Cu atoms located 0.22(4) Å from substitutional sites and $f_R = 57\%$, or a fraction $f_1 = 10(2)\%$ at substitutional sites, a fraction $f_2 = 50(5)\%$ at mean isotropic displacement of 0.5 Å from substitutional sites, and a 'random' fraction $f_R = 40\%$.

Keywords: diamond, Cu lattice location, emission channelling.

Contact author :

K. Bharuth-Ram, School of Physics, University of Natal, Durban 4041, South Africa

Email: bharuthramk@nu.ac.za; Fax.: + 27 31 2616550; Tel.: +27 31 2602775

1. Introduction

Interest in transition metal (TM) defects in diamond arises from their influence on growth conditions and on the material properties of the crystals produced. TM atoms play a crucial solvent-catalyst role in the synthesis of single crystal diamonds in the high temperature high pressure (HTHP) process [1]. In the case of natural diamonds, as well as diamonds synthesized in the CVD process, the goal is to produce diamonds with tailored semiconducting properties through the incorporation of desired impurities. A considerable boost to such studies has been given recently by the synthesis of single crystal diamonds of exceptional purity in a CVD process which, with boron incorporation during growth, showed electron and hole mobilities as high as 4500 and 3800 cm^2/Vs , respectively [2]. Except for boron and lithium, the formation energies of other potential dopant atoms in diamond are relatively high [3], thus favouring ion implantation as a means of incorporating the dopant atoms in the diamond lattice. Radioactive TM nuclides, such as ^{59}Fe , ^{57}Fe and ^{67}Cu , are ideal probes for investigations on implantation parameters and the annealing of radiation-induced lattice damage, as well as on the location of implanted atoms and the defect complexes that they form.

Electron paramagnetic resonance (epr) studies on Ni and Co in HTHP-synthesized diamonds [4-8] have identified three main lattice sites for these impurity atoms: substitutional, tetrahedral (T_d) interstitial, and the 'divacancy' site in which the impurity atom is located at the bond center between two neighbouring vacancies. Little direct information exists on other TM atoms such as Fe, Cu and Ti, and the defects they form in diamond, although Baker [9] has argued that the W36 centre observed in epr measurements on a type IIb diamond may be related to Cu in the divacancy. We reported recently on our studies on the lattice location of ^{59}Fe atoms in diamond [10]. In the present contribution we report on our investigations on the lattice location and annealing properties of Cu atoms in diamond, determined from emission channeling (EC) measurements on β -particles and conversion electrons emitted in the decay of ion implanted radioactive ^{67}Cu probe atoms.

2. Experimental Details

In emission channeling (EC) measurements [11-13] with electron emitting radioactive isotopes the yield of β particles or conversion electrons, emitted in the decay of probe ions implanted in single crystal samples, is measured outside the sample as a function of angle relative to the principal axial directions. The trajectories of the emitted electrons through the crystal lattice are strongly influenced by their Coulomb interactions with the positively charged atomic rows. This results in anisotropic emission yields whose angular pattern is characteristic of the lattice location of the emitter. The identities of the lattice location of the probe atoms and their fractional population at a particular site are then deduced from fits of simulations based on the many beam formalism of electron diffraction through the crystal to the experimental channeling patterns.

Radioactive ion beams of $^{67}\text{Cu}^+$ were produced at the online isotope separator facility, ISOLDE, at CERN, using 1.4 GeV proton-induced nuclear fission in a UC_2 target followed by two-stage laser ionization. Mass separated,

clean beams of $^{67}\text{Cu}^+$ ions were accelerated to 60 keV and implanted into a type IIa natural diamond single crystal at room temperature in an implantation chamber. About 2×10^{12} ions/cm² were implanted into the sample.

The ^{67}Cu probe nucleus decays, with $t_{1/2} = 61.8$ h, to the ground and excited states of ^{67}Zn through the emission of β^- particles with end point energies of 577 keV (20%), 484 keV (35%) and 395 keV (45%). The electrons emitted in the decay of ^{67}Cu were detected in a position sensitive Si detector of 30×30 mm² area, which was segmented on one surface into 22×22 pads, each 1.3×1.3 mm² [13]. Two dimensional channeling patterns of the β^- particles emitted by ^{67}Cu were collected along the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ crystallographic directions, from the as-implanted sample (room temperature) and after annealing under vacuum for 10 min. at 1200 K. In addition, channeling data was also collected on the conversion electrons emitted in the decay of the $^{67}\text{Zn}^*$, 93.3 keV state ($t_{1/2} = 9.16$ μs).

3. Analysis

Energy windows of 97-600 keV and 80-97 keV were set on the emission data to extract the β^- and conversion electron channeling patterns, respectively. The channeling patterns were corrected for the contribution of back-scattered electrons to the data by subtracting constant backgrounds which were estimated for the axial directions investigated by Monte Carlo simulations.

Characteristic two-dimensional patterns of electron emission probability were calculated, within the many beam formalism [11,12], for x - and y -angular ranges of $\pm 3.0^\circ$ around the $\langle 110 \rangle$, $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, in steps of $\Delta x, \Delta y = 0.05^\circ$. For the β^- patterns, the calculations were made in energy steps of 25 keV over the energy window of 97-600 keV, and the results averaged according to the theoretical total β^- energy distribution.

The theoretical emission patterns, $X_{\text{theor}}(\vartheta, \varphi)$, where ϑ and φ denote polar and azimuthal angles from the axis, were smoothed using a Gaussian of $\sigma = 0.1^\circ$ to account for contribution to the angular resolution of the 1 mm beam spot on the sample and the size and shape of the detector pads, and were fitted to the experimental yields X_{exp} according to

$$X_{\text{exp}}(\vartheta, \varphi) = S \left[\sum_i f_i (X_{\text{theor},i}(\vartheta, \varphi) - 1) + 1 \right]. \quad (1)$$

S is a scaling factor common to all angles in a pattern, and f_i denote the fractions of emitter atoms at sites i . The remaining fraction, $f_R = 1 - \sum f_i$, the ‘random’ fraction, accounts for emitters that produce isotropic emission yields and which may be at sites of low symmetry or of extensive damage. The sites modeled included emitters at substitutional (S), tetrahedral interstitial (T), hexagonal interstitial (H), bond center (BC), anti-bonding (AB), split $\langle 100 \rangle$ sites, and for $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ displacements of emitters between these sites. In addition, simulations were also done for emitters displaced isotropically (with Gaussian profiles) from S and T sites with root mean square (rms) displacement values of 0.05 to 1.0 Å.

After the implantation at 300 K a fraction $f_1 = 25(3)\%$ of the Cu atoms were found to be located at a mean displacement of $0.25(3)$ Å from an S site, with a fraction $f_R = 75\%$ at ‘random’ sites. Annealing at 1200 K results in considerable enhancement of the electron channeling; prominent channeling effects become clearly evident along the $\langle 110 \rangle$ and $\langle 111 \rangle$ axial directions and the $\{111\}$ planes, reflecting a substantial increase in the fraction of emitter atoms close to substitutional sites. This is illustrated for the β^- emission yields in Figs. 1(a) and (b). The simulated channeling patterns of the best fits to the data are shown in Fig.1 (c) and (d). Results of the best fits to the 300 K and 1200 K channeling patterns are summarized in Table 1. The fit to the data, assuming a fraction f_1 at a specified site in the lattice and the remainder at ‘random’ sites, yields a fraction $f_1 = 45(5)\%$ of emitters with an rms isotropic displacement of $0.24(5)$ Å from S sites, and $f_R = 55\%$. An improved fit was obtained for $f_1 = 10(3)\%$ of probe atoms at S sites, $f_2 = 50(10)\%$ at sites with an isotropic rms displacement of $0.5(1)$ Å from an S site, and a fraction $f_R = 40\%$ of emitters giving an isotropic electron yield. Our data excluded any Cu atoms located at tetrahedral and hexagonal interstitial sites.

The channeling effects of the ^{67}Zn conversion electrons were not as pronounced, due both to the lower electron energy and to the poorer statistics. Fig. 2(a) presents the experimental emission yield along the $\langle 110 \rangle$ axial direction, and Fig. 2(b) the corresponding simulation for the best fit, which was obtained for a fraction $f_1 = 50(7)\%$ of the Cu(Zn) atoms located at a mean displacement of $0.24(5)$ Å from S sites, and $f_R = 50\%$. This result shows that the lattice sites of $^{67}\text{Zn}^*$ occupied as a result of the decay of ^{67}Cu are not fundamentally different from those of the mother isotope (the recoil energy imparted to the $^{67}\text{Zn}^*$ nucleus is of the order of 1.2-1.9 eV only).

The present results are in good agreement with our EC measurements on the lattice location of ^{59}Fe atoms implanted in diamond, where after room temperature implantation and annealing at 1250 K, 65(5) % of the Fe atoms were found to be located near substitutional sites in the lattice.

4. Conclusions

Emission channeling measurements have been performed on a diamond single crystal implanted with radioactive ^{67}Cu probes. Analysis of the channeling effects on the ^{67}Cu β^- particles and the $^{67}\text{Zn}^*$ conversion electrons show

that after room temperature implantation and annealing at 1200 K, 10% of the Cu atoms are located at practically undisturbed substitutional sites and 50(5) % are at an isotropic rms displacement of $u \approx 0.5(1)$ Å from S sites. About 40% of the Cu atoms remain at defect complexes or at sites that give isotropic emission yields. Contributing to the relaxation of the majority of the Cu atoms from substitutional sites may be a small fraction trapped in divacancies, as suggested by ref. [9], and a larger fraction of atoms undergoing Jahn-Teller (J-T) relaxation. At a substitutional (S) site the Cu atoms form $n = 4$ covalent bonds, which leaves the unpaired electrons most probably in a $3d^6$ configuration. In the strongly bonded tetrahedral S site the crystal field splits $3d^6$ orbitals into sublevels $e^4 t_2^2$. Jahn-Teller distortions which raise the degeneracy of sub-levels may lead to a relaxation of the Cu atoms away from the S site. The J-T relaxations are expected to occur along $\langle 111 \rangle$ directions. However, in this ion implantation study, each 60 keV Cu ion is estimated to produce about 450 vacancy-self interstitial pairs. Fe-vacancy and Fe-C_i interactions are expected to occur, and may be responsible for small displacements of the Cu atom away from $\langle 111 \rangle$ directions.

Johnston et al. [11] have carried out *ab initio* calculations which predict Cu_s to be the most stable substitutional TM impurity in diamond and Fe_s not very stable, having an enthalpy 30 eV above that of Cu_s. Cu is also predicted to be more stable than Fe at the interstitial and divacancy sites. Our data, however, show that ion implantation results in similar fractions of Fe and Cu atoms being incorporated near substitutional sites in diamond, and no evidence of these TM atoms at interstitial sites.

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Table 1: Summary of results of fits to β^- and conversion electron channeling of ^{67}Cu implanted diamond: f_i are the fraction of atoms at an rms displacement of u_i from an S site.

Temperature T_A	Axial direction	f_1	u_1	f_2	u_2
<u>β^- channelling</u>					
300 K	$\langle 110 \rangle$	0.25(3)	0.22(3) Å	-	
	$\langle 111 \rangle$	0.27(3)	0.20(3) Å	-	
	$\langle 100 \rangle$	0.22(4)	0.30(4) Å	-	
1200 K	$\langle 110 \rangle$	0.44(4)	0.30(4) Å	-	
	$\langle 111 \rangle$	0.42(4)	0.22(4) Å	-	
	$\langle 110 \rangle$	0.11(2)	≤ 0.035 Å	0.48(5)	0.45(7) Å
	$\langle 111 \rangle$	0.10(3)	≤ 0.035 Å	0.50(5)	0.50(5) Å
Conv. electron channelling					
1200 K	$\langle 110 \rangle$	0.55(5)	0.25(5) Å	-

Fig. 1: Emission channeling patterns of β^- particles emitted in the decay of ^{67}Cu : a) and b) observed patterns in the $\langle 110 \rangle$ and $\langle 111 \rangle$ axial directions, after annealing at 1200 K: c) and (d) are best fits of simulated patterns to the experimental yields for 10% emitter atoms at S sites and 48% and 50% emitters, respectively, on sites with a mean projected displacement of 0.5 Å from S sites.

Fig.2: Observed and simulated channeling patterns of conversion electrons emitted in the decay of $^{67}\text{Zn}^*$ in the $\langle 110 \rangle$ axial direction, after annealing at 1200 K.