

## EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN-PPE/95-68

25 April 1995

**LATTICE SITES OF ION-IMPLANTED Li IN DIAMOND**

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**Abstract**

Radioactive Li ions were implanted into natural IIa diamonds at temperatures between 100 K and 900 K. Emission channelling patterns of  $\alpha$ -particles emitted in the nuclear decay of  $^8\text{Li}$  ( $t_{1/2} = 838$  ms) were measured and, from a comparison with calculated emission channelling and blocking effects from Monte Carlo simulations, the lattice sites taken up by the Li ions were quantitatively determined. A fraction of 40(5)% of the implanted Li ions were found to be located on tetrahedral interstitial lattice sites, and 17(5)% on substitutional sites. The fractions of implanted Li on the two lattice sites showed no change with temperature, indicating that Li diffusion does not take place within the time window of our measurements.

*(Submitted to Applied Physics Letters)*

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\*\* Supported by the Deutsche Forschungsgemeinschaft, 53170 Bonn, Germany.



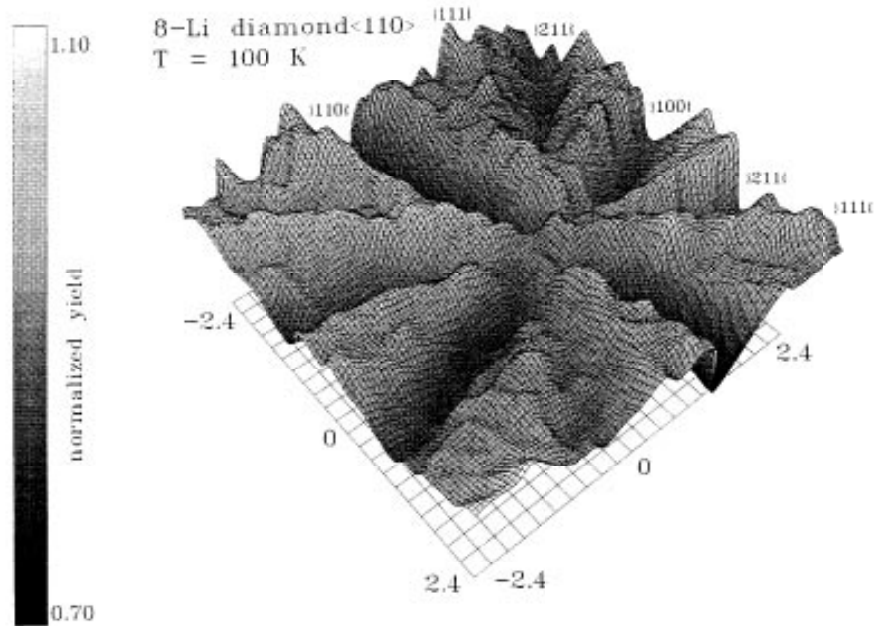
## 1. INTRODUCTION

Diamonds have several outstanding properties with regard to electronic applications. For the realization of semiconducting devices effective p- and n-type conductivity is needed. Boron doped diamonds are p-type semiconducting and are available both as natural type IIb and synthetic samples produced either by thermal growth methods [1] or by ion-implantation [2]. In contrast, n-type doping has proved to be very difficult. The equilibrium solubility of the most likely n-type doping atoms in diamond is very low [3], making thermal diffusion or in situ doping during growth unsuitable methods to achieve n-type conductivity. Considered to be more promising is ion implantation, which is solubility independent. However, successful doping by ion implantation requires incorporation of the doping atoms on electrically active sites and removal of radiation damage through appropriate annealing procedures. Attempts at n-type doping by ion implantation with group V elements such as P and As, reported as being effective n-type dopants in Si, were not, however, very successful [4]. For the group I elements Na and Li, calculations indicate that the most stable lattice sites are tetrahedral interstitial sites, where the dopants should act as shallow donors with ionization energies of 0.3 and 0.1 eV, respectively [3]. The formation of substitutional Li with acceptor character was also regarded as possible [5]. Since on the experimental side electrical measurements on Li-implanted diamonds [6], [7] did show increased conductivity, lattice site determination would be useful for supplementary information. Direct site determinations of Li in diamond are rare since standard methods like Rutherford backscattering channelling or particle-induced X-ray-emission channelling fail in the case of Li owing to its low atomic number. The single reported work in this regard are the nuclear reaction analysis (NRA) channelling measurements of Braunstein et al. [8] which indicated, only qualitatively, that an appreciable fraction of the implanted Li were on non-substitutional lattice sites.

## 2. EXPERIMENT

In this letter, we present a direct and quantitative determination of the lattice location of ion-implanted Li in diamond using the emission channelling technique [9]. In this technique, lattice sites of radioactive atoms are determined from channelling and blocking effect measurements of emitted charged particles. In contrast with NRA channelling no probing beam is needed and therefore crystal damage during analysis is greatly reduced. As our probe we used the isotope  $^8\text{Li}$  ( $t_{1/2} = 0.838$  s) which decays via  $\beta^-$  emission to an excited state of  $^8\text{Be}$  which, within  $4 \times 10^{-22}$  s, breaks up into two  $\alpha$  particles with energies continuously distributed around 1.6 MeV. Thus, the emitted  $\alpha$  particles reflect the lattice sites occupied by  $^8\text{Li}$  within a time window of a few seconds between implantation and decay. The diamond samples were  $\langle 110 \rangle$ -oriented natural single crystal diamonds (type IIa) supplied by DRUKKER International. They were mounted on a two-axes goniometer, which allowed

cooling to about 50 K and heating to about 900 K. At the on-line isotope separator PSB-ISOLDE at CERN [10]  $^8\text{Li}$  was produced and was available as an isotopically pure 60 keV  $^8\text{Li}^+$  beam. The ions were implanted into the diamond crystals in a collimated beam of 0.5 mm diameter. The  $\alpha$ -emission yields along different crystallographic directions were measured as a function of implantation temperature using a two-dimensional position-sensitive Si-detector [11] centred at  $152^\circ$  with respect to the implantation direction. The position resolution of the detector together with the size of the implantation spot give a total angular resolution of  $0.13^\circ$  (standard deviation). Data acquisition was accomplished using the set-up described in Ref. [12]. The implantation dose needed to acquire a single spectrum such as shown in Fig. 1 was below  $1 \times 10^{12} \text{ cm}^{-2}$  and the total implantation dose per sample did not exceed  $2 \times 10^{13} \text{ atoms cm}^{-2}$ . An added advantage of this technique is that after the decay of the  $^8\text{Li}$  ions no decay products, except for some stopped  $\alpha$  particles, remain in the diamond crystal.



**Fig. 1:**  $\alpha$ -emission pattern measured around the  $\langle 110 \rangle$  axial direction during implantation of 60 keV  $^8\text{Li}$  ions into diamond at a temperature of 100 K. The angular range displayed is  $\pm 2.4^\circ$  in x- and y-directions.

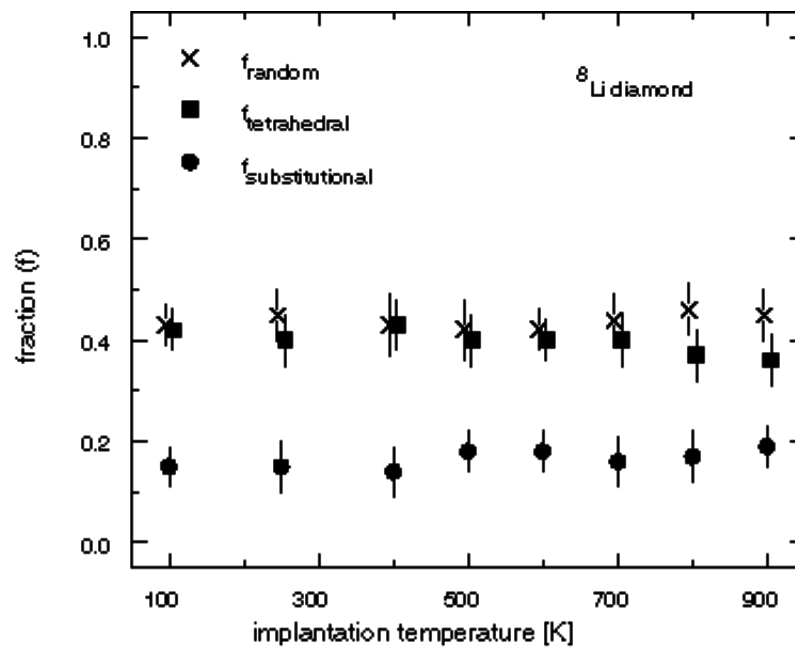
### 3. RESULTS AND DISCUSSION

Figure 1 shows a two dimensional  $\alpha$ -emission channelling pattern measured around the  $\langle 110 \rangle$  axis at 100 K. Clearly resolved are channelling effects along the  $\{111\}$ -planes and blocking effects along the  $\{110\}$ - and  $\{100\}$ -planes showing unambiguously that Li occupies mainly tetrahedral interstitial sites. In order to derive quantitatively the fractions of  $^8\text{Li}$  atoms on different lattice sites, theoretical calculations of the  $\alpha$ -emission channelling patterns were

carried out using the Monte Carlo simulation program FLUX [13], modified for simulating emission channelling effects [14]. In the simulation we used as input values the mean range of the Li implantation profile  $d = 150$  nm (FWHM 67 nm) calculated by TRIM [15] and a Debye temperature  $\Theta_D(\text{diamond}) = 1860$  K [16]. The calculated patterns were then fitted to the experimentally observed channelling patterns in the form of one-dimensional scans, as described in Ref. [14]. For all temperatures a scan through the  $\langle 110 \rangle$  axis along a  $\{110\}$ -plane shows clearly a channelling peak, and strong blocking effects through the  $\langle 100 \rangle$  and the  $\langle 111 \rangle$  axes. Excellent fits to the blocking effects in the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions were obtained by taking into account only lattice sites which are aligned with these two axes, i.e. tetrahedral (T) or substitutional (S) sites, and a fraction at irregular sites (R). The ‘R sites’ include all sites of very low symmetry which are assumed to produce negligible anisotropy in  $\alpha$ -emission yield. The blocking effects in the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions yielded site fractions  $f_{T+S} = 0.57(5)$  and  $f_R = 0.43(5)$ . In contrast with the  $\langle 111 \rangle$  and  $\langle 110 \rangle$  directions, the emission effects observed in the  $\langle 110 \rangle$  direction allow a clear discrimination between the T and S sites since along this axis emitter ions at the T sites give a channelling effect while those at S sites give a blocking effect. Our data when analysed for Li ions located at tetrahedral interstitial, substitutional, and irregular sites yield site fractions  $f_T = 0.40(5)$ ,  $f_S = 0.17(5)$  and  $f_R = 0.43(5)$  for the three sites, respectively. If only T and R sites are allowed, a poorer fit to the data is obtained with fractions  $f_T = 0.20(5)$  and  $f_R = 0.80(5)$ . This is in conflict with the random fraction of 0.43(5) derived from the results in the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions. The site fractions ( $f_R$ ,  $f_T$ ,  $f_S$ ) of Li ions at the different lattice sites determined in our work are plotted in Fig. 2, showing no significant dependence on temperature. In the calculations, the one-dimensional vibration amplitude  $u_1$  of the  $^8\text{Li}$  atoms in the diamond lattice and static displacements from the ideal lattice sites were treated as additional fit parameters. Best results were obtained for vibration amplitudes corresponding to a Debye temperature of  $\Theta_D(\text{Li}) \approx 2280$  K and no static displacements, but there are indications of Li(S) with increased vibration amplitudes or static displacements up to 0.2 Å.

Our results thus show that in the temperature range 100–900 K, Li atoms implanted into diamond prefer interstitial sites, but a significant fraction are also incorporated on substitutional sites even at low temperatures. This latter effect may be related to implantation-assisted processes such as kinetic replacement collisions with lattice atoms. The appreciable value of  $f_R$  (i.e. random sites) could be due to Li atoms being located at more extended defects such as multiple vacancies or dislocations. The fact that the fractions on different lattice sites do not depend markedly on the implantation temperature indicate that within a time window of our measurement there is no diffusion of the Li atoms. Assuming that the mean diffusion length  $(Dt)^{1/2} = (D_0 t \exp(-E_A/kT))^{1/2}$  of  $^8\text{Li}$  during its lifetime  $t$  is smaller than the implantation depth  $d$ , the activation energy for diffusion  $E_A$  can be estimated to  $E_A > 1.25$  eV according to  $E_A > k_B T \ln(D_0/d^2)$  and  $D_0 = (1/6) a^2 \omega_D$ , where  $a$  is the distance between adjacent T sites and  $\omega_D$  the Debye frequency of Li in diamond derived from our experiments. The absence of Li diffusion is in agreement with the recent results of Cytermann et al. [17]. In our experiments we can only probe the lattice sites of Li within a

time window of a few seconds after implantation. No subsequent thermal processing of the implanted sample, such as annealing, is possible. Therefore it is not possible to make direct comparison with annealing studies such as performed by Praver et al. [7]. Nevertheless, the partial incorporation of Li on substitutional sites even at rather low temperatures indicates that the difficulties in n-doping of diamond by Li implantation may be due to the compensation of Li(T) donors by Li(S) acceptors. In addition, the Li observed at irregular sites suggests that an appreciable fraction of the Li ions become bound in defect complexes where they are most probably electrically inactive.



**Fig. 2:** Fractions of Li atoms located on tetrahedral interstitial sites ( $f_T$ ), substitutional sites ( $f_S$ ), and random fraction ( $f_R$ ) as a function of temperature for diamond.

## Acknowledgements

We gratefully acknowledge the financial support of the Bundesministerium für Forschung und Technologie and the Deutsche Forschungsgemeinschaft.

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