Declaration

I declare that this is my own work. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of Candidate)

_____ day of _____ 20_____

ABSTRACT

Electron Paramagnetic Resonance (EPR) has been used to study radiation damage centres in type Ib diamonds which were either electron- or neutron irradiated. The isochronal annealing behaviour has been determined for a number of EPR centres up to 850 ^{o}C. The centres W11, W2, W13 and W14 as well as the interstitial centres R1 and R2 are produced under the irradiation beam and anneal out after about 450 ^{o}C. The centres W15, W29, R4/W6, W33, W37, W46 and W47 are observed following annealing at temperatures starting after about 400 ^{o}C. Of these centres only W33 and W15 are still growing in intensity after annealing at 850 ^{o}C - the temperature at which all the others are annealing out. The concentration measurements were determined for each annealing stage with the aid of a well-calibrated type Ib diamond as a standard.

The central region or g=2 region of our spectra consists mainly of the a-line. This is a centre whose complex nature has been understood a bit better based on the annealing curves obtained in this work. The S1 or negative vacancy superimposes with the centre and hence made the concentration measurements of the cenre (S1) difficult. This was obtained indirectly using its ^{13}C hyperfine lines.

New work on four EPR centres namely W33, W37, W46 and W47 has been made. Their spin Hamiltonian parameters have been determined and have shown that their structural symmetries are very close to <111>. Of the centres W33, W46 and W47 have effective spins S=1 whereas W37 has an unusually large effective spin S=2. From the annealing behaviour and the spin Hamiltonian parameters, their structural models have been proposed.

The effective spin S=3/2 for the W11, W12, W13 and W14 EPR centres have been verified in this work by employing EPR $\Delta m_s = 2$ transitions. The annealing curves for the centres suggest that the nitrogen may not be directly involved but donates electrons necessary for the formation of the centres.

The W29 is an EPR centre that was found to have many similarities with R4/W6, the neutral divacancy centre in diamond. Their symmetries are both close to <111>; they have a large D-values and E-terms. In addition their g-tensors are isotropic and very close to free spin value. We have proposed that the W29 is a negative divacancy.

The linewidths of the centres W29 and R4/W6 have been measured in the temperature range 6-300 K; large variations in this range were found i.e 2 - 7 G for W29 and 1.8 - 14 G for the R4/W6 centre.

The spin lattice relaxation times T_1 for the R4/W6 and the W29 centres in neutron-irradiated type Ib diamond have been made using the CW saturation methods. The dominant relaxation mechanism at very low temperatures (below 50 K for R4/W6 and below 70 for W29 centre) is the direct process. The Orbach process is dominant in the higher temperature regions for both centres. The results suggest excited states 15.5 meV and 25.8 meV for W29 and R4/W6, respectively.

To

Pauline Chepkemoi Kirui, my wife

and our children

Winnie Chemutai, Caleb Kibet and Gerald Kipruto

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