Investigation of the introduction and annealing behaviour of the donor-vacancy complex in alpha-particle irradiated germanium

Abraham W. Barnard, Walter E.Meyer, F. Danie Auret, Phuti N.M. Ngoepe and Sergio M.M. Coelho

Department of Physics, University of Pretoria, Private bag X20, Hatfield 0028, Pretoria

E-mail: u10688112@tuks.co.za

Abstract. The annealing behaviour of the donor vacancy complex (E-centre) in Ge has been investigated by high resolution (Laplace) deep level transient spectroscopy (L-DLTS). In this study Sb-doped Ge was used and the defect was introduced by irradiating the Ge sample with alpha particles from an Am-241 source. The Sb-vacancy complex has an activation energy of 0.37 eV ($E_{0.37}$) for electron emission as determined by L-DLTS. The E-centre in Ge has been observed to anneal out in a two stage process. In the first stage the defect concentration decreases rapidly when the sample is heated to approximately 320 K, and then remains relatively constant with annealing temperature. In the second final stage, at a temperature of approximately 370 K, the defect concentration decreases quite rapidly until the defect finally anneals out completely. A possible hypothesis is that the E-centre observed is in fact two different defects corresponding to the fast and slow annealing components. However, in this study, we found that both the slow and the fast annealing components of the E-centre have the same L-DLTS signatures (activation energy and apparent capture cross section) as well as the same true capture cross section. In effect, both the fast and the slowly annealing components of the E-centre seem to be the same defect. We investigated this phenomenon by investigating different irradiation and annealing procedures and suggest that the fast annealing component of the E-centre can be explained by Ge self-interstitials, released from other radiation induced defects recombining with the vacancy in the E-centre.

1. Introduction

Germanium shares unique properties with silicon in which both have 4 valence electrons that results in the formation of tetrahedral crystal lattice. This dramatically changes the electrical properties when substitution atoms are introduced [1]. It is mainly used in a highly pure form as a detector material and is not extensively used in devices due to the overwhelming success of silicon in applied fields. This material has however gained a lot of interest recently as a semiconductor material due to improved epitaxial growth techniques for electronic and opto-electronic applications. When compared to Si, Ge is a possible candidate for fast switching transistors or complimentary metal-oxide-semiconductor (CMOS) devices due to its higher hole and electron mobility [4].

The donor vacancy pairs (E-centre) formed by introducing vacancies into the antimony doped germanium crystal lattice through alpha or electron radiation has been identified to be trap with an

activation energy of 0.37 eV, which will be indicated as $E_{0.37}$. The rate of $E_{0.37}$ introduction depends on the concentration of the Sb in the material [3]. When high concentrations of Sb are present, the $E_{0.37}$ peak dominates and becomes the sole observed peak with other defects being secondary that grow over time. Defects within germanium are removed by low annealing temperatures between 625 K and 675 K with the E-centre annealing out by dissociation and diffusion of the vacancy. Annealing with a reverse bias delays or prevents annealing of the E-centre in Ge which is a contrast to the annealing of the E centre in Si which has a bias enhancement [2].

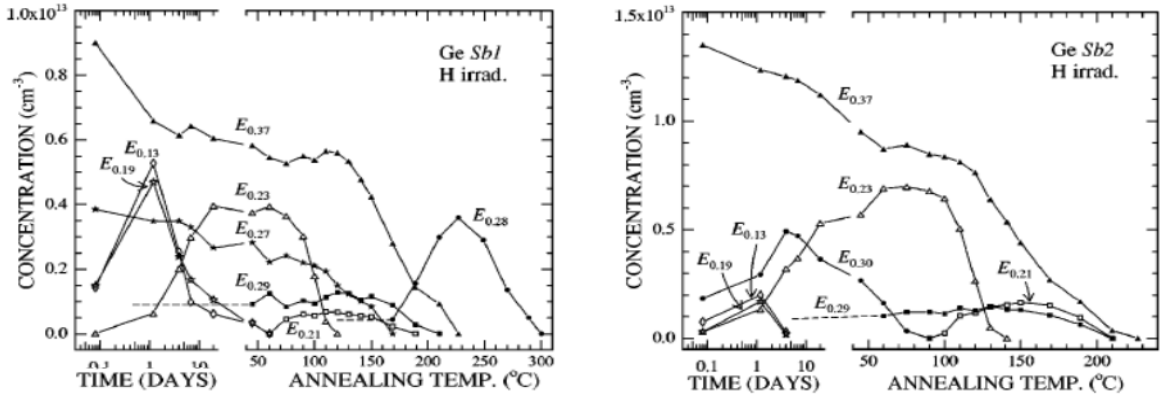

Figure 1. Isothermal annealing at room temperature followed by isochronal annealing at intervals of 15 minutes for two germanium samples Sb1 and Sb2 after exposure to proton radiation [2].

The $E_{0.37}$ observed by J. Fage-Pedersen and A. Nylandsted Larsen in figure 1 showed a reduction in concentration when exposed to room temperature and a further reduction once exposed to temperatures greater than 400 K. It was found that a major fraction of $E_{0.37}$ anneals at approximately 450 K. Over a large temperature span, thermally activated diffusion or association would not proceed. Thus if the $E_{0.37}$ peaks don't contain large contributions from other defects there has to be some kind of unstable source created during the irradiation that release mobile species at room temperature that consumes the E-centre [3].

2. Experimental details

The Ge supplied by Umicore used in this study was bulk grown (100) n-type germanium. Multiple samples of approximately 6 mm by 3 mm were first degreased with trichloroethylene, isopropanol and methanol for 5 minutes each then etched in a mixture of H_2O_2:H_2O with a ratio of 1:5 for 1 minute and dried with nitrogen. Immediately after cleaning a layer of 80 nm AuSb was deposited on the backside forming the ohmic contacts through resistive evaporation. After formation of the ohmic contacts, the samples were rinsed of with isopropanol for 5 minutes and dried off with nitrogen before being annealed at 650 K for 10 minutes in an environment flushed with argon at a rate of 0.1 litres per minute. The samples were cleaned with isopropanol for 5 minutes again and etched with the same mixture of H_2O_2:H_2O for 1 minute before being dried off with nitrogen. Gold circular dots, 100 nm thick, with a diameter of approximately 0.6 mm were grown at a rate of 0.1 nm per second through resistive evaporation on the front of the samples.

Three doping densities were deployed and are denoted as GeSb1, GeSb2 and GeSb3 with the first two approximated to contain 1×10^{15} cm^{-3} Sb and the third measured to have 2.6×10^{15} cm^{-3}. One contact on GeSb1 was exposed to Am-241 in intervals of 30 minutes and annealed at 330 K for 60 minutes after each exposure. L-DLTS was performed at 195 K after each exposure and annealing, up to a resultant exposure of 180 minutes. The second sample (GeSb2) underwent the same procedure but was exposed in intervals of 40 minutes with the third exposure being 50 minutes. Three other contacts on GeSb1 were exposed for the full length of 180 minutes then annealed at 330K for 60 minutes with a L-DLTS

spectrum taken at 195K. Another contact on GeSb2 and a contact on GeSb3 were exposed at intervals of 30 minutes with a Laplace transient recorded after each exposure.

In this paper we have studied the introduction and annealing kinetics of two defects that have a similar energy level which has previously been identified as the E-centre.

3. **Experimental results**

The energy level $E_{0.37}$ may represent at least two defects with very similar energy levels that cannot be distinguished through conventional DLTS methods due to the resolution not being high enough. For convenience sake we will denote the first reduction as the removal of the $E'_{0.37}$ and the second reduction as the removal of the E-centre ($E_{0.37}$) that was observed by many. This peak was identified to lie approximately at 195 K on the conventional DLTS spectrum, thus we used L-DLTS at this temperature for higher resolution [5]. However even using this high resolution technique, it was not possible to distinguish between the two traps.

3.1 Introduction kinetics of $E_{0.37}$

The introduction rate of the $E_{0.37}$ was determined by introducing both defects through alpha radiation as seen in figure 2 and removing only the $E'_{0.37}$ from the two germanium samples by means of low temperature annealing. The introduction of $E_{0.37}$ was tested by introducing both defects for the full exposure time period on multiple points on the GeSb1 sample. After removing the $E'_{0.37}$ defect it was found that the introduction of the $E_{0.37}$ was linear and did not depend on whether the $E'_{0.37}$ was annealed out during or after the irradiation. This is shown clearly in figure 2 where the concentration after annealing (red dots) showed a linear relationship with irradiation time, irrespective of the annealing occurring in one step after irradiation or in shorter steps between irradiations. The introduction kinetics for $E_{0.37}$ was observed to be linear which suggests that is was of a first order introduction which is consistent with vacancies captured by Sb.

3.2 Introduction kinetics of $E'_{0.37}$

The combined introduction rate of $E'_{0.37}$ and $E_{0.37}$ through alpha particle radiation was determined to be that of a quadratic function. This was determined by introducing both defects into the crystals at intervals of 30 minutes and then modelling their combined introduction rate against the equation

$$Nt = At^B$$

where *Nt* is the trap concentration and t is the total exposure time to alpha radiation. In figure 3 the best fit with the equation, GeSb2 was found to have $A = 6.67 \times 10^9$ with $B = 2.04$ and GeSb3 was found to have $A = 1.02 \times 10^{10}$ with $B = 2.02$. This suggests an introduction rate for the simultaneous introduction of both defects to be that of a quadratic nature. Since it was earlier determined that the introduction kinetics of the $E_{0.37}$ was that of a linear nature, it can easily be seen that the introduction kinetics of the $E'_{0.37}$ is that of a second order process.

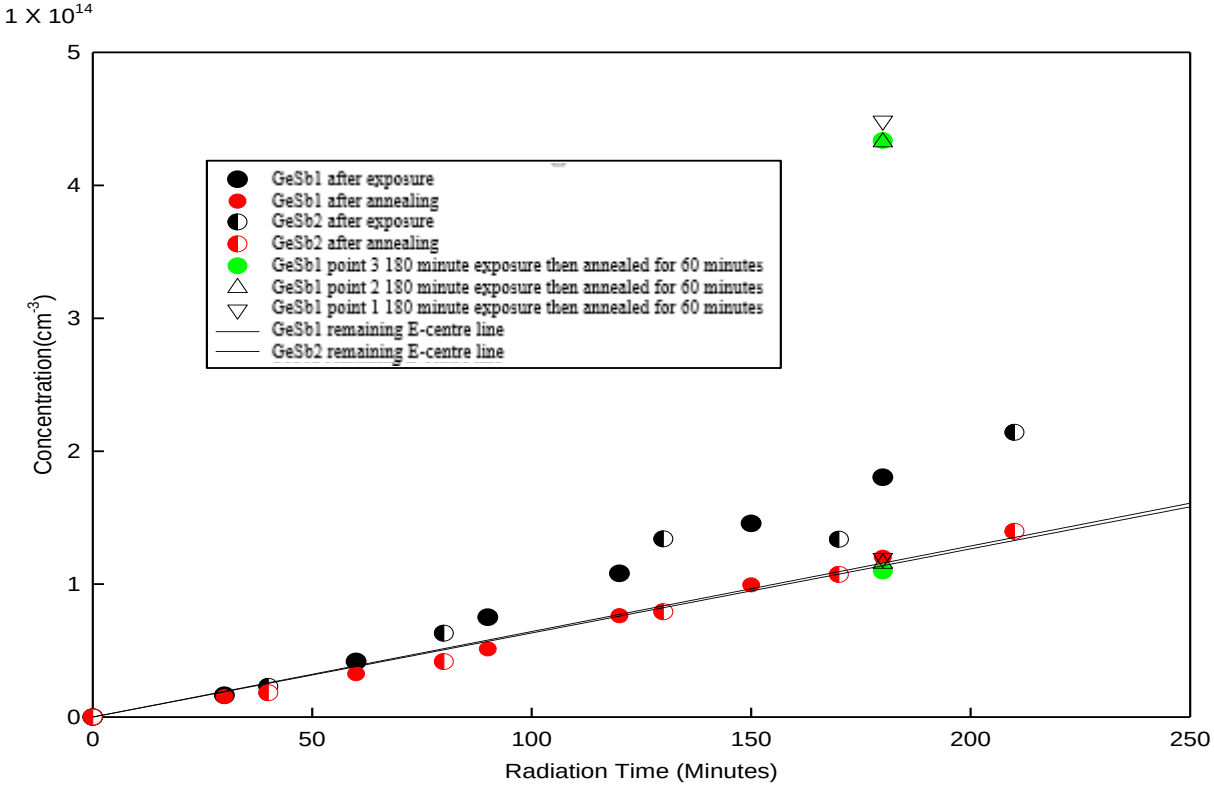

Figure 2. GeSb1 exposed to alpha radiation at 30 minute intervals with 60 minutes 330 K annealing after each exposure. GeSb2 exposed to alpha radiation at 40 minute intervals with same annealing procedure with the third exposure being 50 minutes. Three GeSb1 points exposed to alphas for 180 minutes then annealed at 330 K for 60 minutes.

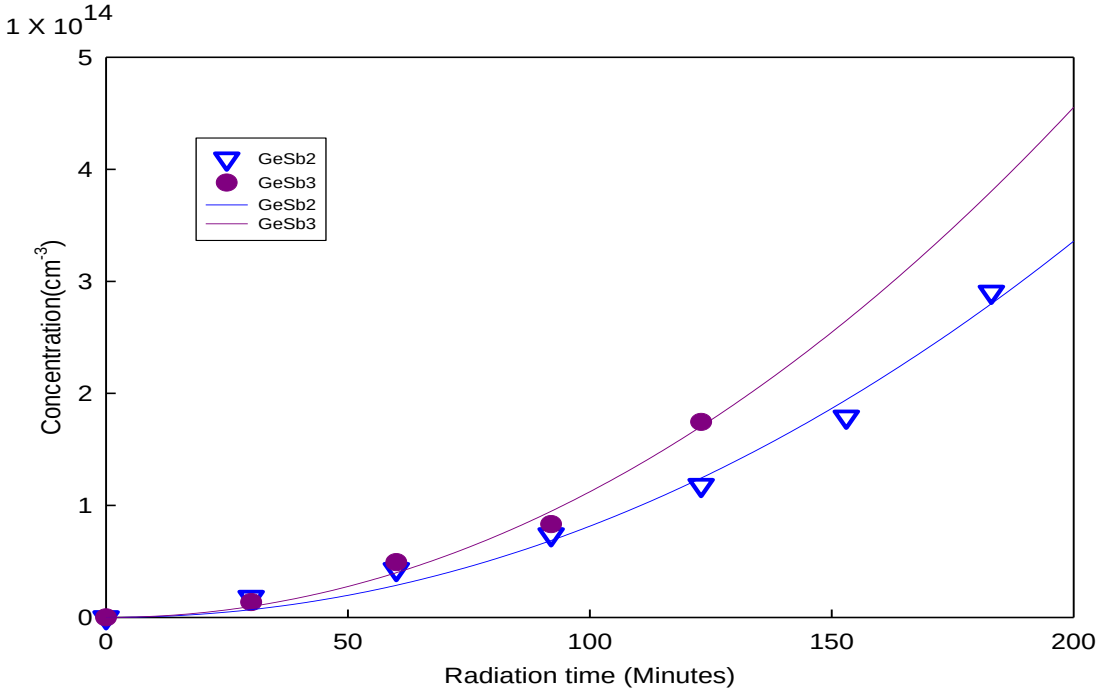

Figure 3. The concentration of the simultaneous introduction of $E'_{0.37}$ and $E_{0.37}$ in the samples GeSb2 and GeSb3 which were exposed to AM-241 at intervals of 30 minutes.

3.3 Annealing behaviour of $E_{0.37}$ and $E'_{0.37}$

This annealing behaviour of the $E'_{0.37}$ peak that is observed through Laplace DLTS was reconfirmed by exposing one of the germanium samples to alpha radiation and immediately doing isothermal annealing measurements on it. It was found that the annealing behaviour at room temperature (300K) was described as exponential decay to a constant concentration. This is consistent with first order decay of the first component with a second component remaining. This annealing behaviour was also confirmed in figure 4 at temperatures of 315 K and 330 K where exponential decay with greater decay constants were observed. We will refer to the component that anneals out in this first stage as the $E'_{0.37}$ defect. Annealing at 330 K for 60 minutes has been found to guarantee the removal of the $E'_{0.37}$ for experimental purposes. Only once the sample was exposed to temperatures greater than 400 K which is seen in isochronal annealing's in figure 5, did the rest of the $E_{0.37}$ peak that is observed in Laplace DLTS anneal away.

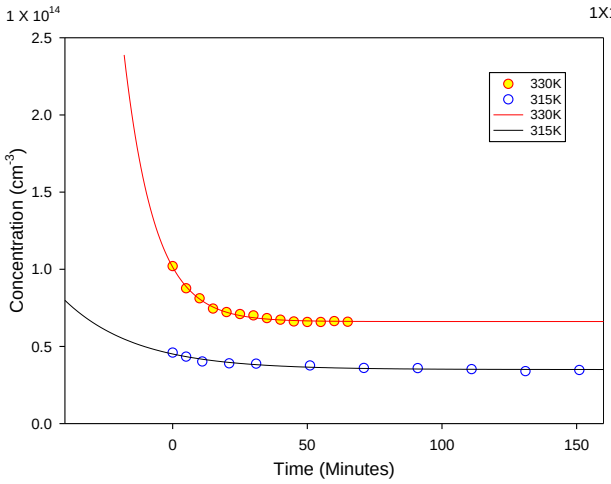

Figure 4. Isothermal annealing of the $E'_{0.37}$ defect at 315 K and 330 K.

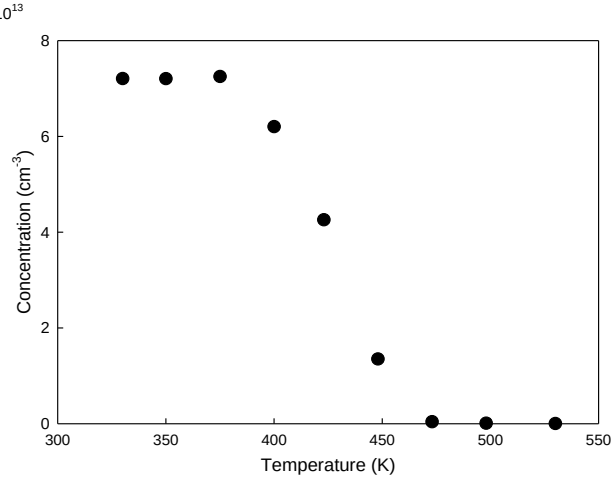

Figure 5. Isochronal annealing of the $E_{0.37}$ defect at time intervals of 15 minutes at 25 K increments.

4. Conclusion

It was found that the two defects $E'_{0.37}$ and $E_{0.37}$ cannot be distinguished through DLTS or through high resolution techniques such as L-DLTS. The introduction kinetics of the $E_{0.37}$ was found to be linear and the introduction kinetics of the $E'_{0.37}$ was found to be quadratic. The annealing of both the $E_{0.37}$ and $E'_{0.37}$ through isochronal annealing was found to exhibit exponential decay. The $E'_{0.37}$ anneals out first at temperatures as low as room temperature with the $E_{0.37}$ which experiences annealing at temperatures greater than 400K. Since the introduction rate of the $E_{0.37}$ is linear it is consistent with the theory of vacancies captured by Sb. The quadratic nature of the $E'_{0.37}$ suggests the reaction of newly introduced defects with previously introduced defects through radiation. A possible theory that will still need to be investigated through density functional theory would be that there may be a self-interstitial captured by the E centre defect which is then seen as the $E'_{0.37}$ defect.

5. References

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