Lattice location and stability of implanted Cu in Ge

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Abstract

We report on emission channeling experiments using the radioactive isotope ^{67}Cu implanted into single crystalline *i*-Ge at a dose of $2.4 \times 10^{12} \text{ cm}^{-2}$. The lattice location of ^{67}Cu was determined from the angular-dependent β^- emission yield, which was measured by means of a position-sensitive detector around the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. We find that already in the as-implanted state a considerable fraction of Cu (20-25%) occupies ideal substitutional lattice positions, a similar fraction is located on positions that are displaced around 0.5-0.6 Å from substitutional sites. Following annealing at 300°C for 10 min, the substitutional fraction of implanted Cu increased to 45% while the fraction of displaced Cu decreased to 23%. Upon further annealing at 400°C, channeling effects disappeared completely and around 10% of ^{67}Cu diffused out of the Ge sample. From this we can estimate the activation energy for dissociation of substitutional Cu to be around 1.6-1.9 eV.

Keywords: Ge, Cu, lattice location, emission channeling

Cu in Ge represents the prototype case of the so-called Frank-Turnbull or dissociative diffusion mechanism [1]. This diffusion mechanism assumes that a substitutional impurity atom is ejected into the interstitial region, followed by fast interstitial migration until it is trapped again by a vacancy. Possible candidates for dissociative diffusion are foreign atoms whose interstitial solubility is low but whose interstitial diffusivity very high, while their substitutional diffusivity is very low and their substitutional solubility moderate to high. The hypothesis by Frank and Turnbull regarding the Cu diffusion in Ge was confirmed by various authors with increasing experimental accuracy [2-5]. A striking consequence of the Frank-Turnbull diffusion mechanism is that the substitutional Cu-concentration in intrinsic Ge effectively maps the Ge vacancy profiles and can hence be used to extract information on the diffusivity and solubility of the Ge vacancy [5]. While the dissociative mechanism was able to consistently explain the phenomenology of Cu diffusion in Ge, one of its basic assumptions, the substitutional incorporation of Cu, has not yet been verified directly. However, Cu was found to act as a triple acceptor in Ge [6], and it is generally accepted that this is due to isolated substitutional Cu [6-9].

We report here on direct lattice location experiments of implanted radioactive ^{67}Cu in Ge by means of the emission channeling technique. Previously, we have used this method to investigate the lattice sites of implanted Cu in Si [10-12]. The sample was an undoped *i*-Ge single crystal with a $\langle 111 \rangle$ surface, resistivity $>30 \text{ } \Omega\text{cm}$, etch pit density $<5000 \text{ cm}^{-2}$, from Eagle Picher Technologies. Room temperature 60 keV implantation of ^{67}Cu up to a fluence of $2.4 \times 10^{12} \text{ cm}^{-2}$ was done at CERN's on-line isotope separator ISOLDE under an angle of 7° to the surface normal. These implantation parameters result in a mean Cu depth profile of 315(160) Å with a maximum concentration around $6 \times 10^{17} \text{ cm}^{-3}$. The isotope ^{67}Cu ($t_{1/2}=61.9 \text{ h}$) decays into stable ^{67}Zn via the emission of β^- particles, the emission yield of which was measured as a function of angle towards different crystallographic directions using a position-sensitive Si detector.

Simulations of emission channeling patterns were done with the manybeam formalism with a number of 16 beams. We used a lattice constant of 5.657 Å and Ge room temperature root mean square displacements (rms) of 0.066 Å. Characteristic two-dimensional patterns of electron emission yield were calculated for substitutional (S), tetrahedral interstitial (T), hexagonal interstitial (H), bond center (BC), anti bonding (AB), split $\langle 100 \rangle$ (SP) and the so-called Y and C sites, as well as $\langle 111 \rangle$ and $\langle 100 \rangle$ displacements between these sites. Quantitative information on the occupied sites was obtained by comparing the fit of simulated patterns to the observed yields. More details on the experimental setup, the simulation calculations, the considered sites, and the data analysis procedures are given in Refs. [10-12].

We first tried to fit all experimental patterns by allowing only, besides random sites, for a single fraction of ^{67}Cu , either on substitutional sites, varying its rms displacement, or on near-substitutional sites displaced along the $\langle 111 \rangle$ or $\langle 100 \rangle$ directions. However, we obtained substitutional or near-substitutional fractions and displacements (either static or rms) that differed by more than a factor of three among the three different crystal

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directions. Only upon allowing for Cu on both ideal substitutional sites and displaced substitutional positions the resulting fractions showed better consistency and, moreover, the chi square of fit improved by up to 10%. As an example, Figs. 1 (a), (b) and (c) show the measured β^- emission yields in the vicinity of the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, following room temperature implantation and annealing up to 300°C. The fact that channeling is observed along all major axes and planes is clear evidence that a large fraction of Cu atoms is located on or near substitutional sites. The best fit results are shown in Figs. 1 (d), (e) and (f), and correspond to 46%, 35% and 54% of Cu atoms on ideal substitutional sites with rms displacements of 0.066 Å, and 16%, 28% and 25% on sites that are halfway in between substitutional and bond center sites, and the remainder on random sites. However, the identification of the second component as being displaced along $\langle 111 \rangle$ from S to BC is not unique. Other positions that have a similar displacement around 0.5-0.6 Å from the S site, e.g., midway between S and AB sites or close to the split $\langle 100 \rangle$ SP position might be involved as well. Although we explored the possibility of Cu on well-defined interstitial sites such as T or H, we found no indication and estimate possible fractions to be lower than 5%.

Fig. 2 summarizes the lattice location results obtained in the as-implanted state and following 10-min annealing steps at 100°C, 200°C, 300°C and 400°C under vacuum. In all cases the patterns were fitted allowing only for fractions on ideal S sites, on sites midway between S and BC (abbreviated in the following as "near-S"), and on random sites. As can be seen from the figure, in the as-implanted state S and near-S sites are both occupied with fractions around 20-25% each. Following annealing to 100°C and 200°C both fractions increase somewhat to around 33-38%, while upon annealing at 300°C the fraction on S sites grows further to 45% while the fraction on near-S sites decreases to 23%. Finally, the 400°C anneal step resulted in the complete vanishing of all channeling effects and was accompanied by the outdiffusion of roughly 10% of the ^{67}Cu probe atoms from the sample.

In order to interpret the substitutional and near-substitutional sites of Cu and their annealing behaviour, we propose the following scenario. While Cu on ideal S sites most likely represents Cu atoms inside a single vacancy, the near-substitutional Cu is suggested to be due to Cu in more extended vacancy-like complexes such as divacancies. The initial increase of both fractions around 100-200°C results from the general annealing of implantation damage, which restores the crystalline quality of the lattice to a large extent. Around 300°C the extended vacancy-like defects start to dissolve, resulting in a higher fraction of ideal substitutional Cu. While this scenario is similar to the case of Cu in Si [10-12] and also to Ag in Si [13], there is a major difference: in Si Cu on ideal substitutional sites was only observed in highly *n*-doped material [12]. We note that our model supports the suggestion of Kamiura et al, who proposed, based on resistivity and Hall effect measurements performed after quenching Ge from 800°C, that a complex of substitutional Cu and an additional vacancy in Ge transforms into ideal substitutional Cu between 200-300°C with an activation energy of 1.3 eV [14].

We can estimate an upper boundary for the activation energy E_a for dissociation of the *ideal* substitutional Cu defects using a one-step Arrhenius model, as described in Ref. [11], which neglects the possible influence of Cu being retrapped at S sites. Using a detection limit of 0.05 for the fraction of Cu remaining on substitutional sites following the 400°C anneal, we derive a dissociation energy of 1.9 eV. As was also outlined in Ref. [11], taking into account Cu retrapping at vacancies from the implantation damage (roughly 1100 vacancies per implanted Cu atom) in the model yields a lower boundary for E_a , around 1.6 eV for Ge. Bracht et al have reported [4] that the effective diffusivity D_{eff} of Cu in Ge due to the dissociative mechanism can be interpolated by $D_{\text{eff}} = 5.5 \text{ cm}^2 \text{ s}^{-1} \exp[-1.55 \text{ eV/kT}]$. The apparent activation energy for diffusion in their formula is hence somewhat smaller than our estimate of the activation energy for dissociation of the ideal substitutional Cu defects.

Summarizing, we have found clear evidence that a large fraction of implanted Cu atoms is found on substitutional sites following annealing at 300°C. The activation energy for the dissociation of ideal substitutional Cu is estimated to be around 1.6-1.9 eV. We also observed Cu on displaced substitutional sites, which showed lower thermal stability and started to disappear above 200°C already.

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Fig. 1: Angular dependent β^- emission yields from ^{67}Cu in Ge around the $\langle 111 \rangle$ (a), $\langle 100 \rangle$ (b) and $\langle 110 \rangle$ (c) direction following annealing at 300°C. Panels (d), (e) and (f) are best fits to the experimental patterns, considering contributions from Cu on ideal S sites, sites midway between S and BC positions, and random sites (as described in the text).

Fig. 2: Fractions of Cu on ideal substitutional (S) and near-substitutional (near_S) sites and the sum of both in the as-implanted state and following 10-min annealing steps.