Lattice location of implanted Cu in highly doped Si

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We report on the lattice location of ion-implanted ^{67}Cu in p^+ - and n^+ -Si using the emission channeling technique. Following room-temperature implantation, the majority of Cu was found on near-substitutional sites in both p^+ - and n^+ -Si. Annealing in the temperature range 200-600°C resulted in changes of near-substitutional Cu to random sites in p^+ -Si, while in n^+ -Si all of the near-substitutional Cu was converted to ideal substitutional lattice sites. The activation energy for dissociation is estimated to be 1.7-2.0 eV for near-substitutional Cu in p^+ -Si and 2.9(2) eV for ideal substitutional Cu in n^+ -Si.

Cu and the other 3d transition metals Fe, Ni and Co may severely harm the performance of Si-based electronic circuits [1,2], acting as deep centers which reduce the lifetime of charge carriers and increase junction leakage. In order to remove the transition metals from the active regions of devices, various gettering procedures have been developed. Among these are the so-called intrinsic or internal gettering by O-related precipitates [3], gettering at implantation damage sites [4-6] or within voids [7,8], segregation gettering in heavily n^+ - or p^+ -doped regions [5,9,10], or gettering by P diffusion via the POCl_3 or PBr_3 processes [4,8,11].

In the case of Fe the formation of pairs between interstitial Fe_i^+ and substitutional B^- provides an efficient gettering mechanism in p^+ -doped regions [5]. On the other hand, $(\text{Cu}_i^+\text{B}^-)$ pairs are unstable at room temperature and p^+ -doped regions represent poor gettering sites for Cu [10]. In contrast to interstitial Cu, which acts as a fast-diffusing shallow donor, it has been suggested that substitutional Cu should form a triple acceptor [9]. This was mainly based on the observation that the solubility of Cu in n^+ -Si is greatly enhanced with respect to intrinsic material [9]. Meek and Seidel have given a theoretical description of the Cu solubility enhancement in n^+ -Si [11], predicting that in thermal equilibrium all Cu atoms should be bound in $(\text{Cu}^{3+}\text{P}^-)$ pairs with Cu and P atoms on neighboring substitutional sites. Using the Rutherford backscattering/channeling technique, it was found that up to 90% of Cu atoms gettered after phosphorus diffusion by means of the PBr_3 process were aligned with the Si $\langle 110 \rangle$ axis [4], indicating the formation of substitutional Cu.

We have shown recently by means of β^- emission channeling that ion implanted ^{67}Cu occupies near-

substitutional sites in low and moderately doped p - and n -Si [12,13]. The study of possible lattice sites of Cu in highly doped material may aid in further understanding its gettering mechanisms, and in this letter we report on the lattice location of implanted Cu in p^+ - and n^+ -Si.

Si samples were implanted with 60 keV ^{67}Cu ($t_{1/2}=61.9$ h) ions at CERN's on-line radioactive isotope separator facility ISOLDE. Three Si single crystals were investigated, one p^+ -type B-doped Czochralski (CZ) grown sample (resistivity 0.002 Ωcm , $\langle 100 \rangle$ surface, implanted ^{67}Cu dose $3.3 \times 10^{12} \text{ cm}^{-2}$, sample A), and two n^+ -type As-doped CZ crystals ($<0.001 \Omega\text{cm}$, $\langle 111 \rangle$, $1.3 \times 10^{12} \text{ cm}^{-2}$ in sample B and $1.6 \times 10^{12} \text{ cm}^{-2}$ in sample C). Emission channeling [14] makes use of the fact that charged particles emitted from radioactive isotopes in single crystals experience channeling or blocking effects along low-index crystal directions. This leads to an anisotropic particle emission yield from the crystal surface which depends in a characteristic way on the lattice sites occupied by the emitter atoms and is recorded by means of a position sensitive detector. Channeling patterns were extracted from the β^- energy window 93-577 keV. Corrections for electrons backscattered into the detector were implemented by subtracting a flat background from every pattern. In contrast to Refs. [12,13], where we estimated a count rate increase by a factor of 1.31 from empirical relations for backscattered electrons from a semi-infinite Si substrate, we have now quantified the backscattering contribution by means of Monte Carlo electron scattering simulations using the EGS4 code [15]. These simulations take into account the relevant elemental composition and main geometrical features of the sample, the Mo sample holder and the stainless steel vacuum chamber, thus giving a more realistic description of

Figure 1[†]: (a), (b), (c): Normalized emission yields of the integral β^- intensity in the vicinity of $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions following room temperature implantation of ^{67}Cu into $n^+\text{-Si:As}$ (sample C) and annealing at 300°C . (d), (e) and (f) are best fits of simulated patterns to the experimental yields, corresponding to 92%, 94%, and 86% of emitter atoms on sites which are displaced by $0.50 \text{ \AA}$ from the S towards the BC position.

the background (count rate increase ≈ 1.50). The fraction of Cu atoms assigned to random lattice sites ($>20\%$) in Refs. [12,13] was thus found to be somewhat overestimated due to an underestimation of the background contribution. More details on the sample production, channeling measurements and data analysis procedures can be found in Refs. [12,13].

Figure 1 (a-c)[†] shows the emission channeling patterns from the $n^+\text{-Si:As}$ sample C following annealing at 300°C . In order to identify the occupied Cu sites, the experimental channeling data are fitted by simulated patterns. We have considered substitutional (S), tetrahedral interstitial (T), hexagonal (H), bond center (BC), anti bonding (AB), split $\langle 100 \rangle$ (SP) and the so-called Y and C sites, as well as various $\langle 111 \rangle$ and $\langle 100 \rangle$ displacements between these sites [12]. The best two-fraction fit results are shown in Fig. 1 (d-e),[†] giving evidence for 91(4)% of Cu on near-substitutional sites with a most probable displacement of $0.50 \text{ \AA}$ from the S site towards the BC site, and the remainder from random (R) sites. The near-S sites are identical to the Cu lattice positions in low-doped p - and n -Si [12,13]. However, upon annealing this sample to 600°C the emission channeling patterns changed markedly [Fig. 2 (a-c)[†]]. The most striking difference is that the normalized yield along the axial directions increased by a factor of 2-3 with respect to unity, which can only be explained by a more perfect substitutional incorporation of Cu atoms in the Si lattice. Considering only one lattice site in addition to random sites, best fit results were obtained for substitui-

Figure 2[†]: (a), (b), (c): Channeling patterns following annealing of the $n^+\text{-Si:As}$ sample C at 600°C . (d), (e) and (f) are best fits of simulated patterns to the experimental yields with 82%, 85% and 90% on ideal S and 10%, 15% and 8% on displaced S sites.

tional sites with a root mean square (rms) displacement of $u_1(\text{Cu})=0.09(2) \text{ \AA}$. The fitted Cu rms displacement is hence comparable to the room temperature vibration amplitude of Si, $u_1(\text{Si})=0.080 \text{ \AA}$ [16], which shows that the Cu atoms occupy more or less ideal S sites. Allowing also for a fraction on displaced S sites, the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ patterns were fitted best by 82%, 85% and 90% on ideal S sites, 10%, 15% and 8% on displaced S sites, and the remainder on R sites [Fig. 2 (d-f)[†]].

Figure 3[†] shows the near-substitutional and substitutional fractions of Cu as a function of annealing temperature. In contrast to the highly doped samples A, B and C, sample D ($p\text{-Si:B}$ CZ, $0.17\text{-}0.23 \text{ }\Omega\text{cm}$, implanted dose $2.2 \times 10^{12} \text{ cm}^{-2}$) and sample E ($n\text{-Si:P}$ CZ, $0.09 \text{ }\Omega\text{cm}$, $3.6 \times 10^{12} \text{ cm}^{-2}$) are typical for lower-doped p - and n -Si. Note that the experimental data from samples D and E [12,13] have been reanalyzed taking into account the improved background correction.

Following room temperature implantation and annealing up to 200°C , similar behavior is observed in all investigated types of Si. Around 80-95% of Cu atoms are found on displaced S sites. The fraction on ideal S sites is small and only shown for the $n^+\text{-Si:As}$ samples B and C. In the lower-doped samples D and E and the highly p -doped sample A, Cu begins to change to random lattice sites for annealing temperatures above 200°C , the near-S fractions decreasing continuously. In the highly n -doped samples B and C, on the other hand, the near-S fraction of Cu is stable up to 400°C , and then Cu on ideal S sites grows in. Following annealing at 600°C , the near-S fraction is almost completely converted to Cu on ideal S sites. Eventually, in all types of Si a drop in the β^- count rate by roughly

Figure 3[†]: Fractions of Cu atoms on near-substitutional (S→BC) and ideal substitutional lattice sites as a function of isochronal (10 min) annealing temperature.

a factor of two was observed, which is characteristic for long-range diffusion of Cu and caused by β^- particles being stopped in the bulk of the Si crystals [13]. However, while this effect occurred in the lower-doped samples D and E only after the annealing step at 600°C and in n^+ -Si after 800°C, the p^+ -sample showed long-range diffusion already following annealing at 400°C. We have estimated the activation energy for dissociation of the Cu-related defects using an Arrhenius model [13]. For near-S Cu we obtain 1.7-2.0 eV in p^+ -Si and 1.8-2.2 eV in moderately doped Si, while the dissociation energy of ideal substitutional Cu in n^+ -Si is 2.9(2) eV.

As previously discussed [13] and also supported by theory [17], we believe that the near-S Cu is related to Cu in multi-vacancy complexes, e.g., divacancies. This interpretation takes into account that single vacancies from the implantation are highly mobile at room temperature, forming either clusters or complexes with other impurities [18], and that Cu is preferentially trapped in vacancy-rich regions [6]. The fact that we observe the same lattice sites in both n - and p -type material as well as O-lean FZ and O-rich CZ Si [13], indicates that neither dopant nor O atoms are required to form near-S Cu. With respect to the incorporation of Cu on ideal S sites in n^+ -Si: As two scenarios seem likely. Firstly, the multi-vacancy complexes partly anneal around 600°C, leaving Cu in a single vacancy. The absence of ideal substitutional Cu in lower-doped n -Si and in p -Si would then imply that Cu within a mono-vacancy is only stable if the Fermi level is close to the conduction band. Secondly, Cu on undisplaced S sites is due to pairing with substitutional As donors, as was suggested by Meek and Seidel for (CuP) pairs [11]. This scenario requires either the substitutional diffusion of Cu towards As dopants or of interstitial Cu towards vacancy-As (VAs) pairs. (VAs) pairs, however, are reported to be unstable above 180°C [18].

Finally let us discuss the implications with respect to Cu gettering. Our results suggest that Cu is trapped at vacancy-related defects in all doping-types of Si, hence these reactions may play a role in those gettering techniques where vacancies are abundant, e.g., gettering by implantation-related defects or via the POCl₃ process. On the other

hand, the stability of Cu in vacancy-related defects is lowest in p^+ -Si, intermediate in moderately doped Si, and highest in n^+ -Si, where Cu can be trapped on ideal substitutional lattice sites. In conclusion, radiation damaged n^+ -Si may offer the most effective gettering sites for Cu. It has been observed recently by transmission electron microscopy that the gettering of Cu in n -type Si is accompanied by the formation of copper-silicide precipitates [10]. The enhanced Cu precipitation in n -type Si was explained by the formation of precipitates that are negatively charged or neutral in n -Si, hence attracting interstitial Cu_i^+ , but positively charged in p -Si [19,10]. We would like to point out that acceptor-like substitutional Cu_s^{n-} should form efficient nucleation centers for the precipitation of Cu_i^+ atoms. Hence the formation of Cu_s^{n-} can provide a supplementary mechanism in order to enhance Cu precipitation in n -type Si.

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- [1] A. Istratov and E.R. Weber, Appl. Phys. A 66, 123 (1998).
- [2] A.A. Istratov and E.R. Weber, Appl. Phys. A 69, 13 (1999).
- [3] B. Shen, T. Sekiguchi, J. Jablonski, and K. Sumino, J. Appl. Phys. 76, 4541 (1994).
- [4] T.E. Seidel and R.L. Meek, in Ion Implantation in Semiconductors and Other Materials, edited by B.L. Crowder, Plenum Press, New York (1973) p. 305.
- [5] J.L. Benton, P.A. Stolk, D.J. Eaglesham, D.C. Jacobson, J.Y. Cheng, J.M. Poate, N.T. Ha, T.E. Haynes, and S.M. Myers, J. Appl. Phys. 80, 3275 (1996).
- [6] S. Koveshnikov and O. Kononchuk, Appl. Phys. Lett. 73, 2340 (1998).
- [7] S.M. Myers and D.M. Follstaedt, J. Appl. Phys. 79, 1337 (1996).
- [8] V. Raineri, Sol. St. Phenomena 57-58, 43 (1997).
- [9] R.N. Hall and J.H. Racette, J. Appl. Phys. 35, 379 (1964).
- [10] A.A. Istratov, C. Flink, H. Hieslmair, S.A. McHugo, and E.R. Weber, Mater. Sci. Eng. B 72, 99 (2000).
- [11] R.L. Meek and T.E. Seidel, J. Phys. Chem. Solids 36, 731 (1975).
- [12] U. Wahl, J.G. Correia, A. Vantomme, G. Langouche, and the ISOLDE collaboration, Physica B 273-274, 367 (1999).
- [13] U. Wahl, J.G. Correia, A. Vantomme, G. Langouche, and the ISOLDE collaboration, Phys. Rev. Lett. 84, 1495 (2000).
- [14] H. Hofsäuss and G. Lindner, Phys. Rep. 210, 121 (1991).
- [15] W.R. Nelson, H. Hirayama and D.W.O. Rogers, The EGS4 Code System, SLAC-Report-265, Dec. 1985; <http://www.slac.stanford.edu/pubs/slacreports/slac-r-265.html>
- [16] L.V. Hau, E. Lægsgaard, and J.U. Andersen, Nucl. Instr. Meth. B 48, 244 (1990).
- [17] S.K. Estreicher, Phys. Rev. B 60, 5375 (1999).
- [18] G. Watkins, in Deep Centers in Semiconductors, edited by S.T. Pantelides, Gordon and Breach, New York (1986) p. 147.
- [19] A.A. Istratov, H. Hedemann, M. Seibt, O.F. Vyvenko, W. Schröter, T. Heiser, C. Flink, H. Hieslmair, and E.R. Weber, J. Electrochem. Soc. 145, 3889 (1998).

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