Lattice location of implanted Cu in Si

U. Wahl^{a*}, J.G. Correia^b, A. Vantomme^a, G. Langouche^a, and the ISOLDE collaboration^b

^aInstituut voor Kern- en Stralingsfysica, University of Leuven, B-3001 Leuven, Belgium

^bCERN-EP, CH-1211 Geneva 23, Switzerland

Abstract

We have implanted the radioactive probe atom ^{67}Cu ($t_{1/2}=61.9$ h) into single-crystalline Si. Monitoring the β^- emission yield from the decay of ^{67}Cu to ^{67}Zn as a function of angle from different crystallographic directions allows to determine the lattice location of the Cu atoms by means of the emission channeling effect. We give direct evidence that the majority of implanted Cu occupies near-substitutional sites. As most-likely lattice location we suggest a displacement of $0.51(7)$ Å along $\langle 111 \rangle$ directions from substitutional sites to bond center positions. The annealing behavior shows that near-substitutional Cu is remarkably stable, and we estimate a dissociation energy of $2.2(3)$ eV.

Keywords: Cu in Si, lattice location, implantation, gettering

Introduction

Cu represents a widespread contaminant in Si processing [1] and is responsible for several deep levels [2]. These deep levels act as recombination centers for electrons and holes, and hence are usually detrimental for the performance of electronic devices. Since Cu is also the fastest interstitial diffuser in Si (migration energy $E_m=0.18$ eV) [3] with a very low intrinsic room temperature solubility, it shows a strong tendency to precipitate or to react with various defects (cf. Ref. [1] and references therein). Among these are acceptors, and damage-related centers such as divacancies [4], dislocations, implantation defects, or voids [5]. The binding of Cu to these defects may be used beneficially in order to getter Cu within regions away from the active region of electronic devices.

The basic knowledge on the lattice sites of Cu in Si is very poor [1], despite its significance as a deep impurity and its technological role as potential contaminant in Si processing. Theory [6-8] as well as analogies to the other $3d$ and IB metals in Si [9, 10] and to Cu in Ge [11, 12] suggest that both tetrahedral interstitial and substitutional Cu may exist. Electron paramagnetic resonance (EPR) [13] and photoluminescence (PL) [14] have been able to detect a number of Cu related signals with less than cubic symmetry which are supposed to be due to Cu-Cu pairs. *Direct* lattice location techniques such as ion beam channeling cannot be applied at low Cu concentrations, and at higher concentrations Cu forms precipitates.

In this contribution we report on first results of β^- emission channeling [15] lattice location experiments using the radioactive isotope ^{67}Cu ($t_{1/2}=61.9$ h) implanted into single-crystalline Si. The β^- particles emitted during the decay from ^{67}Cu to ^{67}Zn (maximum energy 577 keV) experience channeling effects along major crystal axes and planes. Monitoring the angular-dependent β^- emission yield by means of a position-sensitive electron detector as a function of angle from $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions allows to directly determine the lattice location of ^{67}Cu .

Method

Clean beams of 60 keV radioactive Cu isotopes are available from newly developed laser ion sources at CERN's on-line isotope separator ISOLDE [16]. Implantations of ^{67}Cu into an n -Si:P float zone (FZ) grown single crystal (resistivity 700-1300 Ωcm , $\langle 111 \rangle$ orientation, implanted dose $3.8 \times 10^{12} \text{ cm}^{-2}$) were done at room temperature, under 7° towards the surface normal of the sample and using a 1 mm beam spot. A position-sensitive Si detector was used in order to detect the emitted β^- particles. The same detection system was already applied in our previous experiments on the lattice location of rare earths in Si, and is described in more detail in Refs. [17, 18]. Emission channeling patterns were extracted for the integral energy range from 97 keV to 600 keV. The value of 97 keV has been chosen as lower boundary in order to exclude the 84 and 92 keV conversion electrons emitted from the well-known 9.2 μs Mössbauer state in ^{67}Zn , which is populated from the ^{67}Cu decay.

In order to deduce the Cu lattice location from the β^- emission patterns we have carried out computer simulations of β^- emission yields, based on the dynamical theory of electron diffraction [15]. To approximate the continuous β^- energy spectrum of ^{67}Cu , simulations were done for electron energies from 100 keV to 550 keV in steps of 25 keV, and the results were averaged according to the theoretical spectral β^- distribution. We calculated characteristic two-dimensional patterns of electron emission probability within a range of $\pm 3^\circ$ around the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in steps of $\Delta x = \Delta y = 0.05^\circ$. Due to limitations in computing time, however, we had to restrict ourselves to lattice

sites with trigonal or tetragonal symmetry, and we 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 (Fig. 1), as well as various $\langle 111 \rangle$ and $\langle 100 \rangle$ displacements between these sites. Quantitative information on the occupied sites was then obtained by comparing the fit of simulated patterns to the observed yields. The fit procedures used for this purpose have been discussed earlier [18].

Fig.1. High-symmetric lattice sites in Si. Cubic symmetry: S=substitutional, T=tetrahedral interstitial; trigonal symmetry: BC=bond center, AB=anti-bonding, H=hexagonal; tetragonal symmetry: SP=split $\langle 100 \rangle$, Y=so-called Yb sites, and C so called C-sites.

Results and discussion

Figs. 2 (a), (b) and (c) show the normalized β^- emission yields measured in the vicinity of the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions following room temperature implantation of ^{67}Cu and annealing for 10 min at 100°C, 150°C and 200°C. An enhancement of β^- emission yield is visible along all of the axial directions, and also along the $\{111\}$ and $\{110\}$ planes. This proves that the majority of Cu is located close to substitutional sites, leading to channeling of emitted β^- particles along the closest-packed axial and planar directions. While $\{100\}$ planar channeling in Si is usually not very pronounced (a few per cent above unity), in our case we even observe an electron emission yield below unity along the $\{100\}$ planes. This gives evidence that the Cu atoms exhibit a significant displacement from ideal substitutional lattice sites.

More specific information on the occupied lattice sites is obtained by fitting the experimental yields with theoretical patterns. Figs. 3 (a)-(c) show the calculated yields for 100% of emitter atoms on ideal S sites, assuming a root mean square (rms) thermal vibration amplitude of $u_1=0.079$ Å for the Cu atoms. For a fraction of 20% of emitter atoms on S sites and 80% on random sites these patterns reproduced most of the general features of the experimental yields shown in Figs. 2 (a)-(c). Note that random sites are sites which cause an isotropic emission yield, for instance sites of very low crystal symmetry or in heavily damaged surroundings. However, the quality of fit considerably improved by introducing displacements from ideal S sites. The best fits, assuming a single Cu lattice site in addition to random sites, are shown in Figs. 2 (d), (e) and (f) and correspond to 70%, 62% and 76% of emitter atoms displaced from ideal S sites by 0.51(7) Å along $\langle 111 \rangle$ directions towards the bond center positions. The decrease in the chi square of fit, χ^2 , compared to S sites was significant (20-40%). We also tried $\langle 100 \rangle$ displacements from S to SP (S $\rightarrow$ SP) and $\langle 111 \rangle$ displacements from S to AB (S $\rightarrow$ AB) sites. In the case of S $\rightarrow$ SP a local minimum of χ^2 was found for a distance of 0.41 Å from the S site, but the absolute χ^2 values were up to 32% worse than for S $\rightarrow$ BC. Since the $\langle 111 \rangle$ and $\langle 100 \rangle$ channeling patterns for S $\rightarrow$ BC and S $\rightarrow$ AB sites are identical, only the $\langle 110 \rangle$ pattern could be used in order to test for S $\rightarrow$ AB displacements. While a local minimum was found for a displacement around 0.51 Å from S to AB, the χ^2 values were 19% worse than for S $\rightarrow$ BC, and hence Cu on S $\rightarrow$ AB sites is less likely. We

also considered Gaussian distributions of Cu atoms centered at the S sites. For an rms displacement of $u_1=0.40$ Å, these were also in agreement with the experimental data, so that an ensemble of Cu atoms with small but varying displacements from S sites can not be ruled out.

Fig. 2. (a), (b) and (c): β^- channeling patterns following room temperature implantation of $3.8 \times 10^{12} \text{ cm}^{-2}$ of ^{67}Cu into $n\text{-Si:P}$ FZ and annealing at 200°C . Shown are normalized emission yields from the integral β^- intensity in the vicinity of $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. (d), (e) and (f) are best fits of simulated patterns to the experimental yields, corresponding to 70%, 62%, and 76% of emitter atoms on sites which are displaced by 0.51 Å from the S site towards the BC site.

On the other hand, major fractions of Cu on sites with displacements from the substitutional position larger than 0.6 Å were all clearly not in accordance with the experimental data. As an example we show the patterns due to the bond center positions [Figs. 3 (d)-(f)], which are located at 1.17 Å from the S sites. Finally we also investigated the possibility that, besides the near-substitutional Cu fraction, additional smaller fractions might be located on other high-symmetric sites. However, only the fits where we considered a combination of near-S sites and bond centered sites were compatible with the experimental data, indicating that a substantial part of the random fraction might be due to the occupancy of BC sites. Since the channeling patterns from BC sites are generally weak [Figs. 3 (d)-(f)], an unambiguous identification of such a BC fraction will require measurements with improved statistics, though. In summary, we consider it most likely that the majority of Cu [69(6)%] is located at a position around 0.4 - 0.5 times the distance from S to BC sites, and the remainder on random sites. However, since we did not test these sites, we can not exclude that the ~ 0.51 Å displacement occurs along other crystal directions such as $\langle 110 \rangle$ or $\langle 211 \rangle$, leading to a lower symmetry than trigonal or tetragonal.

In order to interpret the incorporation of Cu into near-substitutional sites, we have to consider the defect situation following ion implantation, which we have simulated using the MARLOWE code [19]. The mean implantation depth of $60 \text{ keV } ^{67}\text{Cu}$ in Si is 494 Å with a straggling of 186 Å. The simulations indicate that around 800 vacancies are created for every implanted Cu atom, and that the mean distance to the nearest vacancy is less than 5 Å. Hence, Cu should have ample possibility to be trapped within vacancy-related defects.

Fig. 3. (a), (b) and (c): Simulated angular-dependent β^- emission yields for 100% of ^{67}Cu atoms on ideal substitutional sites. (d), (e) and (f): Simulated yields for 100% on bond center positions. The angular resolution and orientation have been chosen corresponding to the experimental channeling patterns shown in Fig. 2 (a), (b) and (c).

Fig. 4 shows the isochronal (10 min) annealing behavior of the fraction of Cu on near-S sites for temperatures up to 600°C. Already in the as-implanted state we found 56% of Cu atoms close to substitutional sites. Upon annealing to 200°C, the near-S fraction reached a maximum (cf. Fig. 2), and decreased continuously at higher temperatures along with an increase in the random fraction. Since the implantation damage, which is to some extent responsible for the random Cu fraction, decreases with increasing annealing temperature, the growth of the random Cu fraction must be associated with either a change in the local surroundings, or with Cu atoms changing to lattice sites of lower symmetry. A direct proof that Cu lattice site changes are involved, comes from the fact that following the anneal step at 600°C, the β^- count rate dropped by a factor of two. Since there was no detectable contamination outside the sample, we conclude that the radioactive Cu must have diffused throughout the bulk of the crystal. Assuming that the dissociation of Cu from near-substitutional sites follows an Arrhenius behavior with an attempt frequency of the order of the lattice vibrations ($\sim 10^{12}$ Hz), we estimate an activation energy of 2.2(3) eV for this process. This compares to the thermal stability of high-dose Cu implants into single-crystalline Si (> 2.2 eV), Cu in Cu_3Si precipitates (2.2 eV) and Cu within voids (2.7 eV) [5], but is considerably higher than in amorphous Si, where an activation energy of 1.2 eV has been reported for Cu diffusion [20].

Fig. 4. Isochronal annealing sequence (10 min, measurements at 20°C) for the fraction of ^{67}Cu on near-substitutional sites.

Conclusions

We have given direct evidence that the majority of implanted Cu occupies near-substitutional sites in Si. The displacement from S sites amounts to 0.51(7) Å and occurs most likely along the $\langle 111 \rangle$ directions towards the bond center positions. We suggest that this lattice position is due to Cu within a single or double vacancy. The annealing behavior shows that near-S Cu is remarkably stable, and that the room temperature diffusion of Cu is suppressed once it occupies substitutional sites. This indicates that the formation of substitutional Cu is also involved in the initial stages of the radiation damage gettering mechanism.

Finally, the radioactive isotope ^{67}Cu has been found very suitable for lattice location studies of implanted Cu in semiconductors. Further experiments will be undertaken to study possible influences of doping type, crystal growth mode (FZ, CZ, epitaxial), or additional impurities on the lattice sites and stability of Cu in Si.

This work was partially funded by the TMR-LSF program of the European Union (U.W.) and the FCT and ITN, Portugal, through project CERN/S/FIS/1048/98 (J.G.C.).

References

- [1] A. Istratov and E.R. Weber, Appl. Phys. A 66 (1998) 123.
- [2] S.D. Brotherton, J.R. Ayres, A. Gill, H.W. van Kesteren and F.J.A.M. Greidanus, J. Appl. Phys. 62 (1987) 1826.
- [3] A. Istratov, C. Flink, H. Hieslmair and E.R. Weber, Phys. Rev. Lett. 81 (1998) 1243.
- [4] M.O. Aboelfotoh and B.G. Svensson, Phys. Rev. B 52 (1995) 2522.
- [5] S.M. Myers and D.M. Follstaedt, J. Appl. Phys. 79 (1996) 1337.
- [6] A. Fazzio, M.J. Caldas and A. Zunger, Phys. Rev. B 32 (1985) 934.
- [7] F. Beeler, O.K. Andersen and M. Scheffler, Phys. Rev. B 41 (1990) 1603.
- [8] S.K. Estreicher and J.L. Hastings, Mater. Sci. Eng. B 58 (1999) 155.
- [9] G.W. Ludwig and H.H. Woodbury, Solid State Physics 13 (1962) 223.
- [10] E.R. Weber, Appl. Phys. A 30 (1983) 1.
- [11] F.C. Frank and D. Turnbull, Phys. Rev. 105 (1956) 617.
- [12] R.N. Hall and J.H. Racette, J. Appl. Phys. 35 (1964) 379.
- [13] P.N. Hai, T. Gregorkiewicz, C.A.J. Ammerlaan and D.T. Don, Phys. Rev. B 56 (1997) 4620.
- [14] J. Weber, H. Bauch and R. Sauer, Phys. Rev. B 25 (1982) 7688.
- [15] H. Hofsäss and G. Lindner, Phys. Rep. 210 (1991) 121.
- [16] J. Lettry, R. Catherall, G.J. Focker, O.C. Jonsson, E. Kugler, H. Ravn, C. Tamburella, V. Fedoseyev, V.I. Mishin, G. Huber, V. Sebastian, M. Koizumi, U. Köster and the ISOLDE collaboration, Rev. Sci. Instr. 69 (1998) 761.
- [17] U. Wahl, A. Vantomme, J. De Wachter, R. Moons, G. Langouche, J.G. Marques, J.G. Correia and the ISOLDE collaboration, Phys. Rev. Lett. 79 (1997) 2069.
- [18] U. Wahl, J.G. Correia, S. Cardoso, J.G. Marques, A. Vantomme, G. Langouche and the ISOLDE collaboration, Nucl. Instr. Meth. B 136 (1998) 744.
- [19] M.T. Robinson, Phys. Rev. B 40 (1989) 10717.
- [20] S. Coffa, J.M. Poate, D.C. Jacobson, W. Frank and W. Gustin, Phys. Rev. B 45 (1992) 8355.