Lattice Location and Stability of Ion Implanted Cu in Si

U. Wahl,* A. Vantomme, and G. Langouche
Instituut voor Kern- en Stralingsfysica, University of Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium

J. G. Correia and ISOLDE Collaboration
CERN-EP, CH-1211 Geneva 23, Switzerland

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We report on the lattice location of ion implanted Cu in Si using the emission channeling technique. The angular distribution of β^- particles emitted by the radioactive isotope ^{67}Cu was monitored following room temperature implantation into Si single crystals and annealing up to 600 °C. The majority of Cu was found close to substitutional sites, however, with a significant displacement, most likely 0.50(8) Å along the $\langle 111\rangle$ directions towards the bond center position. The activation energy for the dissociation of near-substitutional Cu is estimated to be 1.8–2.2 eV.

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The behavior of Cu in Si has been studied extensively in the past (for a recent review see Ref. [1]). From the viewpoint of fundamental semiconductor physics this is due to the variety of physical phenomena which are associated with Cu in semiconductors. Positively charged Cu^+ is the fastest interstitial diffuser in Si, with a migration energy of only 0.18 eV [2,3]. At elevated temperatures the intrinsic solubility of Cu is the highest among all transition metals (at 1100 °C, e.g., 9×10^{17} cm^{-3}) [4,5]; the solubility at room temperature is not known but must be very small (0.013 cm^{-3} extrapolated from high temperatures). As a consequence, while Cu is easily introduced into Si, it shows a strong tendency to react with various defects and to precipitate. Interstitial Cu_i^+ acts as a donor and may form pairs with acceptors, hence passivating or compensating them. Cu is also responsible for several deep centers [6], i.e., defects which have energy levels deep in the band gap of Si, acting as traps and recombination centers and limiting the lifetime of excited charge carriers. It was speculated long ago that substitutional Cu_S forms a triple acceptor [4] (hence it might be responsible for three of these deep levels), but at present this is still a matter of debate [1].

Together with Fe, Ni, and Co, Cu is the most common transition metal (TM) trace impurity in the manufacturing of Si devices such as integrated circuits or solar cells. In recent years, Cu is also increasingly used for electrical interconnects on top of advanced microchips [7]. It is clear from its above-mentioned properties that Cu contamination forms a major source of concern in Si processing and must be carefully controlled. This is also true for the other transition metals, which act in many respects similarly to Cu. Therefore, in addition to isolating them from the Si wafer production and processing, the additional strategy was adopted to getter the remaining TM impurities outside the active region of devices. One possibility of gettering is trapping at deliberately created radiation damage sites or within cavities [8].

Despite its fundamental importance as a deep impurity and its technological relevance as a potential contaminant in Si processing, the actual knowledge on the lattice sites of Cu in Si is very poor [1]. Direct lattice location techniques such as ion beam channeling cannot be used at low Cu concentrations, whereas at higher concentrations Cu forms precipitates. In analogy to other $3d$ and group IB metals in Si [5,9,10] and to Cu in Ge [4], both tetrahedral interstitial (T) Cu_T and substitutional (S) Cu_S were suggested, which is also supported by recent Hartree-Fock calculations [11]. While theory has made a number of predictions regarding the electronic properties of isolated Cu impurities on T and S sites in Si [9–11], an unambiguous experimental identification of these defects has not been possible [1].

In this Letter we present the first direct lattice location experiments of Cu in Si. We used the β^- emission channeling technique [12], which 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 emission yield from the crystal surface which depends in a characteristic way on the lattice sites occupied by the emitter atoms.

The radioactive probe atom ^{67}Cu ($t_{1/2} = 61.9$ h) decays into stable ^{67}Zn via the emission of β^- particles with a maximum energy of 577 keV. Beams of radioactive Cu isotopes are produced at the ISOLDE facility at CERN, using 1 GeV proton induced nuclear fission from UC_2 targets and recently developed laser ion sources [13]. From the variety of elements produced in nuclear fission reactions, Cu atoms are chemically selected via multiphoton resonant laser ionization and acceleration to 60 keV. Following mass separation, clean beams of ^{67}Cu are obtained with an isobaric contamination of other elements below 0.3%.

Five Si single crystals were investigated, two p-type B-doped Czochralski (CZ) grown crystals (samples A and B, resistivity 0.17–0.23 Ω cm, $\langle 100\rangle$ orientation, implanted doses 2.2×10^{12} and 8.0×10^{12} cm^{-2}), one n-Si:P CZ (sample C, 0.09 Ω cm, $\langle 100\rangle$, 3.6×10^{12} cm^{-2}), one n-Si:P float zone (FZ) grown (sample D, 700–1300 Ω cm, $\langle 111\rangle$, 3.8×10^{12} cm^{-2}), and one n-Si:P CZ (sample E, 7.3–12 Ω cm, $\langle 111\rangle$, 3.3×10^{12} cm^{-2}). Prior to the implantation the samples were dipped in HF acid in order to remove the native oxide layer. Following room temperature implantation of ^{67}Cu under an angle of 7° towards the surface direction, the Si crystals were mounted on a goniometer using sample holders entirely made of Ta and Mo. Annealing up to 600 °C was done *in situ* under vacuum better than 10^{-6} mbar. The β^- emission yield as a function of angle towards different crystallographic directions was measured using the position-sensitive detector systems described in Refs. [14,15]. Angular-dependent β^- emission patterns were extracted for the integral energy window from 97 to 600 keV, and corrected for electrons backscattered from the bulk of the sample by subtraction of a flat background. The amount of backscattered electrons has small energy and angle dependence and is mainly determined by the atomic number of the scattering material [16,17]; in the case of Si it amounts to approximately 31%.

In order to deduce the Cu lattice location from the β^- emission patterns we have carried out computer simulations of β^- emission yields for a variety of sites. The concept of electron emission channeling simulations is based on the dynamical theory of electron diffraction and is described in detail in Ref. [12]. To approximate the continuous β^- energy spectrum of ^{67}Cu, simulations were done for electron energies from 100 to 550 keV in steps of 25 keV, and the results averaged according to the theoretical spectral β^- distribution. We calculated characteristic two-dimensional patterns of electron emission probability within a range of $\pm 3°$ around the $\langle 100\rangle$, $\langle 110\rangle$, $\langle 111\rangle$, and $\langle 211\rangle$ directions in steps of $\Delta x = \Delta y = 0.05°$ for S, T, hexagonal interstitial (H), bond center (BC), antibonding (AB), split $\langle 100\rangle$ (SP), and the so-called Y and C sites (cf. Ref. [18]), as well as $\langle 111\rangle$ 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 are described in detail in Ref. [15].

Figures 1(a), 1(b), 1(e), and 1(f) show the measured β^- emission yield in the vicinity of the $\langle 111\rangle$, $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 211\rangle$ directions of sample B, directly following room temperature implantation of ^{67}Cu. The fact that prominent channeling is observed along all major axes and the closest-packed planes [{110} and {111}] is clear evidence that the majority of Cu atoms is located near substitutional sites. On the other hand, the absence of channeling effects from the weaker planes such as {100} or {311} indicates that there exists some displacement from the ideal lattice positions.

Figures 1(c), 1(d), 1(g), and 1(h) show the best fit results, which were obtained for a displacement of $d = 0.50(8)$ Å along the $\langle 111\rangle$ directions from the S towards the BC site. Ideal S sites did not satisfactorily describe the experimental patterns, leading to a roughly 40% increase in the chi square of fit. We also tried $\langle 111\rangle$ displacements from S to AB and $\langle 100\rangle$ displacements from S to SP sites, as well as Gaussian distributions of Cu atoms centered at the S site, but in all those cases the quality of fit was inferior. We therefore consider it most likely that the majority of as-implanted Cu [62(4)%] 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, we cannot definitely rule out that the 0.5 Å displacement occurs along other, higher-index directions, resulting in Cu defects with lower symmetry than trigonal or tetragonal. On the other hand, including more than one site in the fit resulted only in insignificant improvements in the quality of fit. In particular, possible fractions of Cu on distinct sites of high symmetry, such as BC or AB, are estimated to be less than 10%.

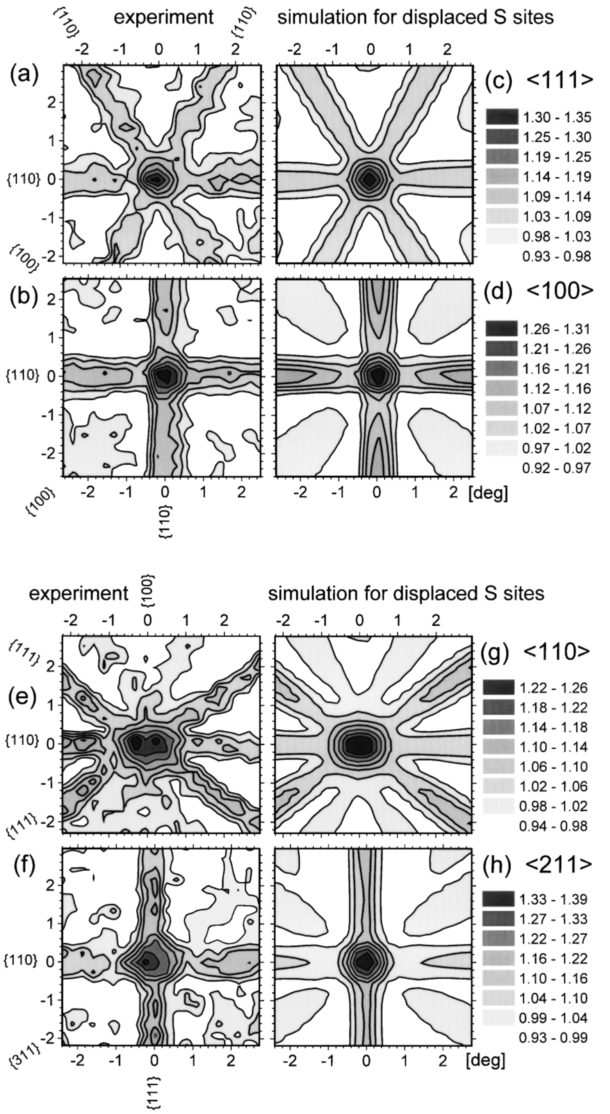

FIG. 1. (a), (b), (e), (f): Normalized emission yields of the integral ^{67}Cu β^- intensity in the vicinity of $\langle 111\rangle$, $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 211\rangle$ directions following room temperature implantation of sample B. (c), (d), (g), and (h) are best fits of simulated patterns to the experimental yields, corresponding to 65%, 67%, 58%, and 59% of emitter atoms on sites which are displaced by 0.50 Å from the S site towards the BC site.

In all samples the fraction of Cu on near-substitutional sites increased upon annealing, reaching a maximum around 200 °C, and decreased continuously for annealing at higher temperatures (Fig. 2). Within the limits of the doping types studied, we found no major differences, either in the lattice site preference or in the annealing behavior, between Cu in p- and n-type material or in FZ and CZ Si. Upon annealing at 600 °C, at least half of the Cu impurities penetrated deep into the bulk of the crystals. This is evident from the fact that in all cases the β^- count rate dropped by a factor of 2 without any detectable contamination outside the samples. Note that the dechanneling lengths for 577 keV end point β^- in Si are around 1000 Å, while the half-thickness for absorption is 80 μm [17], which is still much less than the sample thickness of 630 μm.

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 keV ^{67}Cu in Si is 494 Å with a straggling of 186 Å. The local Cu concentrations are relatively high, in the peak of the profile up to 8×10^{17} cm^{-3} (17 ppm) for an implanted dose of 4×10^{12} cm^{-2}. The simulations indicate that initially around 800 vacancies are created per implanted atom, and that the mean distance from Cu to the nearest vacancy is less than 5 Å. Hence, Cu should have ample possibility to be immediately trapped within vacancy-related defects. This is also backed up by *ab initio* Hartree-Fock calculations on Cu-related complexes [11]. These calculations have predicted an energy gain of 2.71 eV for the reaction $\mathrm{Cu}_i^+ + V^0 \rightarrow \mathrm{Cu}_S^+$ of interstitial Cu with a neutral Si vacancy, although the suggested structure of Cu_S^+ is of cubic symmetry with 0.08 Å breathing mode relaxations of neighboring Si atoms and no displacement of the Cu atom. We cannot *a priori* exclude that the displaced-substitutional Cu is due to reactions with Si interstitials, or due to the formation of Cu_i-Cu_i or Cu_i-Cu_S pairs. However, this seems possible only if Cu would be unstable within vacancy-related defects. In conclusion, we believe to have observed isolated Cu within a single or, more probably, a double vacancy. We ascribe the fact that we did not observe major differences between n- and p-type Si to the damage created during ion implantation, which exceeds the doping level of all our samples by orders of magnitude. It is well known that implanted Si tends to become intrinsic [20]. The relative insensitivity to the implanted dose indicates that the Cu atoms mainly react with vacancies from their own defect cascade.

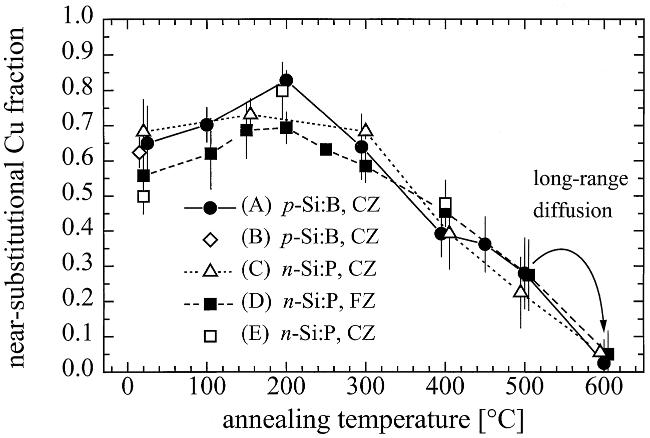

FIG. 2. Isochronal annealing sequences (10 min, measurements at 20 °C) for the fraction of ^{67}Cu on near-substitutional sites. Sample B was only measured as-implanted.

The activation energy E_a for the dissociation of the near-substitutional Cu defect may be estimated from the following considerations. Assuming a simple one-step model and neglecting possible effects of retrapping, which corresponds to an Arrhenius behavior with an attempt frequency, ν_0, of the order of the lattice vibrations, E_a should be related to the near-substitutional Cu fractions $f_{T_{n-1}}$ and f_{T_n} observed after the $(n-1)$th and nth annealing step via $E_a = k_B T_n \ln[\nu_0 \Delta t / \ln(f_{T_{n-1}}/f_{T_n})]$, where T_n and Δt are the temperature and duration of the nth annealing step. Using a typical value of $\nu_0 = 10^{12}$ s^{-1}, we thus derive a dissociation energy of 2.2 eV. On the other hand, the fact that the annealing of Cu_S does not take place within a narrow temperature regime, but starts at 250 °C and is not yet finished at 500 °C, indicates that there are effects from retrapping. The number of times a diffusing atom is captured before it escapes either to the bulk of the sample or towards the surface, starting from the center of a trap profile with a sheet density ϕ, is of the order of magnitude $3\pi R^2 \phi$, where R is the capture radius. Assuming $R = 10$ Å and $\phi = 4 \times 10^{12}$ cm^{-2} $\times$ 800 vacancies, one estimates on average 300 trapping events per Cu atom, resulting in a derived activation energy of 1.8 eV. However, since most vacancies will annihilate during annealing or form higher order complexes, we conclude that 2.2 eV is probably closer to the real value for E_A.

In Table I we have compared tentative models and the activation energies for annealing of various Cu-related defects reported in the literature. The activation energy for dissociation of near-S Cu is comparable to what has been observed previously for the release of Cu from implantation related defects (>2.2 eV) or from $\mathrm{Cu}_3\mathrm{Si}$ precipitates (2.2 eV) [8]. On the other hand, in samples where interstitial Cu was quenched from diffusion at high temperatures, the 1.014 eV photoluminescence (PL) signal was maximized after heating for 30 min at 150–175 °C [21,22], and disappeared again for prolonged annealing, especially above 300 °C. This PL signal has generally been attributed to a ⟨111⟩-oriented pair of Cu atoms, although it has recently been suggested that the underlying defect consists of a single, bond-centered Cu atom [23]. The author of Ref. [22] assumed that the annealing of this center also follows an Arrhenius behavior, fitting both the activation energy and the attempt frequency, which resulted in the unusual combination of $\nu_0 = 4.2$ s^{-1} and $E_a = 0.47$ eV. In our opinion, this approach may not be appropriate, since retrapping tends to flatten the Cu release curves, so that E_a

TABLE I. Experimentally observed Cu-related centers in Si. E_a: activation energy for annealing; EPR: electron paramagnetic resonance; PL: photoluminescence; and DLTS: deep level transient spectroscopy.

Cu center	Symmetry	Tentative model	E_a (eV)	Ref.
Cu-B pairs	⟨111⟩	B_S-$\mathrm{Cu}_{\mathrm{AB}}$	0.61	[24,25]
Cu-Al, Cu-Ga	···		0.70	[24]
Cu-In	⟨111⟩		0.70	[2]
Cu-Pt	···		0.85	[24]
EPR	⟨100⟩	Cu_i-Cu_i	···	[26]
PL 1.014 eV	⟨111⟩	$\mathrm{Cu}_{\mathrm{BC}}$	0.47(5)	[22,23]
	⟨111⟩	Cu_i-Cu_i Cu_i-Cu_S		[21]
DLTS $E_c - 0.15$ eV	···	Cu_i	0.56(3)	[27]
DLTS $E_v + 0.09$ eV	···	Cu_i-Cu_S	1.02(7)	[28]
Cu traps in amorphous Si	···	···	1.2	[29]
$\mathrm{Cu}_3\mathrm{Si}$	···	···	2.2	[8]
Implanted Cu	···	···	>2.2	[8]
Cu in cavities	···	···	2.7(2)	[8]
Near-S Cu	⟨111⟩	···	1.8–2.2	this work

may be largely underestimated if the attempt frequency is also allowed to vary in the fit. We therefore infer that the annealing behavior of the defect showing PL at 1.014 eV is also similar to the displaced-substitutional Cu in our experiments.

In summary, we have shown that room temperature ion implanted Cu in Si occupies predominantly displaced substitutional sites, with a most likely displacement of 0.50(8) Å towards the BC position. Room temperature diffusion is suppressed for near-substitutional Cu. Its thermal stability is high and its annealing behavior similar to the defect characterized by PL at 1.014 eV [22] or to the dissociation of Cu from $\mathrm{Cu}_3\mathrm{Si}$ [8]. The activation energy for dissociation of near-S Cu is estimated to be 1.8–2.2 eV. While Cu is, of course, not to be intentionally implanted in semiconductor processing, we conclude that emission channeling lattice location studies of implanted $^{67}\mathrm{Cu}$ may be used to explore the question whether substitutional Cu exists, and can also give further insight into the gettering behavior of radiation damage.

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*Corresponding author.
Electronic address: ulrich.wahl@fys.kuleuven.ac.be