

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN-EP/86-190
18 November 1986

DIRECT EVIDENCE FOR SUBSTITUTIONAL ION-IMPLANTED
INDIUM DOPANTS IN SILICON

G. Lindner¹, H. Hofsäss¹, S. Winter¹,
B. Besold¹ and E. Recknagel¹,

G. Weyer²,

J.W. Petersen³,

and

the ISOLDE Collaboration, CERN, Geneva, Switzerland

Submitted to Physical Review Letters

Geneva, November 1986

¹ Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, F.R.G.

² Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

³ CERN, CH-1211 Geneva 23, Switzerland

Abstract

Channeling and blocking effects of electrons and positrons emitted from ion-implanted radioactive In dopants in silicon have been utilized for lattice location of In in ppm concentrations. A majority of In atoms occupies substitutional sites after implantation at room temperature. Defect recovery, which is observed after annealing at 700 K, increases the channeling effects. These results corroborate conclusions from previous Mössbauer studies on the same system under identical implantation conditions. The nature of the damage cascades of the individual implanted impurity probe atoms is discussed.

PACS numbers: 61.70.Sk, 61.80.Mk, 61.70.At.

Ion implantation of impurities, which is commonly applied for the doping of semiconductors, is a rather violent technique leaving the implanted sample in a highly non-equilibrium state especially for implantation temperatures far below the melting point. Since the electrical activity of the dopants depends strongly on their lattice site and local defect surrounding, sound structural information on an atomic scale is needed for an understanding of their electronic configuration. To this end numerous ion beam channeling experiments utilizing Rutherford backscattering techniques have been performed for lattice location studies of impurities¹⁾. In general rather high dopant concentrations are needed for this type of channeling experiments (typical ion fluences for implantation energies of 10 - 100 keV are of the order of 10^{14} cm⁻²). However, such fluences cause severe radiation damage in the lattice and may render the implanted layer amorphous. Therefore, annealing is necessary prior to any channeling measurements and consequently information about the as-implanted state is not obtainable. In an effort to overcome this problem Frerichs and Kalbitzer²⁾ have chosen to keep the radiation damage below a critical value by implanting at low energies (2-3 keV) in a comprehensive lattice-location study for as-implanted impurities in silicon. From the systematic trends in the occupancy of substitutional sites by various different dopants it was concluded that chemical effects, i.e. the tendency of a formation of tetrahedrally coordinated sp³ orbitals with the impurity valence electrons^{3,4)}, rather than kinetic replacement mechanisms govern the selection of lattice sites.

However, these experiments still suffer from the inherent constraints of ion-beam channeling techniques, i.e. a high impurity concentration of about 0.1 at.% exceeding the solid-solubility limit²⁾. Additionally, the shallow dopant profile close to the surface (projected range about 7 nm) may yield results, which are not equivalent to a real bulk situation.

In this letter it is demonstrated that a channeling technique based on the observation of the angular distributions of electrons and positrons emitted in nuclear decays from implanted radioactive impurities allows to determine the lattice location of dilute impurities in the bulk at low damage concentrations, i.e. in a situation, where the local defect environment of each dopant is determined entirely by its own slowing-down process. Moreover an immediate combination with other nuclear techniques like Mössbauer spectroscopy (MS) or perturbed $\gamma\gamma$ -angular correlation (PAC) is possible^{5,6)}. These methods are both sensitive to the atomic structure in the neighbourhood of the implant as well as to its electronic configuration; in semiconductors, however, a separation of both influences is difficult. Therefore a complementation of these measurements with a channeling technique offering directly crystallographic information under identical experimental conditions allows for a synoptic interpretation of their results. The system InSi has been studied previously by MS using ¹¹⁹In isotopes⁷⁻⁹⁾, by PAC using ¹¹¹In¹⁰⁻¹³⁾. For this reason and because the isotopes ¹¹²In and ¹¹⁴In are especially well suited for electron- and positron-channeling

measurements this system has been chosen. From the observed channeling and blocking effects a high degree of substitutionality of the In dopants and the conservation of the crystalline lattice structure in the sample volume traced by the emitted electrons and positrons immediately becomes apparent.

As in the case of the MS studies, implantations were performed at the ISOLDE facility at CERN¹⁴⁾, which supplies intense beams of radioactive isotopes at an energy of 60 keV. $^{112\text{m}}\text{In}$ ($T_{1/2} = 20.9$ m) was implanted at room temperature into n-type (0.11 cm), float zone refined silicon single crystals mounted on a two-axis goniometer. Conversion electrons as well as electrons and positrons emitted in the β -decays to ^{112}Sn and ^{112}Cd , respectively, were detected during implantation by a 4 mm thick Si surface barrier detector. When the saturation of activity was reached in the sample, for measurements of the angular dependence of the respective emission yields, the samples were tilted with respect to the detector within a narrow angular regime around crystal axes normal to the surfaces. The total ion fluence was about 10^{11} cm⁻² in the whole experiment, corresponding to a mean dopant concentration in the implanted layer of about 2 at.-ppm. From the blocking dips of positrons and the emission maxima of conversion electrons observed for both (110)- and (111)-cut crystals (fig. 1) it is concluded that (i) the crystalline structure of the samples is conserved to a large extent during implantation and (ii) a large fraction of impurity atoms occupies substitutional

lattice sites, since only electrons and positrons emitted from those sites contribute equally to the channeling effects in both the $\langle 110 \rangle$ and the $\langle 111 \rangle$ directions at comparable depth distributions of the implanted probe atoms. Since pronounced electron channeling effects are only observable for emitter atoms located within a narrow (< 0.02 nm) regime around the respective crystal axes, each probe atom displaced away from one of these axes at larger distances would not contribute to the corresponding channeling effect and therefore the maximum yields of the respective channeling effects would be different. Of course, on the basis of a comparison of only two axial channeling directions, an equal number of emitter atoms displaced away from the $\langle 110 \rangle$ and $\langle 111 \rangle$ atomic strings might simulate a high degree of substitutionality, however, this rather unrealistic coincidence can be excluded from the MS results^{7,8}). (Regarding the positron angular scans it should be noted that these are not corrected for background.)

This result corroborates the interpretation of a dominating line in the Mössbauer spectrum from ^{119}In in Si as due to substitutional In atoms^{7,8}). One has to bear in mind, however, that the Mössbauer spectra are measured for the 24 keV γ radiation of the ^{119}Sn daughter and therefore the relevant electronic structure for the interpretation of the Mössbauer parameters is associated with Sn. However, the Sn position and local lattice environment is assumed to be inherited from the ^{119}In parent atom⁸). The channeling results provide a direct proof of a dominating substitutional site occupancy

of implanted In ions in a crystalline Si lattice. These results are at variance with the interpretation of PAC measurements for the same system by Dezsi et al.¹¹⁾, who derive a substitutional fraction of only 20% in an as-implanted sample at comparable ion fluences. Recent PAC investigations indicate, that the strong perturbations observed in the PAC spectra are mainly caused by defects in the electronic structure rather than by lattice defects^{12,13)}. The implanted radioactive ^{111}In decays by electron capture to the deep-level impurity ^{111}Cd , which is the PAC probe. The ^{111}Cd atoms are left in highly-ionised states after the decay and hence various possible band-gap states of substitutional Cd¹⁵⁾ may be populated during the lifetime of the intermediate state in the $\gamma\gamma$ -cascade of ^{111}Cd , which is probing the quadrupole interaction. For such a system also Jahn-Teller distortions might be suspected¹⁶⁾. No such effects are expected for the ^{119}Sn Mössbauer probe, since isoelectronic Sn has no band-gap states.

Besides the substitutional line in the as-implanted ^{119}Sn Mössbauer spectra further lines were identified with different defect complexes, which anneal below 610 K⁷⁾. This defect annealing was followed up here by electron channeling in another (111) Si crystal of the same material as described above, which was implanted with ^{114}In to a fluence of about 10^{11} cm^{-2} . Owing to the long halflife of 49.5 days of the isotope, the sample could be transferred to Konstanz and conversion-electron channeling effects were measured with a 3-axis goniometer along the three principal crystal

axes. Also in this sample pronounced axial emission maxima were observed in all three directions (fig. 2), evidencing the predominant occupation of substitutional sites. Annealing at 700 K for 10 min causes an additional increase of the yield maxima, which is slightly different (5 - 10%) for the various directions. This indicates local rearrangements of In atoms with respect to these axes besides a removal of radiation damage distributed in the lattice. Though it is beyond the scope of this letter to discuss possible geometrical models of such rearrangements - either the dissolution of defects containing non-tetrahedral interstitial In atoms as e.g. attributed to the dominating defect line no. 1 in the Mössbauer spectra^{7,8)} or the formation of vacancy complexes around In atoms on tetrahedral interstitial sites may be considered - more detailed annealing studies, which are in progress, promise new insight into the defect structures formed by ion implantation. If one adopts a substitutional In fraction of more than 90% from the Mössbauer effect measurements for an annealed sample, which seems also reasonable from theoretical estimates of the yield maximum based on dynamical theory of electron diffraction including dechanneling corrections¹⁸⁾, a substitutional fraction of 55 - 60 % is calculated for the as-implanted sample even though additional dechanneling by radiation damage is neglected. Regarding this value as a lower limit for the actual substitutional fraction, a satisfactory agreement is obtained with a 70% fraction of Sn daughter atoms localized on substitutional lattice sites as deduced from the MS measurements, whereas the 50% substitutional fraction measured by Frerichs

and Kalbitzer²⁾ is surpassed. In those channeling measurements the exceedingly high local In concentration and an overlap of damage cascades may cause a reduction of the substitutional fractions.

In addition to information about the lattice site occupancy of the implanted In isotopes the observed channeling effects provide insight into the nature of cascade damage after room temperature heavy ion implantation. Because most of the electrons and positrons have to transverse the damage cascade produced by their own emitter atom on their way towards the crystal surface, the mere existence of the channeling effects rules out a complete amorphization of the cascade volume as well as the existence of highly disordered regions in the neighbourhood of the final position of a majority of the implanted atoms. This is in contradiction to conclusions drawn by Dezsi et al. from their PAC measurements¹¹⁾. Furthermore, also from TEM investigations of ion-irradiated Si it is found, that rather extended highly disordered regions are produced within the cascade volume under comparable implantation conditions¹⁹⁾. Presumably the channeling effects would be destroyed for those electrons and positrons, which are transversing these regions. The rather pronounced annealing of the channeling effects as compared to metal crystals⁶⁾ may also serve as an indication for the existence of such highly disordered regions at room temperature. Their sizes, however, have to be rather small, because a majority of the emitted electrons and positrons does not suffer severe dechanneling. Taking dechanneling into account the

fraction of probe atoms located in highly disordered regions has to be even smaller than the apparent non-substitutional fraction. Adopting furthermore from the MS results^{7,8)} a strong affinity of In atoms to form vacancy complexes, which partly results in displacements into interstitial sites, any evidence for the existence of amorphous regions around the implanted probe atoms at room temperature is further diminished.

In conclusion it may be stated that the radioactive channeling technique established at an on-line isotope separator like ISOLDE appears to be a unique tool for the determination of substitutional lattice sites in particular for implanted impurities in their as-implanted state in semiconductors, where low ion implantation fluences and very dilute concentrations are crucial conditions. The method is rather universal with respect to impurity elements, since most of the radioactive isotopes produced by such an isotope separator can be employed by utilizing conversion electrons as well as electrons or positrons from β -decays. Furthermore, in combination with nuclear hyperfine interaction methods like MS and PAC such techniques may pave the way also to investigations of the impurity location in defect complexes formed in ion implantations.

The authors would like to appreciate valuable discussions with Th. Wichert, M. Deicher and F. Pleiter. Financial support of this project from the Bundesminister für Forschung und Technologie and the Danish Accelerator Physics Council is gratefully acknowledged.

References

- 1) L.C. Feldmann, J.W. Mayer and S.T. Picraux: "Materials Analysis by Ion Channeling" (Academic Press, New York, 1982).
- 2) H.P. Frerichs and S. Kalbitzer, Rad. Eff. 83, 135 (1984).
- 3) E. Antoncik, Nucl. Instr. and Meth. B14, 193 (1986).
- 4) E. Antoncik, Rad. Eff. 88, 217 (1986).
- 5) H. Hofsäss, G. Lindner, S. Winter, B. Besold, E. Recknagel and G. Weyer, Nucl. Instr. and Meth. B13, 71 (1986).
- 6) Th. Wichert, G. Lindner, M. Deicher and E. Recknagel, Phys. Rev. B24, 7467 (1981).
- 7) G. Weyer, S. Damgaard, J.W. Petersen and J. Heinemeier, Hyp. Int. 7, 449 (1980).
- 8) G. Weyer, S. Damgaard, J.W. Petersen and J. Heinemeier, Nucl. Instr. and Meth. 199, 441 (1982).
- 9) G. Weyer, J.W. Petersen and S. Damgaard, Hyp. Int. 10, 775, (1981).
- 10) E.N. Kaufmann, R. Kalish, R.A. Naumann and S. Lis, J. Appl. Phys. 48, 3332 (1977).
- 11) I. Dezzi, L. Hermans, J. van Cauteren and M. Rots, Rad. Eff. Lett. 85, 277 (1985).
- 12) M. Deicher, G. Grübel, E. Recknagel, Th. Wichert and D. Forkel, Nucl. Instr. and Meth. B13, 499 (1986).
- 13) M. Deicher, G. Grübel, H. Hofsäss, E. Recknagel and Th. Wichert, Nucl. Instr. and Meth. B15, 418 (1986).

- 14) H. Ravn, L.C. Carraz, J. Denimal, E. Kugler, M. Skarestad, S. Sundell and L. Westgaard, Nucl. Instr. and Meth. 139, 267 (1976).
- 15) S.S. Dyunaidov, N.A. Urmanov and M.V. Gafurova, Phys. Stat. Sol. (a)66, K79 (1981).
- 16) F. Pleiter, private communication
- 17) J. Lindhard, in: " Atomic collision phenomena in solids", eds. D. Palmer, M. Thomson and P. Townsend (North Holland, Amsterdam, 1970) p. 1.
- 18) H. Hofsäss, G. Lindner, E. Recknagel and Th. Wichert, Nucl. Instr. and Meth. B2, 13 (1984).
- 19) D.A. Thompson, Rad. Eff. 56, 105 (1981).

Figure captions

Fig. 1:

Axial angular scans of the normalized emission yields of positrons with energies above 700 keV and of conversion electrons with energies of 130 keV measured on-line at ISOLDE during implantation of ^{112}In into (110) and (111) Si crystals (fluences 10^{11}cm^{-2}).

Fig. 2:

Axial channeling effects of 170 keV conversion electrons from the decay of ^{114}In measured at a Si crystal after room temperature implantation at ISOLDE with a fluence of 10^{11}cm^{-2} (top) and after subsequent annealing at 700 K (bottom). The data were fitted with a theoretical function, whose angular dependence was proposed by Lindhard¹⁷).

Fig. 1

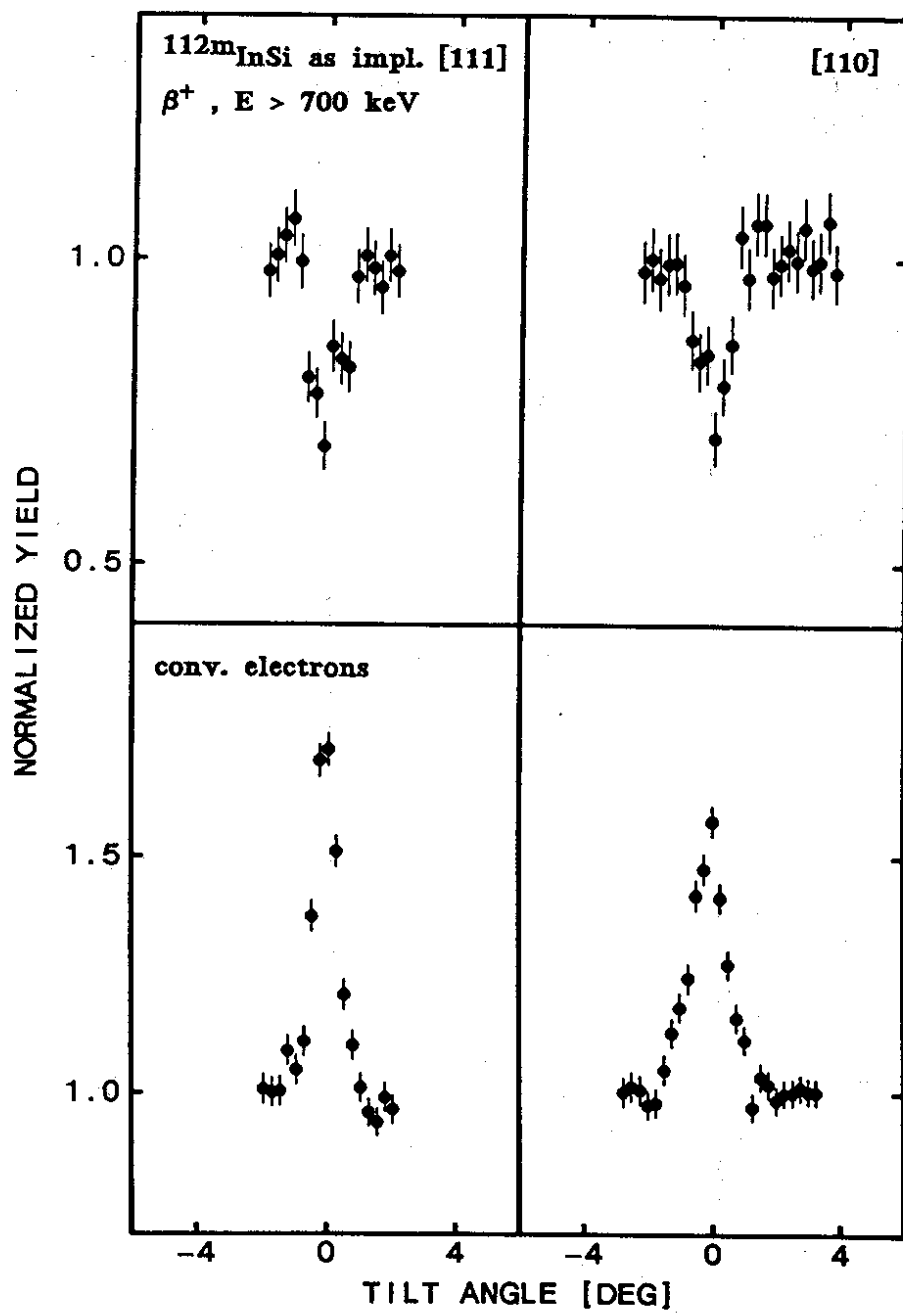


Fig. 2

