Direct Evidence for Substitutional Ion-Implanted Indium Dopants in Silicon

G. Lindner, H. Hofsäss, S. Winter, B. Besold, and E. Recknagel
Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Federal Republic of Germany

G. Weyer
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

and

J. W. Petersen
EP Division and the ISOLDE Collaboration, CERN, CH-1211 Geneva 23, Switzerland
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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 parts-per-million 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.

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Ion implantation of impurities, which is commonly applied for the doping of semiconductors, is a rather violent technique that leaves the implanted sample in a highly nonequilibrium 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 surroundings, 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 impurities.[1] 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 Kalbitzer[2] 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 sp^3 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 limit.[2] 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 us 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 neighborhood of the implant as well as its electronic configuration; in semiconductors, however, a separation of the two 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 Si:In has been studied previously by MS with use of ^{119}In isotopes,[7-9] and by PAC with ^{111}In.[10-13] For this reason and because the isotopes ^{112}In and ^{114}In 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 CERN,[14] which supplies intense beams of radioactive isotopes at an energy of 60 keV. ^{112}In^m ($T_{1/2}$=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 substitional lattice sites, since only electrons and positrons emitted from those sites contribute equally to the channeling effects in both the ⟨110⟩ and the ⟨111⟩ 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 ⟨110⟩ and ⟨111⟩ atomic strings might simulate a high degree of substitutionality; however, this rather unrealistic coincidence can be excluded by the MS results.[7,8] (Regarding the positron angular scans it should be noted that these are not corrected for background.)

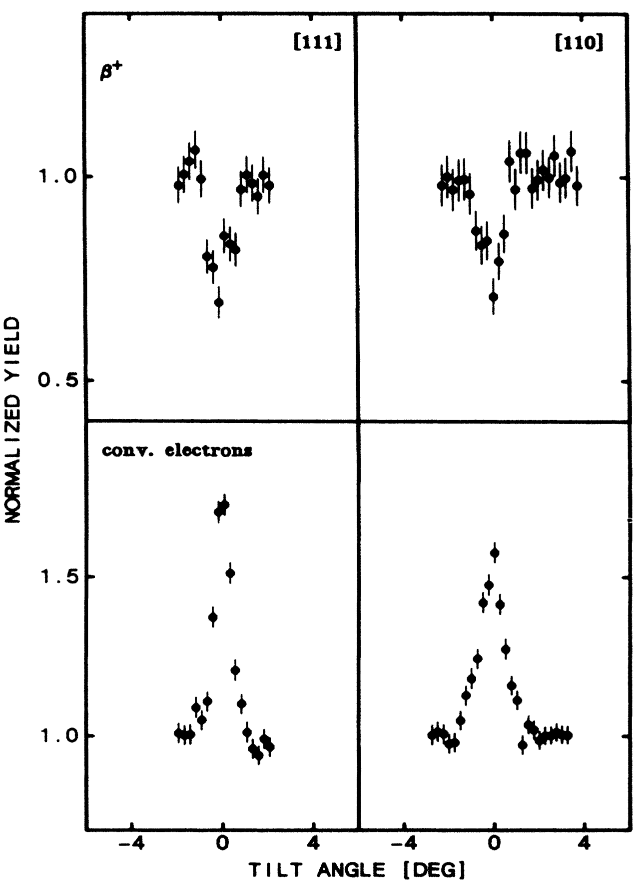

FIG. 1. Axial angular scans of the normalized emission yields of positrons with energies above 700 keV and of conversion electrons with energies of 130 keV measured on line at ISOLDE during implantation of ^{112}In into (110) and (111) Si crystals (fluences 10^{11} cm^{-2}).

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 are assumed to be inherited from the ^{119}In parent atom.[8] 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 ionized states after the decay, and hence various possible band-gap states of substitutional Cd[15] 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 suspected.[16] 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 K.[7] 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}. Because of the long half-life of 49.5 days of the isotope, the sample could be transferred to Konstanz and conversion-electron channeling effects were measured with a three-axis goniometer along the three principal crystal axes. Also in this sample pronounced axial emission maxima were observed in all three directions (Fig. 2), which gave evidence of the predominant occupation of substitutional sites. Annealing at 700 K for 10 min causes an additional increase of the yield maxima, which is slightly dif-

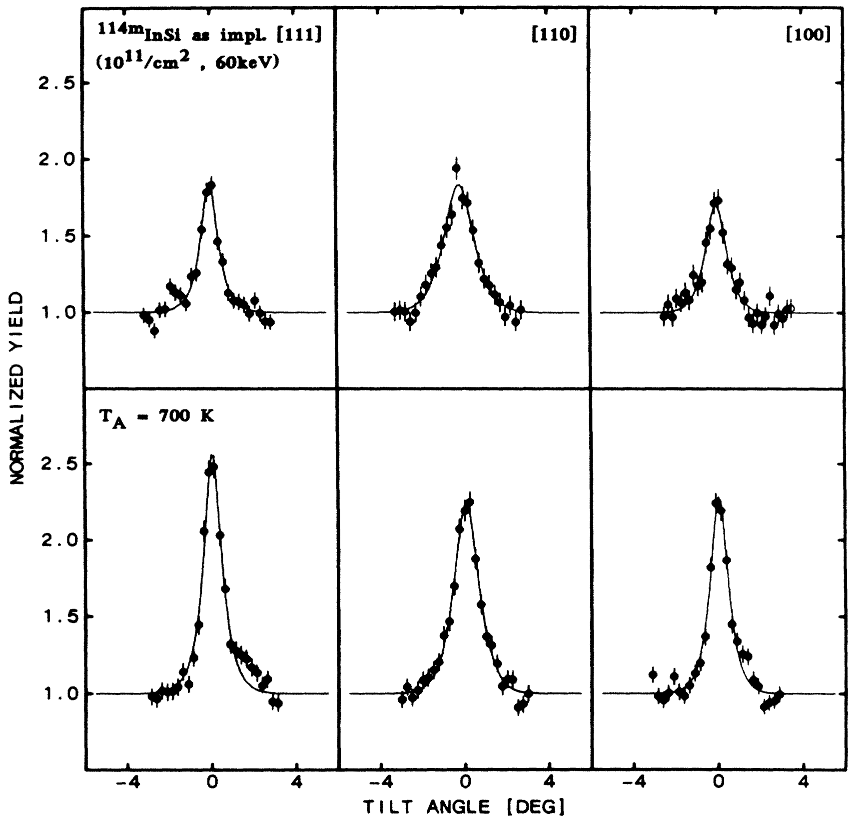

FIG. 2. Axial channeling effects of 170-keV conversion electrons from the decay of ^{114}In measured at a Si crystal after room-temperature implantation at ISOLDE with a fluence of 10^{11} cm^{-2} (top) and after subsequent annealing at 700 K (bottom). The data were fitted with a theoretical function whose angular dependence was proposed by Lindhard (Ref. 17).

ferent (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 nontetrahedral 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 corrections,[18] a substitutional fraction of 55%–60% is calculated for the as-implanted sample even though additional dechanneling by radiation damage is neglected. If we regard 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 Kalbitzer[2] 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 the cascade damage after room-temperature heavy-ion implantation. Because most of the electrons and positrons have to traverse the damage cascade produced by their own emitter atoms 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 neighborhood 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 measurements.[11] Furthermore, also from transmission electron microscopic investigations of ion-irradiated Si it is found that rather extended highly disordered regions are produced within the cascade volume under comparable implantation conditions.[19] Presumably the channeling effects would be destroyed for those electrons and positrons which are traversing these regions. The rather pronounced annealing of the channeling effects as compared to metal crystals[6] 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. When we take dechanneling into account the fraction of probe atoms located in highly disordered regions has to be even smaller than the apparent nonsubstitutional fraction. If we adopt 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 the utilization of 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.

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