Passivation of Shallow Acceptors by H in Si: A Microscopic Study by Perturbed Angular Correlations

Th. Wichert, H. Skudlik, M. Deicher, G. Grübel, R. Keller, E. Recknagel, and L. Song[(a)]
Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, West Germany

(Received 28 July 1987)

The formation of acceptor-hydrogen complexes in silicon is studied via the electric field gradients caused by H atoms at the site of radioactive ^{111}In acceptor atoms, and is measured by means of the perturbed $\gamma\gamma$ angular correlation technique. The identical In-H pairs which are oriented along ⟨111⟩ lattice directions are found in samples hydrogenated by different methods, well known for the passivation of shallow acceptors. They dissociate around 420 K and are more stable than B-H complexes. There is evidence for an influence of the free-hole concentration on the actual structure of the In-H pairs.

PACS numbers: 61.70.Yq, 71.70.Jp, 76.80.+y

In recent years the electrical passivation of shallow acceptors like B, Ga, In, and Al in silicon by hydrogen atoms has been subject of numerous research activities,[1] whereby the passivation is observed after a variety of different procedures, such as charging from a H plasma, boiling in water, avalanche injection in SiO_2, chemical etching, and other common wafer processing steps[2]; they all seem to have in common the introduction of atomic hydrogen into Si. The first observations[3,4] of this process in B-doped Si have stimulated a large number of investigations; among them, important microscopic information arose from infrared experiments,[5-7] passivation studies under electric fields,[8] and Raman-scattering experiments.[9] In spite of this effort, the passivation mechanism and the nature of the hydrogen-acceptor bond have remained a matter of controversy.[10-14]

In this Letter, first results on the formation, stability, and structure of In-H complexes will be given from the perturbed $\gamma\gamma$ angular correlation (PAC) technique. The presence of a H atom next to an In acceptor atom is detected at the In atom itself via the electric field gradient induced by the H atom. This field gradient is characteristic for the H defect and its crystallographic position and because of its r^{-3} dependence a defect has to reside close to the In atom in order to be visible. For the present study radioactive ^{111}In probe atoms were implanted at 350 keV at 295 K into B-doped (100) Si wafers (1×10^{15} to 5.5×10^{17} cm^{-3}, Wacker Chemitronic) resulting in a peak concentration of about 5×10^{16} ^{111}In cm^{-3} at a depth of 1500 Å. The radiation damage caused by the implantation process was removed by annealing at 1170 K for 600 s under flowing N_2; subsequently, the Si samples were charged with hydrogen. At 295 K, eight coincidence spectra were measured by recording of the $\gamma\gamma$ cascade of the decay of ^{111}In to ^{111}Cd with help of a standard four-detector setup. The coincidence spectra were combined into a single PAC time spectrum $R(t)$, which contains the information on the electric field gradient produced at the site of the radioactive probe atom.[15] For probe atoms on regular lattice sites, the field gradient is zero because of the tetragonal symmetry of the electric charge distribution around these atoms and the $R(t)$ spectrum is time independent. A nonzero electric field gradient caused by a H atom next to an In atom gives rise to oscillations in

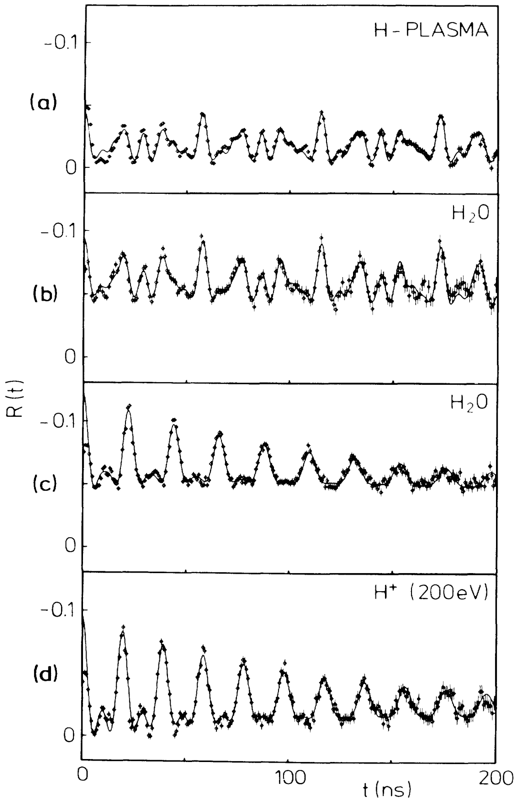


FIG. 1. PAC time spectra for ^{111}In/^{111}Cd probe atoms in Si samples differently charged with H atoms. The spectra, measured at 295 K with γ detectors oriented along ⟨100⟩ and ⟨110⟩ lattice directions, show the formation of In-H complexes. The Si samples were doped with (a),(b) 1×10^{15}, (c) 5.5×10^{17}, and (d) 1.6×10^{17} B cm^{-3}.

the $R(t)$ spectrum, whereby the actually observed amplitudes depend on the fraction of probe atoms associated with such a H atom.

In Fig. 1 PAC spectra are collected for Si samples which were doped with hydrogen under different conditions, all known for passivating acceptor atoms. Spectrum (a) shows the result for a Si sample (10^{15} B cm^{-3}) charged for 15 min by a H plasma (operated at 13.56 MHz, 320 V, and 0.6 mbar). The pronounced oscillations point to the presence of H atoms in the close vicinity of ^{111}In atoms. A least-squares fit to the experimental $R(t)$ spectrum (solid lines in Fig. 1) reveals the presence of two different field gradients, which is more clearly visible in the Fourier transform $F(\omega)$ shown in Fig. 2 (top): The occurrence of two frequency triplets shows the presence of the two different electric field gradients; the frequency ratio and the dependence of the frequency amplitudes on the two different orientations of the γ detectors (top and bottom panel) shows the axial symmetry of both field gradient tensors about a $\langle 111 \rangle$ direction of the Si lattice.[16] Their largest component V_{zz} is expressed by $\nu_Q = eQV_{zz}/h = (10/3\pi)\omega_0$, where Q is the electric quadrupole moment of the isomeric ^{111}Cd state and ω_0 is the smallest frequency of the triplet, so that $\nu_Q = 349(1)$ and 463(1) MHz, respectively.

Spectrum (b) of Fig. 1 shows the result of boiling a Si sample (10^{15} B cm^{-3}) in doubly deionized H_2O for 45 min at 353 K. Since the same field gradients are observed as before, identical In-H complexes are formed after plasma charging and boiling in water, with the 349-MHz complex being dominant in both cases. The last two PAC spectra in Fig. 1 show the results for H-charged Si samples containing a higher B concentration: Spectrum (c) (5.5×10^{17} B cm^{-3}) is observed after boiling in H_2O for 395 min at 353 K and annealing at 410 K and spectrum (d) (1.6×10^{17} B cm^{-3}) following 200-eV H^+ implantation with a dose of 1×10^{14} cm^{-2} at 353 K and annealing at 402 K. In both cases, the higher B concentration causes the exclusive occurrence of the 349-MHz complex, whose actual frequency, however, can be slightly reduced as discussed below.

On the basis of their appearances following boiling in water, the well-defined and strong field gradients can be attributed to In-H complexes where the H atoms reside at a unique lattice site, which is close to the In atom. That means that H forms *close pairs* with the In acceptor atoms, which are oriented along $\langle 111 \rangle$ lattice directions because of the $\langle 111 \rangle$ axial symmetry of the field gradients. On account of the present results, the interpretation of a recent PAC experiment on laser-annealed Si, where the identical field gradients have been associated with the formation of In-vacancy complexes,[17] has to be revised.

The stability of the acceptor-H complexes is studied during isochronal annealing (10 min), as plotted in Fig. 3 for Si samples charged in H_2O (top) or by 200-eV H^+

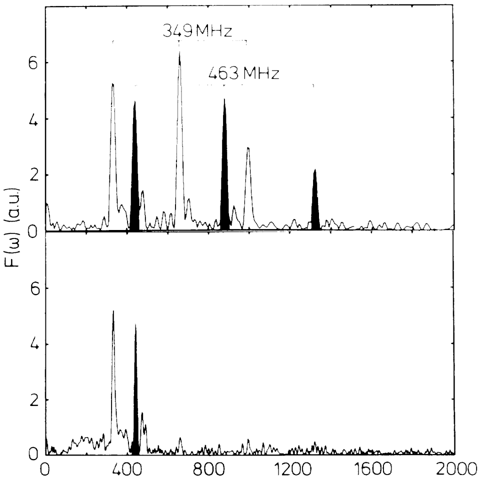


FIG. 2. Fourier transforms $F(\omega)$ of PAC spectra $R(t)$ measured with γ detectors along (top) $\langle 100 \rangle$ and (bottom) $\langle 111 \rangle$ lattice directions at a H-plasma–charged Si sample. The amplitudes of the two electric field gradients, characterized by $\nu_Q = 349$ and 463 MHz, show the $\langle 111 \rangle$ axial symmetry of the In-H complexes.

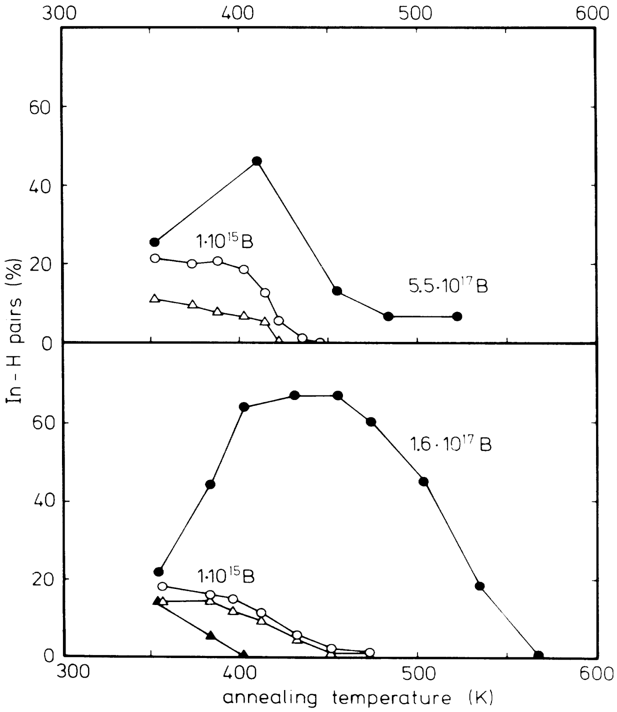
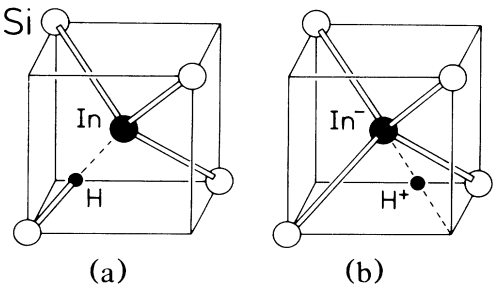


FIG. 3. Fractions of In-H pairs in Si(100) samples doped with ^{111}In atoms (5×10^{16} cm^{-3}) and (top) boiled in H_2O at 353 K or (bottom) implanted with 1×10^{14} 200-eV H^+ cm^{-2} at 353 K. Circles and triangles correspond to the 349- and 463-MHz complexes, respectively.

with a dose of 1×10^{14} cm^{-2} (bottom). In the case of lower B concentration (open symbols), where the Si lattice in the region of the ^{111}In profile is dominated by the 5×10^{16} In cm^{-3}, the panels show a constant fraction of In-H complexes at low annealing temperatures, followed by a decrease of both types of In-H complexes between 373 and about 450 K. On the assumption of a single jump for the dissociation process, a dissociation energy $E_{\text{In-H}}=kT_A\ln(\nu_0 t_A)=1.3$ eV is deduced with use of an annealing temperature $T_A=420$ K for $t_A=600$ s and an assumed attempt frequency $\nu_0=10^{13}$ s^{-1}; this value is significantly lower than the 2.1 eV given by Pearton.[1] In the case of the higher B concentrations (filled symbols), where the Si lattice observed by ^{111}In atoms is B dominated, mainly the fraction of In-H complexes with the lower field gradient (349 MHz) is observed. Obviously, the high B concentration provides a strong source of H for the In atoms, because the In-H fraction still increases at temperatures where the In-H complex already starts to vanish in case of low B concentration. This observation is easily understood if B-H complexes formed during the charging procedure exhibit a lower dissociation energy than In-H complexes, as is also suggested by Sah, Pan, and Hsu.[18] The faster decrease of In-H pairs between 400 and 500 K, observed in the upper panel, is due to the lower H concentration introduced by boiling in water. The high concentration of B-H complexes seems to be also responsible for the observed field-gradient distribution exhibited by the damping in the PAC spectra (c) and (d) of Fig. 1. Furthermore, with increasing B concentration, a remarkable steady decrease of the magnitude of the field gradient during annealing is observed, starting from 349 MHz at 353 K and arriving at about 300 MHz for T_A about 500 K in the case of the highest B concentration. This decrease of the field gradient during annealing indicates a change of the length of the In—H bond that is caused by the increasing concentration of reactivated B atoms or of free holes. In Fig. 4, two arrangements of In-H complexes are sketched which both fulfill the ⟨111⟩ symmetry determined by PAC (possible relaxations are not taken into account); however, the magnitude of the electric field gradients does not allow us to identify either model since reliable theoretical calculations are not available. Model (a), the commonly accepted configuration, was proposed by Pankove *et al.*[5] and DeLeo and Fowler,[11] in order to explain the observed H-related infrared absorption band at 1875 cm^{-1} in passivated, B-doped Si.[5,6] Here, the H atom occupies a site between two neighboring Si atoms (bond-center site) and is covalently bound to one of the four Si atoms surrounding the acceptor atom which then becomes neutral and threefold coordinated. However, these infrared data were also explained by Assali and Leite[12] assuming a covalent bond to the acceptor atom whereby the H atom occupies a nearest-neighbor interstitial site between the acceptor atom and the tetrahedral site (antibonding site). Also, in model (b) of Fig. 4, the H atom resides at the antibonding site; but a Coulombic bond between a H$^+$ and an In$^-$ species is assumed, which was also discussed by Stutzmann[9] and Pantelides[13] for B in Si. A Coulombic bond can most easily account for the observed influence of the free-hole concentration on the magnitude of the field gradient of the 349-MHz complex: The increasing concentration of holes effects a stronger electrostatic screening of the In$^-$ so that the H$^+$ becomes more weakly bound and, consequently, the field gradient of this complex decreases. Since a similar relaxation of the H atom in model (a) is not expected, the 349-MHz complex, which was dominant at 295 K and at higher B concentrations, is interpreted as an In$^-$-H$^+$ complex as in model (b). The occurrence of H at an antibonding site is also supported by recent ion-channeling experiments on Si doped with 5×10^{19} B cm^{-3}, which were performed at 295 K.[19]



(a) (b)

FIG. 4. Two models for the microscopic structure of In-H pairs according to the present PAC results where the H atom resides at either (a) a bond center or (b) an antibonding interstitial site; possible lattice relaxations are not taken into account.

The second, 463-MHz field gradient is indicative of a second, metastable H complex, because its fraction grows whenever the concentration of free holes becomes small: Thus, Fig. 3 already showed that the formation of this complex occurred in case of the lowest B concentration and for the next higher B concentration only directly after passivation. In addition, an increase of the 463-MHz at the expense of the 349-MHz complex is observed, if the sample temperature is decreased below 295 K or the sample, forming a Schottky diode, is reverse biased. Therefore, the 463-MHz field gradient represents a second In-H complex, that might be similar to complex (a) in Fig. 4, which is easily formed in case of low hole concentrations because the H atom can stay neutral. Thus, the two models of Fig. 4 seem to represent two limiting cases for possible In-H arrangements, where models (a) and (b) are typical for lower and higher hole concentrations, respectively; that means also for different sample temperatures. Also, recent infrared experiments by Stavola *et al.*[7] can be interpreted in the framework of such a metastability, where a narrowing and shift of the acceptor-H related absorption bands upon cooling was observed.

Summarizing, it can be stated that (1) H atoms form close In-H pairs along ⟨111⟩ lattice directions in Si and occupy two different, metastable complexes depending on the free-hole concentration; (2) In-H complexes dissociate around 420 K and are more stable than B-H complexes; and (3) all charging procedures studied so far, i.e., plasma charging, boiling in water, or 200-eV H^+ implantation, lead to the formation of the identical In-H complexes. It can be expected that the structure of other shallow acceptor-H complexes is similar to that of the In-H pairs because of their similar vibrational characteristics[7] and thermal stabilities.[18]

It is a pleasure to thank J. Weber, M. Konuma, and M. Singh of the Max-Planck-Institut, Stuttgart, for many stimulating discussions and experimental assistance during plasma charging, and to acknowledge the critical reading of the manuscript by G. Schatz and helpful comments by T. Yussouff. This work was supported by the Bundesminister für Forschung und Technologie.

---

[a] On leave from Nuclear Science Department, Fudan University, Shanghai, People's Republic of China.

[1] S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A **43**, 153 (1987).

[2] C. H. Seager, R. A. Anderson, and J. K. G. Panitz, J. Mater. Res. **2**, 96 (1987).

[3] C. T. Sah, J. Y.-C. Sun, and J. J.-T. Tzou, Appl. Phys. Lett. **43**, 204 (1983).

[4] J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).

[5] J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lucovsky, Appl. Phys. Lett. **46**, 421 (1985).

[6] N. M. Johnson, Phys. Rev. B **31**, 5525 (1985).

[7] M. Stavola, S. J. Pearton, J. Lopata, and W. C. Dautremont-Smith, Appl. Phys. Lett. **50**, 1086 (1987).

[8] A. J. Tavendale, D. Alexiev, and A. A. Williams, Appl. Phys. Lett. **47**, 316 (1985).

[9] M. Stutzmann, Phys. Rev. B **35**, 5921 (1987).

[10] N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B **35**, 4166 (1987).

[11] G. G. DeLeo and W. B. Fowler, Phys. Rev. B **31**, 6861 (1985), and Phys. Rev. Lett. **56**, 402 (1986).

[12] L. V. C. Assali and J. R. Leite, Phys. Rev. Lett. **55**, 980 (1985); and **56**, 403 (1986).

[13] S. T. Pantelides, Appl. Phys. Lett. **50**, 995 (1987).

[14] M. Capizzi and A. Mittiga, Appl. Phys. Lett. **50**, 918 (1987).

[15] Th. Wichert and E. Recknagel, in *Microscopic Methods in Metals,* edited by U. Gonser, Topics in Current Physics, Vol. 40 (Springer-Verlag, Berlin, Heidelberg, 1986), p. 317.

[16] D. Wegner, Hyperfine Interact. **23**, 179 (1985).

[17] G. J. Kemerink and F. Pleiter, Phys. Lett. A **121**, 367 (1987); note that these authors quote ω_0 instead of ν_Q.

[18] C.-T. Sah, S. C.-S. Pan, and C. C.-H. Hsu, J. Appl. Phys. **57**, 5148 (1985).

[19] Th. Wichert, H. Skudlik, H. D. Carstanjen, T. Enders, and M. Stutzmann, to be published.