Shallow hydrogen-related donors in silicon

Joachim Hartung* and Jörg Weber
Max-Planck-Institut für Festkörperforschung, Postfach 800665, D-70506 Stuttgart, Germany
(Received 22 June 1993)

Photothermal ionization spectroscopy on neutron-irradiated and subsequently hydrogen-plasma-treated silicon reveals the existence of new shallow donors. The binding energies of the observed effective-mass-like donors are between 34 and 53 meV. The optical dipole transitions of the different donors are shifted towards higher energies by $\Delta E = 0.1-0.2$ cm^{-1}, when deuterium is used in the plasma instead of hydrogen. This isotope shift of the optical dipole transitions between the electronic levels of the defects is direct proof of the incorporation of hydrogen in these defects.

I. INTRODUCTION

Hydrogen in crystalline semiconductors forms readily chemical bonds with either the host or impurity atoms.[1] In particular in Si the interaction of hydrogen with donors or acceptors was studied intensively and detailed models of the defect structures were proposed.[2,3] In addition to the passivation of shallow defects by hydrogen there exists experimental evidence for the passivation of deep enters.[4]

Proton implantation in Si generates several deep defects, which do not depend on the implanted species. But during annealing of the implanted samples hydrogen was found to become mobile and to bind to the radiation induced defects, leading to their passivation.[4,5] At the same annealing temperatures new donors are formed.[6,7] At least three new shallow donors could be detected by photothermal ionization spectroscopy (PTIS).[8,9] There are also reports on the formation of shallow donors after annealing of neutron transmutation doped (NTD) silicon grown in a hydrogen atmosphere.[10]

In Ref. 11 we have tried to separate the damaging process from the diffusion of atomic hydrogen by diffusing hydrogen from an rf-driven plasma into silicon which was already heavily damaged by neutron irradiation. After this procedure we detect in addition to the donors observed in proton-implanted silicon several new donors which we labeled HD donors.[12] Although there was indication of hydrogen incorporation in these donors, definite proof is still missing.

In the present study we use high-resolution PTIS (Ref. 13) to investigate these shallow donors in detail. We report on five new shallow donors created after hydrogen plasma treatment of neutron-irradiated silicon. The binding energies of the observed effective-mass-like donors are between 34–53 meV. When deuterium is used in the plasma instead of hydrogen the optical dipole transitions of the different donors shift towards higher energies by $\Delta E = 0.1-0.2$ cm^{-1}. An isotope shift of the optical dipole transitions between the electronic levels of the defects proves unambiguously the incorporation of hydrogen in these defects.

II. EXPERIMENTAL DETAILS

In the present study the silicon samples were first irradiated with thermal neutrons (n) as in the neutron transmutation doping process (NTD),[14] but were not annealed to avoid the elimination of the radiation damage and the activation of the phosphorus donors. The neutron flux was 5.6×10^{17} n/cm^2 and the silicon starting material had a resistivity of 3200 Ω cm. The homogeneously damaged floating zone silicon was then subjected to an rf-driven H plasma working at a frequency of 13.56 MHz. The temperature of the H-plasma treatment was chosen between 240 °C–400 °C for 1.5–20 h. Deuterium plasma treatments were at temperatures between 255 °C–360 °C for 4–5 h. The thermal stability of the donors was determined by annealing the samples in inert gas atmospheres at temperatures between 300 °C–600 °C for 1 h. The spreading resistance profiles were taken on a commercial setup, ASR 100 C from Solid State Measurements.

The Ohmic contacts were Ni-Au-Sb-Au alternating layers evaporated onto the plasma exposed sample surface and alloyed by a pulsed Nd-YAG (yttrium aluminum garnet) laser. A Bruker IFS 113v Fourier transform spectrometer was used in this PTIS study. The spectra were recorded with an unapodized spectral resolution of 0.04–0.1 cm^{-1}. The broadening of the instrumental linewidth during apodization according to Norton and Beer[15] is a factor of 1.2 larger compared to the unapodized linewidth.

III. RESULTS

A. Spreading resistance profiles

The spreading resistance profiles of the samples directly after the neutron irradiation and those after additional annealing at 300 °C for 3 h in a H_2 atmosphere are identical. A typical profile of these samples is shown as profile (a) in Fig. 1. The constant high resistance is evidence for the homogeneous damage of the samples. A hydrogen plasma treatment (385 °C, 2 h) of the n-irradiated sample generates a steplike profile [profile (b) in Fig. 1] with a re-

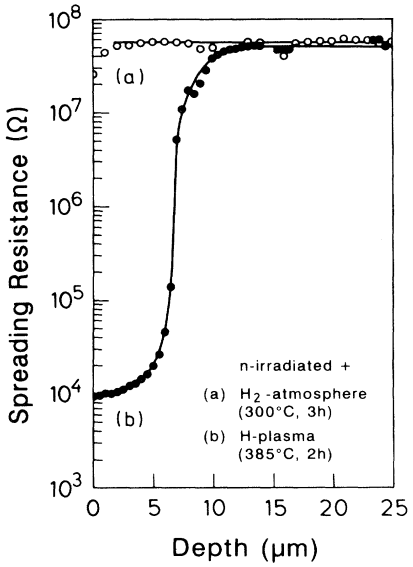

FIG. 1. Spreading resistance profile of neutron-irradiated silicon after (a) annealing in a H_2 atmosphere and (b) hydrogen-plasma treatment.

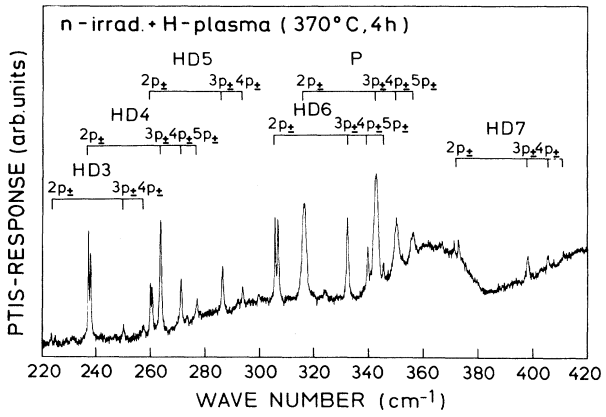

FIG. 2. PTIS spectrum of n-irradiated and H-plasma-treated silicon, measured at $T=18$ K with an unapodized resolution of 0.1 cm^{-1}.

gion of low resistivity directly below the surface which was exposed to the hydrogen plasma. At 10 μm below the surface the resistivity of the H-plasma-treated silicon is identical to the resistivity of n-irradiated silicon without any further treatment. We find no step in the profile of phosphorus doped Si (NTD-Si) after H-plasma treatment. Only neutron-irradiated and subsequently H-plasma-treated silicon samples exhibit the steplike resistivity profile, the surface resistivity and the depth of the resistivity increase vary, however, with the parameters of the H-plasma treatment. The difference in profiles (a) and (b) of Fig. 1 can be attributed to the diffusion of hydrogen into the sample.

B. PTIS signal of the donors HD3–HD7

A typical spectrum of a neutron-irradiated sample which was subsequently annealed in a H plasma at 370 °C for 4 h is shown in Fig. 2. Several sharp photoionization peaks can be resolved and we are able to group them into six sets of lines, marked by HD3–HD7 and P in Fig. 2. In a few samples we detect additional line series HD0–HD2, which are still subject of our investigations.[8] In the spectral region 220–290 cm^{-1} the PTIS spectrum is dominated by the strong line series denoted HD4 and HD5, while at energies higher than 300 cm^{-1} HD6 and P are the most intense lines. The line series HD3 and HD7 show up only with small intensity on a strong background signal.

The line positions of the observed series HD3–HD7 are listed in Table I. A comparison of the line separations with those predicted by the effective-mass theory (EMT) (Refs. 16 and 17) identifies the observed lines as ground- to excited-state transitions of several EMT-like donors, labeled HD3–HD7. The P-line series represent the well known optical dipole transitions of the phosphorus donor,[18] which was generated by n irradiation and thermally activated during the plasma treatment. The ionization energies of the HD donors determined from the $1s\rightarrow 4p_{\pm}$ or $1s\rightarrow 5p_{\pm}$ transitions are between 34–53 meV. Table I lists the ionization energies for all donors along with the deviations—chemical shift—from the ionization energy predicted by the effective-mass theory. The donors HD3 and HD5 show the transitions $1s\rightarrow 2p_{\pm}$ up to $1s\rightarrow 4p_{\pm}$, well resolved with respect to the background signal, in addition for the donors HD4 and HD6 even the dipole transitions from the $1s$ ground state to the $5p_{\pm}$ excited state are detectable. The donors HD3–HD7 exhibit a splitting of the $1s\rightarrow 2p_{\pm}$ transitions. Energies for the resolved splittings are given in Table I. Similar line splittings are common features for EMT donors in Si.[19,20] The linewidths full width at half maximum of the optical dipole transitions lines of the HD donors are between 0.6–0.9 cm^{-1}. Measurements of the PTIS signals at different temperatures in the range of 8–23 K show an increase of the line intensities due to thermal activation. For the donors HD3–HD7 we cannot observe the $1s\rightarrow 2p_0$ EMT donor level transitions. This agrees with other PTIS investigations on donors in doped Si,[17,21] where the same transition is only detected with small signal strengths. The donors HD3–HD7 are observed in neutron-irradiated silicon after H-plasma treatments at temperatures between 350 °C–400 °C. In particular the donors HD4–HD7 are present in all samples treated in the temperature range mentioned above. The donor HD3 can directly be detected only in a few samples investigated, in other samples the optical dipole transitions in HD3 show up after an additional annealing at 400 °C.

In addition we studied the influence of H-plasma treatment on Si samples, which have not been damaged by any other radiation processes before. In such samples we only detected a PTIS signal resulting from the phosphorus dopant. We also failed to resolve a PTIS signal in neutron-irradiated silicon after thermal annealing in inert gas atmospheres of nitrogen, argon, and even hydrogen.

TABLE I. The HD donor energy levels observed by PTIS. The binding energies are determined using the transitions to the $4p_{\pm}$ or $5p_{\pm}$ excited states. The precision of the energies determined in this work is ± 0.05 cm^{-1} throughout the table.

Donor transitions (cm^{-1})	EMT (Ref. 17)	HD3	HD4	HD5	HD6	HD7
		223.4	236.9	259.6	305.4	371.4
$1s \rightarrow 2p_{\pm}$	200.51					
		224.7	237.6	260.2	306.4	372.6
$1s \rightarrow 3p_{\pm}$	226.98	249.8	263.4	286.0	332.0	397.8
$1s \rightarrow 4p_{\pm}$	234.50	257.0	270.8	293.5	339.4	405.4
$1s \rightarrow 5p_{\pm}$	240.46		276.7	299.4	345.1	
E_i (cm^{-1})	252.14	274.6	288.4	311.1	356.8	423.0
E_i (meV)	31.26	34.1	35.8	38.6	44.2	52.5
		26.4	26.5	26.4	26.6	26.4
ΔE $(3p_{\pm} - 2p_{\pm})$	26.47					
		25.1	25.8	25.8	25.6	25.2
ΔE $(4p_{\pm} - 3p_{\pm})$	7.53	7.2	7.4	7.5	7.4	7.6
ΔE $(5p_{\pm} - 4p_{\pm})$	5.95		5.9	5.9	5.7	

C. Isotope shift of the optical dipole transitions of the donors HD4–HD7

Although the HD donors have only been observed in neutron-irradiated silicon after a H-plasma treatment there is no direct proof for the incorporation of hydrogen in the donors. In Figs. 3–5 a comparison of the PTIS spectra for donors HD4–HD7 generated in hydrogen or deuterium plasma is given. The optical dipole transitions in the deuterated samples are shifted towards larger energies relative to the line positions of the donors in the hydrogenated sample. The energy shift differs slightly for the different donors by $\Delta E = 0.1$–0.2 cm^{-1}. The exact values are given in Table II. Within the experimental error the isotope shift is clearly resolved for the transitions from the ground state to the $2p_{\pm}$ excited state up to the transitions into the $4p_{\pm}$ excited states of the different donors HD4–HD7. For the lines of the donor HD3 a clear shift was not observable due to the small signal strength. No shift is observed for the phosphorus lines at 316 and at 342 cm^{-1}.[18] The occurrence of the optical dipole transitions of the phosphorus donor after hydrogen plasma treatment as well as after deuterium treatment at the same photon energy demonstrates the high accuracy of the experimental setup and supports our identification of an isotope shift for the HD donors.

The chemical nature of many defects could be identified by the isotope shift of localized vibrational defect modes. In particular in silicon shallow donor-hydrogen and acceptor-hydrogen complexes were identified by deuterium isotope shifts.[22,23] The vibrational modes of hydrogen-donor and hydrogen-acceptor complexes are shifted to lower energies, when hydrogen is substituted by deuterium. The isotope effects on the optical dipole transitions determined in the present paper are very small compared to those found for the hydrogen local vibrations. Similar isotope shifts for optical transition

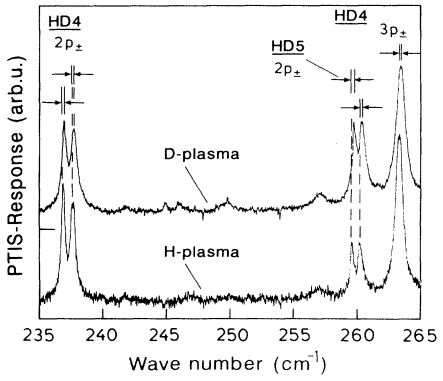

FIG. 3. PTIS signal of the donors HD4 and HD5 from *n*-irradiated silicon after H(D)-plasma treatment of 370 °C (360 °C) for 4 h and subsequent thermal annealing at 400 °C. The spectra were recorded with an unapodized resolution of 0.05 cm^{-1}.

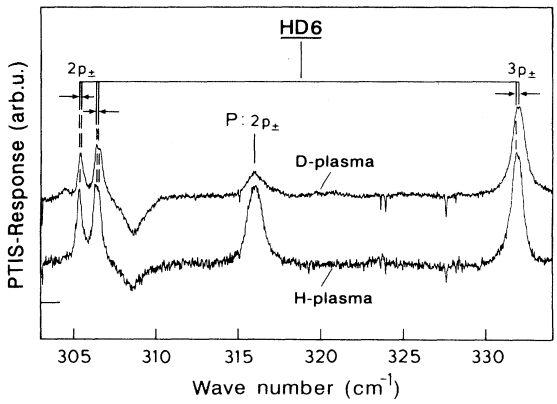

FIG. 4. Effect of the isotope substitution on the $1s \rightarrow 3p_{\pm}$ dipole transitions of the donor HD6. The spectra are taken on *n*-irradiated silicon samples after H-plasma treatment (370 °C, 4 h) or D-plasma treatment (360 °C, 4 h) and thermal annealing at 400 °C for 1 h with an unapodized resolution of 0.05 cm^{-1}.

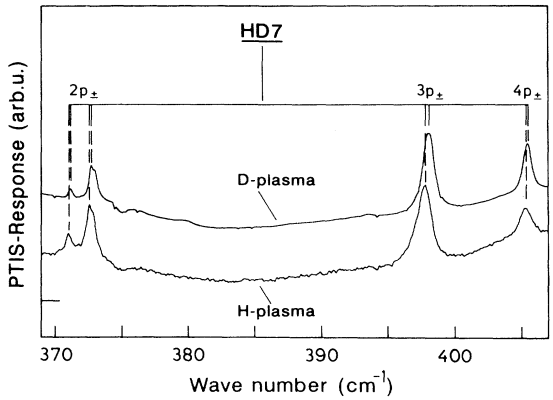

FIG. 5. Isotope shift of the optical dipole transitions of the donor HD7. The PTIS signals were taken on n-irradiated silicon after H(D)-plasma treatment at 320 °C (360 °C) for 3 h (4 h) and subsequent annealing for 1 h at 300 °C and 400 °C with an unapodized resolution of 0.05 cm^{-1}.

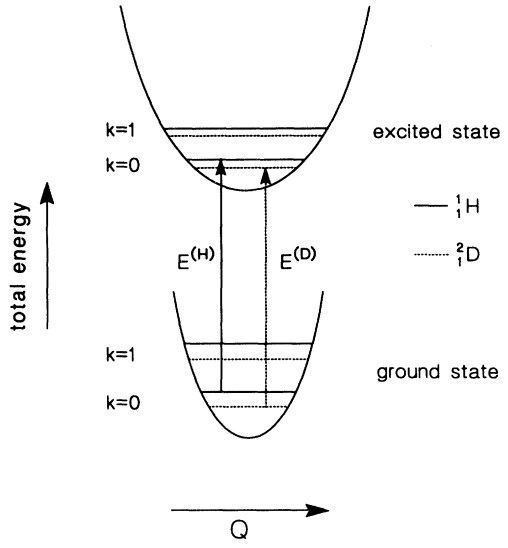

FIG. 6. Total energies of the ground state and the excited states of a donor. The optical dipole transitions between electronic levels are indicated by arrows. The vibrational levels of m_H and m_D are given as well.

between electronic shallow donor or acceptor states were already reported in Ge.[24]

The electronic level scheme for shallow donors is described by the effective-mass theory, however, coupling of the electronic levels with the lattice will modify the total energy of the defect system. To a first approximation the total energy of a defect is a linear combination of electronic and elastic energies. The elastic properties are in most cases described in the harmonic-oscillator approximation. A schematic configuration coordination diagram of the defect is given in Fig. 6.

Optical dipole transitions within this scheme are characterized by the conservation of the lattice deformation coordinate Q (Franck-Condon principle[25]) and are drawn as vertical arrows in Fig. 6. An isotope substitution of a defect atom species introduces a shift of the vibrational oscillator levels. An optical dipole transition is sensitive to such an isotope substitution only if the isotope-induced shifts of the vibronic levels are different in the ground and the excited states.

The sign and the magnitude of the isotope-induced shift of optical dipole transitions between electronic defect levels can be explained in terms of an approach by van Vechten,[26] which is based on a model by Heine and Henry.[27] The isotope shift in the optical dipole transition is attributed to a carrier induced mode softening and the change of the zero point vibration due to the change in impurity mass. The application of this approach to the HD donors suggests different force constants for the vibration of the donors in the ground and the excited states. The strong localization of an electron in the ground state corresponds to an increased polarization of the lattice in the vicinity of the defect compared to the excited states. This leads to a stiffer constant of the defect in the ground state than in the excited states. The substitution of m_H by m_D results in a larger shift of the vibronic levels towards smaller energies in the ground state compared to the excited states. Therefore the optical dipole transitions of the defect containing deuterium E^D appear at higher energies than the ones of the defect with hydrogen E^H (Fig. 6).

TABLE II. Observed isotope shifts ΔE for the donors HD4–HD7.

Donors	HD4	HD5	HD6	HD7
ΔE (cm^{-1})	0.15±0.05	0.20±0.05	0.10±0.05	0.15±0.05

D. Thermal stability of the donors HD3–HD7

The donors HD3–HD7 created in neutron-irradiated silicon during a hydrogen- (deuterium-) plasma treatment are thermally stable up to a temperature of 500 °C. After annealing at $T=600$ °C the PTIS signal vanishes. Figure 7 exhibits the PTIS signals of the donors HD3–HD7 after different annealing stages. Directly after the D-plasma treatment the optical dipole transitions occur on a photoionization continuum, while subsequent annealing at 400 °C leads to a reduction of the continuum especially at energies smaller than 300 cm^{-1}. A further increase of the annealing temperature to 500 °C causes a rapid decrease of the total PTIS signal, leading to the absence of any PTIS signal after annealing at 600 °C.

The different donors show different annealing behavior. The donors HD4, HD5, and HD7 are present directly after the H(D)-plasma treatment. They are also observed after thermal anneals at temperatures of 300 °C–500 °C with varying relative intensities. Directly after the deuterium plasma treatment as shown in Fig. 7(a) and also after a subsequent annealing at 300 °C the dipole transitions of the donor HD4 are the most intense, the transitions of HD5 show up with the same signal strength at an additional annealing step at 400 °C—Fig. 7(b). Increasing the annealing temperature to 500 °C makes the ionization lines of HD5 the main contribution to the total PTIS

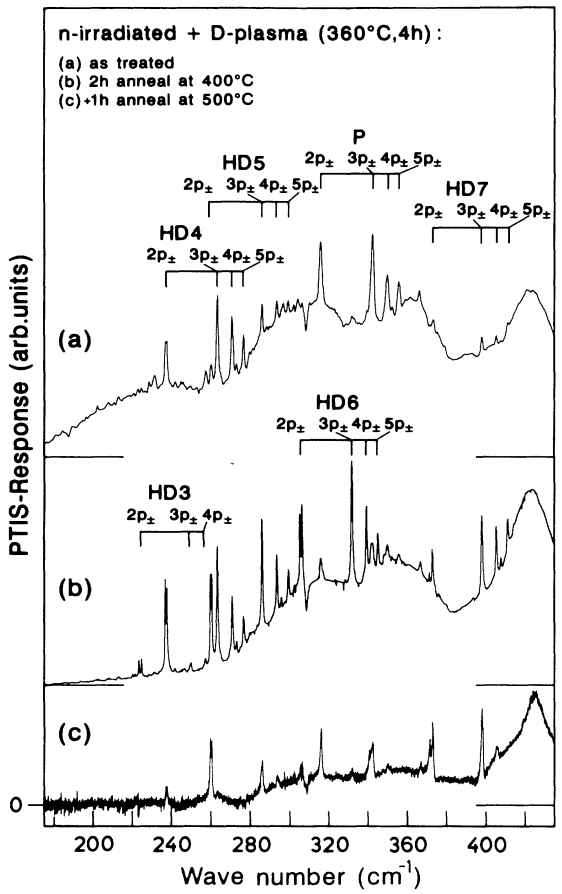

FIG. 7. PTIS signals of donors HD3–HD7 after different annealing processes. The spectra were recorded with the following unapodized resolutions: (a) 0.5 cm^{-1}, (b) and (c) 0.1 cm^{-1}.

signal. The optical dipole transitions of the donor HD6, are not observable without thermal annealing following the D-plasma treatment (contrary to the hydrogen plasma treatment). The PTIS signal of donor HD3 appears only at an annealing temperature of 400 °C.

IV. DISCUSSION

The results obtained by means of photothermal ionization spectroscopy give sufficient information for an understanding of the formation of the new HD donors. In addition to three shallow donors HD4–HD6 which could already be observed at the sensitivity limit of PTIS in proton implanted silicon[9] the hydrogen plasma treatment of *n*-irradiated silicon creates several new donors in much higher concentrations. The more efficient formation of the new donors in the neutron-irradiated and hydrogen-plasma-treated samples can be explained by the more uniform neutron damage process. In the literature shallow donors were already detected using Hall-effect measurements in NTD silicon, which was grown in H_2 ambient.[10] The identity of the donors of Ref. 10 to the shallow donors observed in the present paper cannot be established due to the difference in the measurement techniques used in the two experiments.

The shallow donors HD3–HD7 are detected by PTIS in H-plasma treated silicon crystals which were damaged by neutron irradiation. The donors HD3–HD7 have central-cell corrections ranging from 2.8 to 21.2 meV. No PTIS signal could be observed in neutron-irradiated silicon after thermal annealing in atmospheres of hydrogen, nitrogen, or argon gases. The diffusion of atomic hydrogen ions seems to be necessary for the donor formation. The steplike spreading resistance profile is evidence for a diffusion process of atomic hydrogen from the rf plasma into the sample. Radiation induced defects have to be present in the sample to bind the atomic hydrogen. We interpret the formation of the HD donors as a binding between the radiation induced defects and atomic hydrogen. This reaction takes place at elevated temperatures between 250–400 °C. As the signal strength of the donor HD3 is very small in the PTIS spectrum, we could not detect a clear shift of its optical dipole transitions. However it can be suggested that the donor HD3 also belongs to the HD-donor family.

V. CONCLUSION

Photothermal ionization spectroscopy on neutron-irradiated and subsequently hydrogen-plasma-treated silicon reveals the existence of several new shallow donors. These donors HD3–HD7 having ionization energies between 34–53 meV are well described by the effective-mass theory. The donors are the result of a defect reaction of hydrogen with radiation induced defects. The donors are created at temperatures between 250–400 °C in heavily damaged silicon in the presence of hydrogen. Substituting hydrogen by deuterium leads to a shift of the optical dipole transitions of the donors HD4–HD7 towards higher energies by $\Delta E = 0.1-0.2$ cm^{-1}. The observed hydrogen-induced isotope shift is very small and can be qualitatively interpreted in terms of a model proposed by Heine and Henry.[27] To our knowledge the new hydrogen donors are the first evidence for a hydrogen initiated transformation of deep centers to shallow effective-mass-like centers.

ACKNOWLEDGMENTS

The authors would like to thank L. Genzel and H.-J. Queisser for their interest and continuous support. The technical support of W. Rauscher and H. W. Krause as well as the expert technical advice of W. König is gratefully acknowledged. We thank M. Rinker for this help in the operation of the Nd-YAG laser. We are indebted to W. Zulehner who donated the neutron-irradiated samples. Special thanks are due to W. Wondrak for the spreading resistance measurements.

*Present address: Department of Physics, King's College London, Strand, London WC2R 2LS, U.K.

[1]S. J. Pearton, in *Oxygen, Carbon, Hydrogen, and Nitrogen in Silicon,* edited by J. C. Mikkelsen, S. J. Pearton, J. W. Corbett, and S. J. Pennycook, MRS Symposia Proceedings No. 59 (Materials Research Society, Pittsburgh, 1986), p. 457.

[2]K. Bergmann, M. Stavola, S. J. Pearton, and T. Hayes, Phys. Rev. B **38**, 9643 (1988).

[3]M. Stavola, K. Bergmann, S. J. Pearton, and J. Lopata, Phys. Rev. Lett. **61**, 2786 (1988).

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

[5]J. Krynicki, J. C. Muller, P. Siffert, I. Brylowska, and K. Paprocki, Phys. Status Solidi A **100**, 245 (1987).

[6]Y. Omura, Y. Zohta, and M. Kanazawa, Solid State Commun. **11**, 26 (1972); Phys. Status Solidi A **15**, 93 (1973).

[7]S. R. Wilson, W. M. Paulson, W. F. Krolikowski, D. Fathy, J. D. Gressett, A. H. Hamdi, and F. D. McDaniel in *Ion Implantation and Ion Beam Processing of Materials,* edited by G. K. Hubler, O. W. Holland, C. R. Clayton, and C. W. White, MRS Symposia Proceedings No. 27 (Materials Research Society, Pittsburgh, 1084), p. 287.

[8]J. Hartung, Ph.D. thesis, University of Stuttgart (1991).

[9]J. Hartung and J. Weber (unpublished).

[10]Z. Wang and L. Lin, in *Proceedings of the 4th International Conference Neutron Trans. Dop. Semi.,* edited by R. D. Larrabe (Plenum, New York, 1983), p. 311.

[11]J. Hartung and J. Weber, Mater. Sci. Eng. B **4**, 47 (1989).

[12]J. Hartung, J. Weber, and L. Genzel, Mater. Sci. Forum **65&66**, 157 (1990).

[13]T. M. Lifshits and F. Ya. Nad', Dokl. Akad. Nauk **162**, 801 (1965) [Sov. Phys. Dokl. **10**, 532 (1965)]; for a review see S. Kogan and T. M. Lifshits, Phys. Status Solidi A **39**, 11 (1977).

[14]K. Lark-Horovitz, in *Semiconducting Materials,* edited by H. K. Henisch (Butterworths, London, 1951), p. 47.

[15]R. H. Norton and R. Beer, J. Opt. Soc. Am. **66**, 259 (1976).

[16]W. Kohn, in *Solid State Physics: Research in Physics and Applications,* edited by. F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[17]E. Janzén, R. Stedman, G. Grossman, and H. G. Grimmeiss, Phys. Rev. B **29**, 1907 (1984); R. A. Faulkner, Phys. Rev. **184**, 713 (1969).

[18]R. K. Ramdas and R. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981).

[19]P. Wagner, C. Holm, E. Sirtl, R. Oeder, and W. Zulehner, in *Advances in Solid State Physics (Festkörperprobleme),* edited by P. Grosse (Vieweg, Braunschweig, 1984), Vol. 26, p. 191.

[20]L. T. Ho and A. K. Ramdas, Phys. Rev. B **5**, 462 (1972).

[21]M. S. Skolnick, L. Eaves, R. A. Stradling, J. C. Portal, and S. Askenazy, Solid State Commun. **15**, 1403 (1974).

[22]M. Stavola, S. J. Pearton, J. Lopata, and W. C. Dautremont-Smith, Phys. Rev. B **37**, 8313 (1988).

[23]K. Bergmann, M. Stavola, S. J. Pearton, and J. Lopata, Phys. Rev. B **37**, 2770 (1988).

[24]E. E. Haller, Phys. Rev. Lett. **40**, 584 (1978).

[25]O. Madelung, *Introduction to Solid-State Theory,* edited by M. Cardona, P. Fulde, and H.-J. Queisser, Springer Series in Solid State Sciences Vol. 2 (Springer, Berlin, 1981).

[26]J. A. van Vechten, Phys. Rev. B **13**, 946 (1976).

[27]V. Heine and C. H. Henry, Phys. Rev. **11**, 3795 (1975).