RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 17 15 JUNE 1987-I

Set of five related photoluminescence defects in silicon formed through nitrogen-carbon interactions

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(Received 9 February 1987)

We study four new defect photoluminescence lines, $N2$ (758.0 meV), $N3$ (761.5 meV), $N4$ (767.4 meV), and $N5$ (772.4 meV), appearing in silicon after nitrogen implantation. The defects are closely related to the $N1$ (745.6 meV) defect recently associated with single nitrogen and carbon atoms. It is demonstrated here by annealing studies and isotope shifts that the new defects incorporate nitrogen and carbon as well, and that the $N3$–$N5$ defects need additional interactions with other impurities (probably oxygen) to form. The optical properties suggest that $N1$–$N5$ form a set of defects with similar basic N-C configurations.

Nitrogen, a group-V impurity, does not act as a shallow donor in crystalline silicon as do P, As, Sb, and Bi, but shows exceptional behavior.[1] The incorporation and chemical bonding of nitrogen in silicon have become of particular technological interest (apart from academic studies), since nitrogen is introduced into silicon in a number of processing steps.[1] Several nitrogen-associated defects have been studied in the past by electron spin resonance (ESR),[2-6] deep-level transient spectroscopy (DLTS),[7] and photoluminescence (PL).[8-10] However, no positive identification of the defect structure and the nitrogen partners in these defects has emerged, with the exception of the EPR SL5 spectrum which was ascribed to a trigonally distorted substitutional single nitrogen atom.[2,3] Recent infrared (ir) absorption spectroscopy involving sequential ^{14}N and ^{15}N implantation has shown that nitrogen pairing is the preferential mode for the bonding of N into silicon for a wide range of processing conditions.[11] Interaction of nitrogen with oxygen has been demonstrated by sequential implantation of nitrogen and oxygen with overlapping profiles.[12] Finally, a PL spectrum $N1$ with its no-phonon (NP) line at 745.6 meV has been studied in some detail. Isotope shifts of the NP line and of a local mode satellite showed evidence for optically active single nitrogen and carbon atoms in the defect, demonstrating the importance of nitrogen-carbon interactions as well.[13-15]

In their study of the $N1$ (745.6 meV) photoluminescence spectrum the present authors briefly mentioned four other PL defect lines, $N2$ (758.0 meV), $N3$ (761.5 meV), $N4$ (767.4 meV), and $N5$ (772.4 meV), which likewise seemed to depend on nitrogen and carbon implantation and emerged in distinct annealing stages.[14,15] Here, these lines are studied in detail employing nitrogen- and carbon-isotope implantation and isochronal annealing of samples implanted with N, N plus C, Ar, and C. We confirm that these four defects incorporate (single) nitrogen and carbon atoms and show that their optical properties are very similar to those of $N1$, implying that the defects are closely related.

The implantation doses are in all cases 5×10^{14} cm^{-2}. The following float-zone (FZ) and Czochrazlski-grown (CZ) starting materials are used: (1) Si:P (FZ) 240 Ω cm, (2) Si:P (FZ) 10 Ω cm, (3) Si:B (CZ) 20 Ω cm, (4) Si:B (CZ) 0.3 Ω cm.

Figure 1 is an overview spectrum obtained from the Si:B, 20 Ω cm sample after sequential nitrogen and carimplantation with overlapping profiles and subsequent annealing at 550 °C for 1 h. Observed are the recombination line of boron-bound excitons (BE-TO) and a line at 0.79 eV (1.569 μm) which is not the C line. Other radiative defects due to the damage are annealed out at 550 °C. The lines of interest here are the group between ~1.60 and ~1.67 μm. The lowest energy line is $N1$ at 1.6624 μm (745.6 meV). Our earlier study of this line has shown[13] that it is due to an exciton at a nitrogen-carbon defect of monoclinic (C_{1h}) symmetry, which binds the electron by only ~50 meV but localizes both particles by as much as $E_{\text{loc}} = E_g - h\nu(N1) = 423.9$ meV. Compared to this large electron-hole binding energy the overall spacing of the N lines of 26.8 meV is small, suggesting that the electronic structure of all optical defects is similar. The portion of the PL spectrum with $N1$–$N5$ is represented in Fig. 2 on expanded scales. This reveals a doublet structure of the $N4$ peak. The larger component of the doublet is a different line, the 0.767-eV (P) line, known to emerge in crucible-grown oxygen-rich silicon upon heat treatment at 400–500 °C.[18-22] In our study, this line is already observed in the starting material. Its intensity is reduced as a consequence of the implantation and recovers between

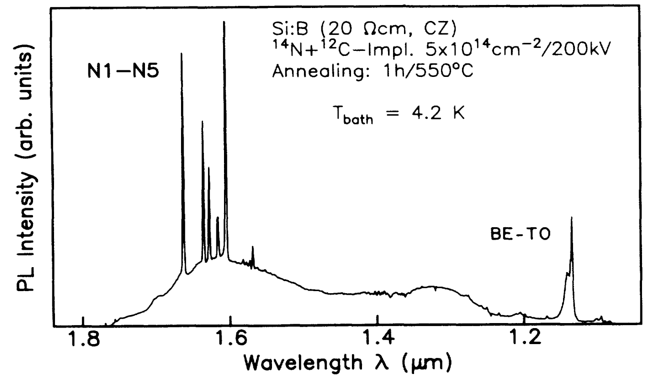

FIG. 1. Photoluminescence overview spectrum of a Si:B (10-Ω cm) sample after sequential ^{14}N and ^{12}C implantation with overlapping profiles and 550 °C annealing for 1 h. The five sharp lines at 1.6 μm and higher wavelengths are $N1$–$N5$ in the order indicated. [The weak sharp line at 1.569 μm is not the C line (Refs. 16 and 17).] (BE)-TO denotes the TO-phonon assisted recombination of boron-bound excitons with the multiple-bound-exciton lines not fully resolved. The spectrum is not corrected for the spectral sensitivity function of the Ge detector employed.

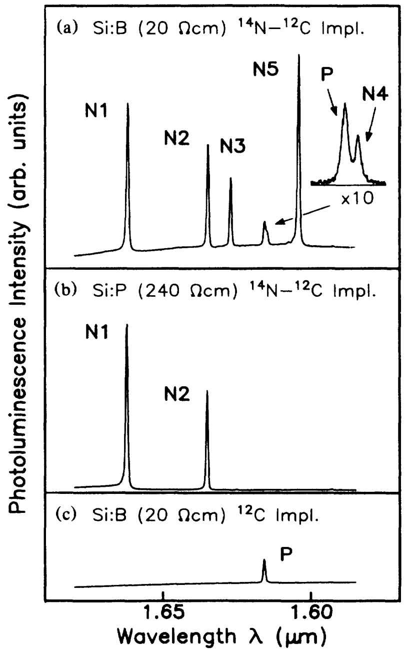

FIG. 2. Comparison of N-line PL spectra in different starting materials: (a) Si:B, 20 Ω cm, sequential implantation of ^{14}N and ^{12}C, annealing at 550 °C for 1 h. (b) Si:P, 240 Ω cm, same treatment as (a). (c) Si:B, 20 Ω cm, implantation of only ^{12}C, annealing at 550 °C for 1 h. The P line is the 0.767-eV emission from an oxygen-dependent heat-induced defect.

500° and 550 °C. The identification of this line is unambiguous due to its spectral position, the characteristic temperature dependence, and its associated excited-state transitions.[19,22,23]

As exemplified in Fig. 2, there is a difference in the appearance of the N lines for oxygen-rich CZ material and oxygen-poor FZ material. The pulled silicon shows first the $N1$ line after nitrogen-carbon implantation and room-temperature annealing. $N1$ increases steadily upon isochronal annealing in steps of 100 °C up to 400 °C with a gain of $\sim$10 in intensity. $N5$ grows in between 200° and 300 °C and becomes about twice as strong as $N1$ at 400 °C. In the relatively small temperature interval between 500° and 550 °C both lines increase by a factor of $\sim$5, and at the same time $N2$–$N4$ emerge. The 550 °C annealing stage shown in Fig. 2(a) represents the maximum intensity for all N lines. Further annealing leads to a drastic reduction of all line intensities: $N3$–$N5$ disappear at 650 °C, $N2$ closely above 650 °C. Only $N1$ retains $\sim$10% of its maximum strength at 650 °C, and hence it is the most stable defect among $N1$–$N5$. These observations have been made for several samples of the CZ 20- and 0.3-Ω cm material. Implantation of these samples with nitrogen alone yields exclusively the $N1$–$N5$ lines, but at much smaller intensities than for nitrogen-carbon implantation. The floating-zone material (240 and 10 Ω cm) shows for all samples studied the emergence and out anneal of $N1$ and $N2$ similar to pulled silicon. Typical spectra are shown in Fig. 2(b). None of the $N3$–$N5$ lines is observed for this material in the whole range of annealing temperatures. As the only exception, $N3$–$N5$ lines appear at 550 °C (but not below 500 °C or above 600 °C) in one sample of Si:P, 240 Ω cm, and a spectrum

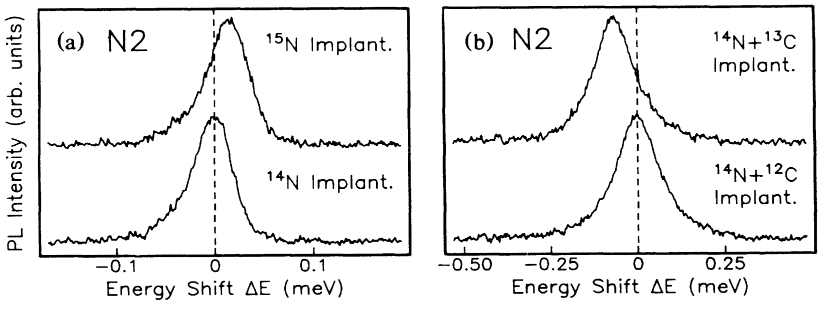

FIG. 3. Isotope shifts of the $N2$ line: (a) ^{14}N and ^{15}N shift in a Si:P, 240-Ω cm sample; (b) ^{12}C and ^{13}C shift in a Si:B, 20-Ω cm sample.

TABLE I. Effect of ^{14}N and ^{15}N isotopic substitution and of ^{12}C and ^{13}C isotopic substitution on the N lines.

Line	Energy (meV)	$E(^{15}\text{N})-E(^{14}\text{N})$ (meV)	$E(^{13}\text{C})-E(^{12}\text{C})$ (meV)
$N1$	745.6	$+0.021\pm0.003$[a]	-0.043 ± 0.007[a]
$N2$	758.0	$+0.015\pm0.003$	-0.067 ± 0.007
$N3$	761.5		-0.064 ± 0.007
$N4$	767.4		-0.059 ± 0.003
$N5$	772.4		-0.051 ± 0.007

[a] Reference 13.

similar to Fig. 2(a) is observed. We conclude that this sample may not be representative. With the inclusion of the latter case a strict relationship can be stated: Samples showing all lines $N1$–$N5$ also exhibit the P line; when the P line is not observed $N3$–$N5$ do not show up either. The relationship suggests that oxygen plays a role in the formation of $N3$–$N5$.

To check further the dependence of the N lines on nitrogen or sequential nitrogen-carbon implantation, samples of Si:P (240 Ω cm), Si:B (20 Ω cm), and Si:B (0.3 Ω cm) were implanted with ^{40}Ar and subjected to the heat treatment described above. Only in the pulled samples the lines $N1$ and $N3$ were detected with intensities smaller by a factor of ~100 than for nitrogen-carbon implantation. We ascribe this effect to small doping concentrations of the starting material with nitrogen and carbon from which the defects can form after damage by the Ar implantation. This is consistent with the previous result[13] that arbitrary ion implantation of nitrogen-doped silicon with subsequent appropriate annealing can generate the $N1$ defect. Finally, the requirement of nitrogen for the formation of the N lines was checked by implantation of Si:B (20 Ω cm) with ^{12}C. Up to 550 °C annealing, none of the N lines appeared after this procedure, merely the P line was observed with approximately the same intensity as in the starting material [Fig. 2(c)].

From these implantation studies it is clear that nitrogen is needed to form any of the N defects. Additional carbon implantation drastically enhances the intensities of $N1$, $N2$, and $N5$, whereas $N3$ and $N4$ need the carbon implantation to be observed at all. Therefore, we conclude that all of the defects form through nitrogen-carbon interactions; however, $N3$–$N5$ need other impurities in addition to form.

Line shifts observed in high-resolution photoluminescence due to isotopic substitution give direct evidence for nitrogen and/or carbon being incorporated in the defects $N2$–$N5$. To record reliably the small shifts involved we proceed as described previously:[13] The monochromator (focal length 1 m) is set fixed at the line position and the spectrum is scanned by rotating an electrically driven quartz plate in the optical path inside the spectrometer. The effects of ^{14}N and ^{15}N isotopic substitution and of ^{12}C and ^{13}C isotopic substitution on the $N2$ line are shown in Fig. 3. Substitution of ^{14}N by ^{15}N [Fig. 3(a)] leads to a high-energy shift of $N2$ by 0.015 meV, close to the corresponding shift of $N1$ (cf. Table I). The line shape of $N2$ exhibits a low-energy tail and is identical to that of $N1$.[13] The shift induced by substitution of ^{12}C by ^{13}C [Fig. 3(b)] is −0.067 meV, also similar to that observed for the $N1$ line.

Sequential nitrogen-carbon implantations are used to study the carbon-isotope effects on the $N3$, $N4$, and $N5$ lines. In all three cases, the ^{12}C and ^{13}C shifts are again close to those exhibited by $N1$ and $N2$. In Fig. 4 and in Fig. 3(b) all lines are broadened compared to the $N2$ line in Fig. 3(a). It is unclear whether the broadening is caused by the carbon implantation or the high oxygen contents of the starting matrial. Irrespective of this ques-

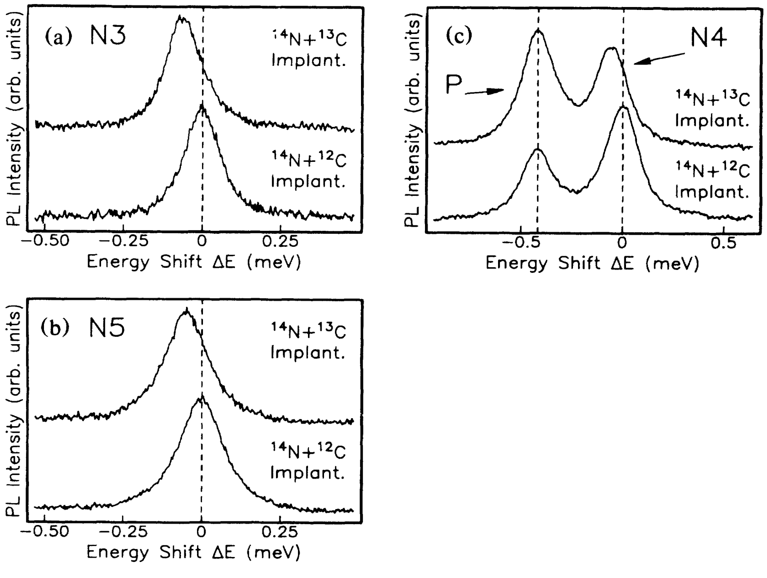

FIG. 4. Isotope shifts of the $N3$, $N4$, and $N5$ lines due to substitution of ^{12}C by ^{13}C after sequential nitrogen-carbon implantation and annealing at 550 °C. In the $N4$ spectrum, the P line is not affected. Starting material in all cases is pulled silicon.

tion, it was made sure by comparison of the $N1$ line in float-zone silicon with pulled silicon (where it was generated by ^{14}N or sequential ^{14}N and ^{12}C implantation, respectively) that the broadening does not affect the line positions. Moreover, as independent proofs neither the P line nor the boron-exciton line show a shift to within an accuracy of ± 0.003 meV. The P line position, in particular, is known to be very sensitive to stress[22] and would easily indicate shifts due to internal strain.

We summarize the conclusions that can be drawn from the present data in conjunction with earlier data on the $N1$ line.[13-15] (1) All N line defects bind an exciton strongly with ~400 meV, much larger than the scatter (~27 meV) between the individual lines. This hints to similar electronic properties. (2) All N-line defects incorporate nitrogen and carbon as shown by implantation and annealing studies and isotope shifts. Comparison of the isotope effects in $N2$–$N5$ to those in $N1$ suggests that single optically active atoms are involved. (3) In all cases studied, corresponding isotope shifts are very similar in size. For nitrogen, they are positive for the heavier isotope; for carbon they are negative for the heavier isotope. The opposite signs of the effects demonstrate that two different local modes are involved. The strikingly similar values of the corresponding shifts suggest equivalent bonding strengths of nitrogen and carbon in all of the defects, and hence, similar microscopic structure. (4) Boron and phosphorus seem to play no role in the formation of the defects; however, oxygen is very likely involved in the defects $N3$–$N5$. (5) $N1$ is the primary and most stable defect. On the basis of the arguments given above, the remaining less-stable defects $N2$–$N5$ can be identified with modifications of $N1$; they are possibly configurations in which additional atoms (like oxygen) are relatively loosely bonded to the primary $N1$ defect and are released at temperatures slightly before $N1$ anneals out.

Local mode spectra of $N2$–$N5$ could prove this concept. Unfortunately, they are not easy to study, since such spectra are obscured by the strong $N1$ line and its local mode spectrum. Symmetry assignments and a study of the yet-missing nitrogen-isotope effects on $N3$, $N4$, and $N5$ defects would also be informative. Such work is in progress. Even with the present lack of such data it is clear that the N defects constitute a set of related centers that form through carbon-nitrogen interactions.

We thank M. H. Pilkuhn for his encouragement of this study. This work was supported by the Deutsche Forschungsgemeinschaft under Contract No. Sa 311/4-1.

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