

ideality factor $n = 1.2$ for over six orders of magnitude. Figure 4 illustrates the reverse breakdown and the photoreponse for these diodes. The reverse breakdown is comparable to that obtained for as-grown or Zn or Cd diffused junctions.¹⁴ C - V data, shown in Fig. 5, yield a linear plot of C^{-2} vs V , indicating an abrupt junction. This result is typical for the rapid anneals.

In conclusion, we have presented results for rapid thermal annealing of Be-implanted InGaAs. These results demonstrate that significant improvements in electrical activation and peak concentration can be achieved using short anneals rather than conventional furnace anneals. Be implantation should provide a controllable alternative to acceptor diffusion for the formation of shallow junctions with acceptor concentrations greater than 10^{18} cm^{-3} .

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Nitrogen in silicon: Towards the identification of the 1.1223-eV (*A,B,C*) photoluminescence lines

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We show that the "new" photoluminescence line in silicon at 1.1223 eV which was recently reported and ascribed to a nitrogen complex is identical with the *A* line of the isoelectronic *A, B, C* exciton system as previously studied. New data are presented which confirm that nitrogen is incorporated in the optical center. Further defect constituents cannot be identified on the basis of the present data.

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Tajima *et al.*¹ have recently reported a "new" photoluminescence (PL) line in silicon at a photon energy of 1.1223 eV (Fig. 1). This line exclusively appeared in samples which were nitrogen doped. The doping was performed by adding either N_2 gas into Ar atmosphere or Si_3N_4 into polycrystalline Si during the crystal growth. The total nitrogen concentration as determined by activation analysis amounted to $3.2 \times 10^{15} \text{ cm}^{-3}$. The nitrogen concentration was also tested by the characteristic IR absorption at wave numbers of 767 and 963 cm^{-1} . Tajima *et al.*¹ and later Tajima² found that the PL intensities of the 1.1223-eV line were directly related with the nitrogen contents of the samples. This correlation led the authors to assume that the line originates in a nitrogen complex as the optical center. In these works,^{1,2} the PL

was recorded at 4.2 K, and even in the samples of the highest *N* concentration the 1.1223-eV line (labelled *N* line) was only weakly observed in comparison with the phosphorus bound exciton and multiple bound exciton spectra (Fig. 1).

This letter reports two findings: first we show that the *N* line is not principally new but is the *A* transition of the well-studied *A, B, C* photoluminescence system.^{3,4} Second we confirm the suggestion that nitrogen is incorporated in the optical defect based on PL measurements on intentionally N-doped silicon crystals.

The *N* line arises at the exact spectral position of the *A* line and suggests that both lines are identical. Thanks to the courtesy of M. Tajima, we could test this suspicion by studying the photoluminescence of the *original* N-doped crystals at 4.2 K and higher temperatures. The important PL feature which gives us confidence as to the identity of the *A* line and the *N* line is the appearance of the excited-state *C* line (cf.

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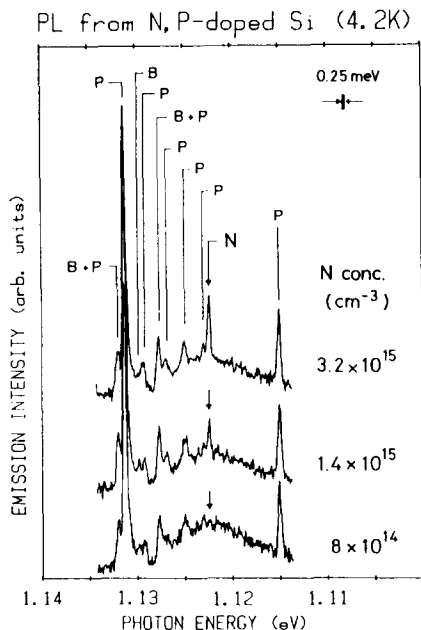


FIG. 1. Photoluminescence spectra of N-doped silicon samples showing the *N* line (1.1223 eV) along with P and B associated bound exciton spectra (from Ref. 2, courtesy of M. Tajima).

Fig. 2) which we observed in the samples provided by M. Tajima when high-resolution spectra were recorded at elevated temperatures up to 15 K.

The *A*, *B*, *C* photoluminescence lines (Fig. 2) were discovered in a few Si samples by Weber *et al.*^{3,4} who demonstrated that they are due to an exciton localized at an isoelectronic defect of axial symmetry around $\langle 111 \rangle$ (C_{3v}). The *A* line at 1.1223 eV originates in the radiative decay of the $J_z = \pm 1$ exciton state to the crystal ground state, $J = 0$. The "forbidden" *B* line at 0.9 meV lower energy is due to the $J_z = \pm 2$ exciton state and shows up only under external perturbations by a magnetic or stress field. The relatively broad *C* line stems from three nearly degenerate excited exciton states at an excess energy of 3.1 meV. It was argued that the electron is primarily bound to the defect capturing the hole by its Coulombic field and suggesting that the localized exciton can be described in terms of an isoelectronic acceptor. In fact, Wagner and Sauer⁵ by photoluminescence excitation spectroscopy with a tunable color center laser detected several highly excited states which could be classified according to an axial pseudoacceptor with an ionization energy of $E_i = 36.7$ meV.

Although the optical properties of the *A*, *B*, *C* lines are well understood the chemical nature of the binding center remained unidentified. A former tentative identification of one trap constituent with carbon³ could not be confirmed in later experiments⁴ and must now be considered insignificant. The present identification of the *N* line with the *A* line suggests that nitrogen is incorporated in the optical center. There is, however, a drastic quantitative discrepancy with respect to the PL intensities in our previous samples exhibiting the *A*, *B*, *C* lines and the N-doped samples from M. Tajima. The discrepancy amounts to an approximate 10^3 : 1 ratio between our previous "standard" sample, Si:Al (2.5 Ω cm) and the sample of the highest nitrogen concentration provided by M. Tajima. The discrepancy refers to the maxi-

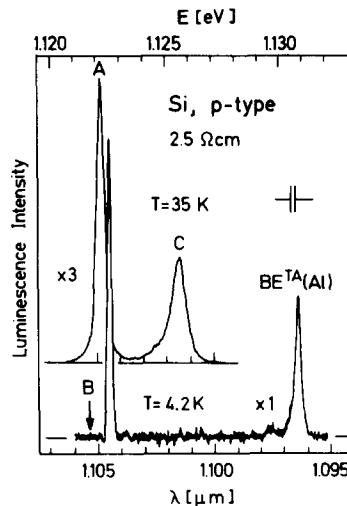


FIG. 2. *A*, *B*, *C* photoluminescence spectrum at two temperatures. The position of the "forbidden" *B* line is indicated by an arrow (see text). Also shown is the TA phonon-assisted bound exciton line due to Al acceptor doping.

mum intensity of either sample exhibited at different temperatures above 4.2 K. The relative weakness of the *N* line may indicate that either a contaminant is incorporated and is optically active in the defect which is unintentionally introduced with N, or a cooperator of N is needed in the defect which is contained in only small concentrations in the samples studied by Tajima and coworkers. It is also possible that N exists in different stages of solution or precipitation, respectively, in the different samples; generally, it is not known at the present time which portion of the absolute N concentration in Si as determined by activation analysis dissolves or precipitates. In any case, the enormous PL discrepancy requires further experiments on new samples to support the nitrogen hypothesis.

We have studied seven new float-zone or crucible pulled Si samples which were intentionally doped with N. The FZ crystals were grown as usual and the doping was performed by working in an ambient with different concentrations of N_2 gas. The CZ crystals were grown from silica crucibles under special conditions using no magnetic field and contain unusually low concentrations of oxygen. They were doped by adding Si_3N_4 powder to the melt. The concentrations of N, C, O and of the shallow impurities B, Al, P were determined by infrared absorption measurements using standard calibration factors. These data are listed in the table.

Our essential result is that *all* new samples exhibit the *A*, *B*, *C* photoluminescence. The intensities are partially almost as strong ($\approx 70\%$) as in the best sample of our previous study.⁴ Thus the above-mentioned discrepancy is also existent for the new samples and remains not understood. We refer to the elusive nature of the defect and recall that the *A*, *B*, *C* lines were heretofore observed in only nine samples among dozens investigated in the previous work,⁴ and was in only one case observed in an independent work.⁶ This is a very scarce appearance and therefore, we consider the present result as strong evidence for N being incorporated in the optical center.

To be more quantitative, we list in the table the maximum PL intensities which were observed for all samples between 12 and 14 K. As an accurate comparison of PL

TABLE I. Growth method, impurity concentrations, and *A* line PL intensities of the present silicon samples. No. 4 is a neutron transmutation doped crystal, the PL was recorded after heating to 770 °C and quenching in silicon oil. No. 5 contains nitride precipitates and dislocations.

Sample No.	Growth method	[N]	[O] (in 10 ¹⁵ cm ⁻³)	[C]	[B]	[Al] (in 10 ¹³ cm ⁻³)	[P]	Shallow impurities according to PL	<i>A</i> line intensity (arb. units)
1	CZ	8.0	390	53	26.0	3.5	...	B, Al, P	140
2	CZ	2.4	380	69	220.0	12.0	...	B, very little Al and P	90
6	FZ	1.2	1.3	13	7.5	P, very little As	66
3	FZ	1.8	3.3	8	< 0.3	< 0.3	13.0	P	62
7	FZ	0.7	1.5	19	0.2	P, little B	20
	FZ								
4	(NTD)	0.6	1.7	6	< 0.3	< 0.3	4.0	P	20
5	CZ	5.7	300	22	28.0	4.0	...	B, Al, P	0.8

intensities from different samples is problematic the numbers given are only an approximate measure of the relative concentrations of the optical defect. With the exception of sample No. 5 where N is known to have precipitated, a rough correlation between the concentration of dissolved N (according to the infrared measuring technique) and the PL intensities exists. There is no evidence for a correlation with any other impurity, neither shallow donors or acceptors nor oxygen or carbon. This negative result is in particular interesting for the group III acceptors because these could be expected to be partners of (substitutional) nitrogen in the formation of the isoelectronic center. We emphasize that a previous estimate of the concentration of the *A* line center⁴ yielded a maximum value of $\approx 10^{13} \text{ cm}^{-3}$. This is much lower than the N concentration of the present samples and indicates that only a small fraction of the N atoms is optically active. This could be understood if the fraction was determined by the concentration of the anticipated cooperators of N in the defect.

Our present *A*, *B*, *C* line center is diamagnetic and seems to be well distinguished from the paramagnetic defect which was reported by Brower^{7,8} in N_2^+ implanted silicon after pulsed-ruby laser annealing. This defect (exhibiting the SL5 spectrum) was interpreted as a single substitutional nitrogen donor distorted off the tetragonal site along $\langle 111 \rangle$. Brower has also described the SL6 and SL7 spectra of C_{3v} symmetry which are associated with N and form in samples containing SL5 upon thermal annealing at 400 °C. More-

over, he has observed two other, isotropic resonances which are possibly associated with N. Finally, Ammerlaan and Sprenger⁹ observed an EPR signal in Si:Al which they could unambiguously ascribe to N and found that the Al doping of the crystal was not essential for observing the signal. In all these cases, except for SL5, the data are too poor to discuss possible relations of the EPR centers with the optical center generating the *A*, *B*, *C* photoluminescence lines.

In conclusion, our data give evidence that N is incorporated in the isoelectronic *A*, *B*, *C* line defect. The present sample data give no indication of further defect constituents as are expected from the optical properties.

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