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# ELECTRON PARAMAGNETIC RESONANCE OF A NITROGEN-RELATED CENTRE IN ELECTRON IRRADIATED SILICON

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The observation by electron paramagnetic resonance of a centre related to nitrogen as an impurity in silicon is reported. While all previously reported nitrogen-related centres in silicon were produced by nitrogen implantation, the present centre is observed after electron irradiation of aluminiumdoped silicon at low temperatures. We tentatively identify the observed spectrum, labeled Si-NL26, with neutral interstitial nitrogen. Possible models for the incorporation of nitrogen in silicon, before the irradiation, after the irradiation and after thermal anneal, are discussed.

## 1. INTRODUCTION

RECENTLY, much attention has been paid to the behaviour of nitrogen as an impurity in silicon crystals. One of the most remarkable facts is that nitrogen behaves drastically different from the other group V impurities (P, As, Sb), which are the common shallow donors.

The solubility of nitrogen in silicon near the melting point is  $4.5 \times 10^{15}$  cm<sup>-3</sup>, as determined by activation analysis [1]. This is at least four orders of magnitude below the solubility of the shallow donors. Also, the electrical behaviour is different. In electrical measurements a donor activity of at most a few percent of the nitrogen concentration was found. Mitchell *et al.* [2] reported a shallow level at  $E_c - 0.017$  eV, determined from the Hall resistivity as a function of temperature in nitrogen-implanted silicon after annealing. More recently, measurements by deep level transient spectroscopy were performed in N-doped silicon [3] which revealed two deep levels probably associated with nitrogen, but again the concentrations were well below 1% of the total nitrogen concentration.

Two infrared absorption bands have been reported, with wavenumbers of 963 and 764 cm<sup>-1</sup> [4]. Their intensities were shown to be proportional to the nitrogen concentration. Furthermore, a photoluminescence band at an energy of 1.1223 eV was associated with nitrogen [5, 20].

Several electron paramagnetic resonance (EPR) observations have been associated with nitrogen. Table 1 summarizes the parameters of these spectra. The spectrum labeled SL5 was investigated in most detail [6-8]. It is ascribed to substitutional nitrogen trigonally distorted from the regular site, behaving as a deep donor

analogous to nitrogen in diamond [9]. It is observed after nitrogen implantation and subsequent annealing, but less than 10% of the implanted amount was observed in EPR.

Table 1 also includes the parameters of the new nitrogen related EPR spectrum NL26, which we observed. The next sections of this paper will describe its parameters and discuss the formation and anneal of the centre.

#### 2. EXPERIMENTAL RESULTS

In a cryostat for combined low-temperature irradiation and EPR measurements (the same as was used in [10]) aluminium-doped float-zone silicon was irradiated at temperatures between 17 and 20 K to a fluence of  $10^{17}$  electrons per cm<sup>2</sup>. The energy of the electrons was 1.5 MeV. Two different materials were used, one with a resistivity of  $10 \Omega$  cm ( $1.5 \times 10^{15}$  Al cm<sup>-3</sup>) and one with a resistivity of  $0.9 \Omega$  cm ( $2 \times 10^{16}$  Al cm<sup>-3</sup>) [11].

In both materials a new EPR spectrum, which we labeled Si-NL26, emerges after a dose large enough to make the Fermi-level rise above the Al acceptor level. The rise of the Fermi-level was evidenced by the emergence of the spectrum Si-G2, associated with the negatively charged lattice vacancy [10, 12]. An example of the NL26 spectrum is given in Fig. 1(a). The parameters of the spectrum are included in Table 1. The spectrum can be understood as arising from a centre with electron spin  $S = \frac{1}{2}$ . The three central lines are due to the hyperfine interaction with a 100% abundant nucleus with nuclear spin I = 1. The only element with these properties is nitrogen. (<sup>14</sup>N is 99.63% abundant.) The satellite lines can be understood as due to hyperfine interactions with 4.7% abundant <sup>29</sup>Si nuclei with nuclear spin  $I = \frac{1}{2}$ .

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Spectrum label of first author	Symmetry	g-value	Hyperfine interaction with <sup>14</sup> N (MHz)	Hyperfine interaction with <sup>29</sup> Si (MHz)	Number of <sup>29</sup> Si atoms	Reference
Matsumori	Cubic	g = 2.041	<i>A</i> = 116			[15]
Matsumori	Cubic	g = 2.0061	N present, value not given	_	_	[15]
Si-SL5	Trigonal	$g_{\parallel} = 2.0026$	$A_{\parallel} = 45.3$	$A_{\parallel} = 397.5$	1	[6-8]
		$g_{\perp} = 2.0089$	$A_{\perp} = 36.3$	$A_{\perp} = 231.7$		
Si-SL6	$\approx$ Trigonal	$g_{\parallel} = 2.0018$	$A_{\parallel} = 23.4$	_		[6-8]
		$g_{\perp} = 2.0085$	$A_{\perp} = 19.2$			
Si-SL7			values not given			[8]
Murakami	Cubic	g = 2.0065	A = 45.5	_	_	[17]
Si-NL26	Cubic	<i>g</i> = 2.0022	<i>A</i> = 12.3	<i>A</i> = 48.6	6(4)	This work
		······································		<sup>13</sup> C	<sup>13</sup> C	
C-P1	Trigonal	$g_{\parallel} = 2.0024$	$A_{\parallel} = 113.984$	$A_{\parallel} = 340$	1	[9, 18, 19]
	-	$g_{\perp} = 2.0024$	$A_{\perp}^{"} = 81.344$	$A_{\perp}^{"} = 142$		

Table 1. Electron paramagnetic resonance spectra of nitrogen related centres in silicon. For comparison the parameters of substitutional nitrogen in diamond (C-P1) are included. All centres have electron spin  $S = \frac{1}{2}$  and contain only one nitrogen atom

As the two outer central lines coincide with such <sup>29</sup>Si hyperfine satellites their intensity is larger than that of the inner line. From the intensities of these satellites the number of equivalent Si nuclei is estimated to be 6. However, because of experimental error, a number of 4 cannot be ruled out completely. Especially at the low field side the spectrum is somewhat disturbed by interference with the Si-G2 vacancy spectrum. In the spectrum shown in Fig. 1(a), the G2 spectrum was tuned out-of-phase on our lock-in detector. The intensity of the nitrogen spectrum is comparable to that of the vacancy spectrum, corresponding to a concentration of 10<sup>15</sup>-10<sup>16</sup> spins per cm<sup>3</sup>, an amount about equal to the solubility of nitrogen in silicon [1]. Attempts to observe electron nuclear double resonance (ENDOR) of NL26 were not successful.

In the experiment on the  $0.9 \,\Omega$  cm material NL26 is not the only nitrogen spectrum present directly after the irradiation. As can be seen in Fig. 1(b), also another spectrum is present, with the same <sup>14</sup>N hyperfine splitting but with a slightly different g-value. Moreover, angular dependence study reveals that the g-value of this spectrum is slightly anisotropic, contrary to the g-value of NL26. Because of the severe overlap with NL26 the spectrum cannot be analysed completely. For the discussion in this paper we will temporarily call it NLx, further experiments are necessary to determine its symmetry and parameters. At this point we can only give the range in which the g-values lie: from  $g_{eff} =$ 2.0023 to  $g_{eff} = 2.0018$ . After an anneal of 15 min at T = 36 K the intensity of spectrum NLx about equals the intensity of NL26. After subsequent 15 min anneal at T = 38.5 K NLx has disappeared completely and the

only spectrum left is NL26 in an intensity of about 10% of the original intensity. However, the linewidth is smaller than that of the original spectrum. Another 15 min anneal to T = 42 K removes all nitrogen spectra. The intensity of other EPR spectra was not influenced by this annealing of the nitrogen spectra. Due to experimental conditions no such detailed annealing studies were performed in the 10  $\Omega$  cm aluminium-doped material. No other traces of nitrogen spectra were found, nor in these materials after warming up to 77 or 300 K, nor during or after illumination of the sample with various kinds of light. Similar experiments as the above in boron-doped silicon did not reveal any trace of nitrogen.

### 3. DISCUSSION

Three questions arise in connection with these, and some other workers' observations:

(1) What is the atomic configuration of the nitrogen before the electron irradiation? From our observation of an EPR spectrum in intensities comparable to the solid solubility it follows that the nitrogen is present in the lattice in an isolated form, and not mainly in clusters of, for example,  $Si_3N_4$ .

(2) What is the effect of irradiation with 1.5 meV electrons? As was shown by Watkins in many experiments (see e.g. [12]) the lattice vacancy in silicon is immobile during irradiation at 18 K, while the selfinterstitials are mobile. Thus, the only mechanism for the production of the NL26 centres seems to be a replacement mechanism analogous to the capture of silicon interstitials by group III acceptor elements, creating interstitial group III atoms [12].



Fig. 1. EPR spectrum Si-NL26 in aluminium doped silicon. The microwave frequency is 23.236 GHz, all spectra are recorded with the spectrometer tuned to dispersion mode at T = 18 K. (a) The spectrum NL26 in 10  $\Omega$  cm material after the irradiation, **B** || [100]. (b) The spectrum in 0.9  $\Omega$  cm material after the irradiation, **B** || [011]. At the high field side of each NL26 line a line of NLx is visible (see text). (c) The spectrum in the same sample as in Fig. 1(b), after a 15 min anneal at T = 38.5 K, with **B** || [100]. Clearly the linewidth is smaller than in Fig. 1(a).

(3) What structure is produced upon annealing of the NL26 centres?

The requirements on models describing the observations can be summarized as follows:

(a) Before irradiation the nitrogen most probably is in a form which is not paramagnetic as the observation of a nitrogen-related spectrum in non-implanted, nonirradiated silicon was never reported. (b) The paramagnetic variety NL26 is produced by interaction with mobile interstitial silicon  $(Si_7)$  atoms.

(c) Anneal at T = 42 K produces non-paramagnetic centres.

(d) Anneal of the nitrogen defects does not produce vacancies or self-interstitials as the concentration of vacancies remains constant upon annealing of NL26, as was monitored by the G2 spectrum ( $V^-$ ).

(e) The model should be consistent with earlier observations of nitrogen in silicon, in particular the EPR spectrum SL5, which has been identified with neutral substitutional nitrogen  $(N_S^0)$  [6, 7, 8].

Requirement (a) and also the electrical inactivity strongly suggest that normally nitrogen is not in a simple atomic form in the crystal. An obvious possibility, which was suggested earlier [13], is that nitrogen remains molecular when incorporated into the silicon lattice. The small size and high stability of the nitrogen molecule make this reasonable. There are three possibilities:

(i) The molecule is interstitial,  $(N_2)_I$ .

(ii) The molecule occupies one lattice site,  $(N_2)_S$ , or

(iii) The molecule occupies two lattice sites,  $N_S \cdot N_S$ .

In the first case the effect of the interstitial in creating NL26 is hard to conceive; in the second and third case replacement is possible:

$$(N_2)_S + Si_I \rightarrow 2N_I$$

or

 $N_{\boldsymbol{S}} \cdot N_{\boldsymbol{S}} + Si_{\boldsymbol{I}} \rightarrow N_{\boldsymbol{S}} + N_{\boldsymbol{I}}.$ 

In both cases the local strain field caused by the nitrogen atoms can provide the attractive force to the silicon interstitial, competing with the substitutional aluminium atoms.

As a model we propose the following:

(i) Before irradiation the nitrogen is present in the crystal in one of the above mentioned molecular forms.

(ii) During the electron irradiation the molecules are broken up by the silicon interstitial, giving either two interstitial nitrogen atoms or an interstitial and a substitutional nitrogen atom.

(iii) The two nitrogen atoms separate far enough to yield a spectrum apparently arising from one isolated interstitial nitrogen atom ( $N_1^{0}$ ), the spectrum NL26.

(iv) In the case of a substitutional nitrogen being present, it is in the non-paramagnetic positive charge state  $(N_s^+)$ , explaining the absence of SL5 in our *p*-type silicon.

(v) As the two nitrogen atoms attract each other, they gradually recombine upon annealing. Spectrum NLx, which is anisotropic, corresponds then to some close pair configuration of the two nitrogen atoms.

(vi) After all pairs have annealed, presumably to  $(N_2)_I$  in the first case and to  $(N_2)_S$  in the second, only those few  $N_r^0$  that have become really isolated from the other nitrogen atoms remain. This corresponds to the small fraction of NL26 remaining after anneal at T = 38.5 K, characterized by narrow EPR lines.

(vii) At still higher temperatures (42 K) also the remaining  $N_T^0$  becomes sufficiently mobile to migrate and disappear.

The present observations can be explained by yet another model. In our Al-doped silicon one can think of the possibility of the presence of aluminium-nitrogen pairs prior to the irradiation. Such bound pairs,  $Al_{s}^{-} \cdot N_{s}^{+}$  can be expected to be very stable. Furthermore AlN is known to be an extremely stable solid, with a melting point as high as 2200°C. As a donoracceptor pair  $Al_{S}^{-} \cdot N_{S}^{+}$  is electrically inactive. In that case the defect production during the irradiation would be:

 $Al_{S} \cdot N_{S} + Si_{I} \rightarrow Al_{S} + N_{I}.$ 

As in the discussion above NL26 comes from interstitial neutral nitrogen,  $N_{I}^{0}$ . Most of the arguments in the previous model can be applied to this case as well, where the annealing product after 42 K anneal would be  $Al_{s} \cdot N_{t}^{+}$ .

Obviously these models are extremely tentative and require further experiments to test them.

A question remaining as regards the above models, is whether two nitrogen atoms or a nitrogen atom and an aluminium atom can be close enough to attract each other, while at the same time they are far enough apart to produce an isotropic NL26 g-value, not reflecting the presence of the other atom by a lower symmetry or additional hyperfine interaction. A possible clue to the solution is provided by the observed hyperfine interactions. The hyperfine parameters of NL26 in Table 1 can be analysed in terms of the wavefunction with the expression for the Fermi contact interaction:

 $a = \frac{8}{3}\pi g\mu_B g_N \mu_N |\Psi(r_0)|^2,$ 

where a is the hyperfine interaction and  $|\Psi(r_0)|^2$  is the probability density of the wavefunction on the nucleus involved. This gives a value for  $|\Psi(r_0)|^2$  which is only 0.84% of the free atom value on the nitrogen nucleus and 1.17% on each silicon nucleus [14]. These figures indicate a fairly delocalised wavefunction. In this situation the effect of a nearby atom on the g-tensor is expected to be small. Also its hyperfine interaction will not be resolved. Only when the two nitrogen atoms, or the nitrogen atom and the aluminium atom, are very close together, i.e., just before annealing to a bound pair, anisotropy becomes noticeable. One could compare this

to the case of diamond, where many EPR spectra are known to be isotropic, whereas the defects giving rise to the spectra are not [9].

## 4. CONCLUSIONS

The most important conclusion of this work is that nitrogen can be incorporated into silicon in a simple form, as molecules or as part of a two-atom complex. The individual atoms can be freed by the silicon interstitial during low temperature electron irradiation. We conclude that the nitrogen is present in our aluminium doped as-grown silicon as nitrogen molecules or as aluminium-nitrogen pairs. In either case, the annealing behaviour suggests an astounding mobility for interstitial atomic nitrogen in the silicon lattice. More experiments are needed to clarify definitely in which way nitrogen is incorporated in the silicon lattice. Such experiments would consist of EPR under different conditions (n-type material, lower irradiation temperature), ENDOR and optical work. Actually, the 1.1223 eV luminescence, ascribed to nitrogen [5, 20], has been observed in our aluminium doped silicon [16].

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