

Evidence of energy levels due to nitrogen dimers in silicon

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ARTICLE INFO

Article history:

Received 23 April 2008

Accepted 1 September 2008

Keywords:

Silicon

Nitrogen

Energy levels

Hall effect

ABSTRACT

Nitrogen-and-boron doped Czochralski Si samples are converted into n-type by annealing at 600 °C due to formation of Shallow Thermal Donors (STDs). The temperature dependence of the electron concentration, measured by Hall effect down to the liquid Helium temperature, is not however consistent with existence of only STDs and compensating boron acceptors; there is clearly an extra acceptor species with a level close to the conduction band, and of a concentration comparable to the total concentration of nitrogen. This acceptor centre is thus identified with the major nitrogen species, N₂ and N₂O. These two species can be distinguished by using samples from the seed-end and tail-end of a crystal: the level due to N₂ is about $E_c - 27$ meV, and that due to N₂O about $E_c - 33$ meV.

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1. Introduction

The major state of the nitrogen impurity in silicon, at the room temperature, is the dimeric interstitial, N₂ [1–3]; this species dominates in Float-Zoned material. In Czochralski (CZ) Si, the dimers are partially “oxidized”, and exist as N₂O complexes [1,4]. Regarding nomenclature: we will refer to both N₂ and N₂O as dimeric nitrogen species. Through the redistribution of the IR bands due to N₂ and N₂O by annealing at various T [5,6], it can be inferred that the transformation of N₂ into N₂O occurs below 700 °C. Therefore the grown-in mixed population of N₂ and N₂O species in CZ samples will depend on the thermal history of the crystal growth process. In a tail-end crystal portion (that is fast cooled) we expect that the high-temperature N₂ species are frozen-in. On the contrary, in the seed-end part (slowly cooled down to about 400 °C) we expect that almost all initial N₂ are transformed into N₂O. In the intermediate positions within a crystal, a mixed population of the two species will generally exist.

The dimeric species N₂ and N₂O are definitely neutral at room temperature since no electrically active centres, in concentrations comparable to that of the total nitrogen concentration, was found. However the presence of nitrogen results in formation of Shallow Thermal Donors (STDs) in CZ samples, upon annealing in a middle-temperature range, 600–700 °C [7–9]. The STDs are present already in as-grown state of nitrogen-doped CZ crystals, but by annealing, their concentration saturates at a specific value that depends on

the total nitrogen concentration, N_{tot} . By this dependence it was concluded [9] that an STD species includes one nitrogen atom and several oxygen atoms, and thus the family of STDs is composed of NO_{*m*} complexes, of different oxygen number *m*, that was concluded to be mostly in a range from 2 to 4 [9,10].

The present work is a continuation of our previous study of STDs. We will discuss a strange behaviour of the temperature dependence of the electron concentration $n(T)$ in boron-doped samples converted into n-type due to STD generation at 600 °C. It is now realized that these data actually imply that the dimeric species are electrically active, in the limit of extremely low temperatures: in this range they trap an electron and become single-negatively charged. In other words, they possess an electronic acceptor level very close to the bottom of the conduction band.

2. Evidence in favour of acceptor levels due to the nitrogen dimers

The first group of studied samples was lightly boron-doped, and co-doped with nitrogen to different levels, up to $2 \times 10^{15} \text{ cm}^{-3}$. The nitrogen concentration N_{tot} was determined by secondary ion mass spectroscopy (SIMS) and also calculated using the known initial concentration in the melt and the segregation coefficient; the two methods give almost coincident values [9]. The samples were annealed at 600 °C for several hours and converted into n-type due to produced STDs while the grown-in double TDs were annihilated. Note that after annealing at higher T (like 650 °C) the produced STD concentration, N_{std} , is lower, and the annealed samples are always of p-type. The concentration of boron acceptors, N_{B} , was determined in a sister sample annealed at 900 °C,

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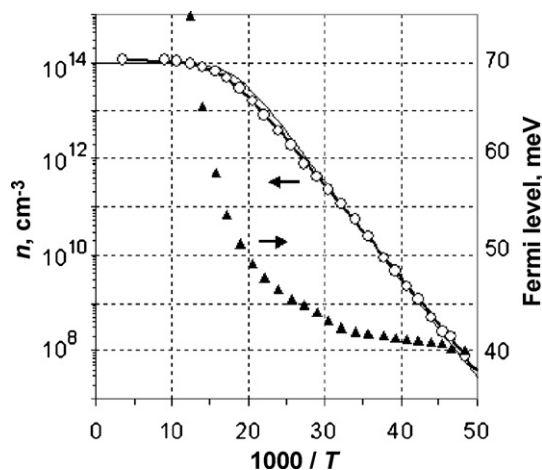


Fig. 1. Temperature dependence of the electron concentration (deduced from Hall effect) for boron- and nitrogen-doped sample annealed at 600 °C for 6 h. The sample is taken from the tail-end of crystal; nitrogen concentration is $2 \times 10^{15} \text{ cm}^{-3}$. The thin curve is drawn assuming that only STDs ($N_{\text{std}} = 5.1 \times 10^{14} \text{ cm}^{-3}$) and boron acceptors ($N_{\text{B}} = 4 \times 10^{14} \text{ cm}^{-3}$) are present. The solid curve is the best-fit theoretical dependence assuming that, along with the STDs and boron, there is also an acceptor level close to the bottom of the conduction band. The best-fit position of this level is at $E_{\text{c}} - 27 \text{ meV}$. The triangles show the Fermi level distance from the bottom of the conduction band.

to destroy STDs. Hence, in n-type samples, we can deduce N_{std} by the room-temperature electron concentration, $n_0 = N_{\text{std}} - N_{\text{B}}$. The temperature dependence of the electron concentration $n(T)$ deduced from the Hall effect, is shown in Fig. 1 for a sample of the highest nitrogen concentration ($N_{\text{tot}} = 2 \times 10^{15} \text{ cm}^{-3}$) cut from the tail-end of the crystal. The curve calculated with the known values of $N_{\text{B}} = 4 \times 10^{14} \text{ cm}^{-3}$ and $N_{\text{std}} = 5.1 \times 10^{14} \text{ cm}^{-3}$, and with the known electronic level of the STDs (around $E_{\text{c}} - 37 \text{ meV}$, according to IR spectra) however does not fit at all the measured dependence $n(T)$, as shown by the thin curve in Fig. 1. If the STD level is used as a fitting parameter, to minimize the deviation of the computed curve from the experimental points in Fig. 1, one should place the STD level at essentially shallower position ($E_{\text{c}} - 31 \text{ meV}$) and – which even more embarrassing – to ascribe to N_{std} and N_{B} non-realistic high values. The straightforward explanation of this difficulty is that the curve shape is controlled by the presence of some ultra-shallow electronic traps, with the energy level that is closer to the bottom of the conduction band than the STD level of $E_{\text{c}} - 37 \text{ meV}$. The concentration of this level should be higher than N_{std} , to compete with a deeper level of STDs. Since N_{std} is smaller than N_{tot} – and yet comparable to it – we should attribute the level to the major (dimeric) nitrogen species. In the present case of a tail-end sample, these are expected to be mostly simple dimers, N_2 . This level should be of course an acceptor level since the dimers are neutral at the room temperature.

Now, with the ultra-shallow traps for electrons, the $n(T)$ curve is well fitted, see the thick curve in Fig. 1. The best-fit acceptor level position is $E_{\text{c}} - 27 \text{ meV}$. An important feature of the acceptor level is the degeneracy factor g – the ratio of the equivalent electronic state numbers for the empty and filled states of the centre [11]. The curve shape is crucially dependent on g , and we have to use g as one of the two fitting parameters (the other one is the energy level position), at a specified concentration N_2 of the dimeric species: $N_2 = (N_{\text{tot}} - N_{\text{std}})/2 = 7.4 \times 10^{14} \text{ cm}^{-3}$. The resulting value, by the best fit shown in Fig. 1 is $g = 0.07$. For a donor level of conventional dopants (like phosphorus) the g -factor is thought to be $1/2$ that corresponds to the two spin orientations of the electron filling the level. An essentially smaller value of g for N_2 acceptor may be understood if the electrons of every of the eight conduc-

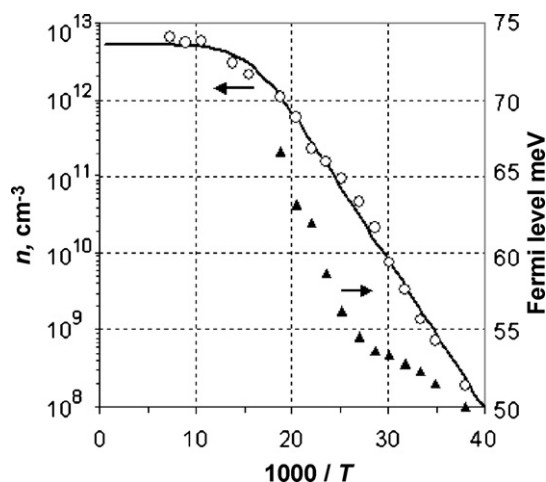


Fig. 2. Temperature dependence of the electron concentration for boron- and nitrogen-doped sample annealed at 600 °C for 3 h. The sample is taken from the seed-end of crystal; nitrogen concentration is $1.1 \times 10^{15} \text{ cm}^{-3}$. The solid curve is the best-fit theoretical dependence assuming that, along with the STDs ($N_{\text{std}} = 2.8 \times 10^{14} \text{ cm}^{-3}$) and boron acceptors ($N_{\text{B}} = 2.77 \times 10^{14} \text{ cm}^{-3}$), there is also an acceptor level close to the bottom of the conduction band. The best-fit position of this level is at $E_{\text{c}} - 33 \text{ meV}$, and the concentration is $N_{\text{ust}} = 3.2 \times 10^{14} \text{ cm}^{-3}$.

tion band minima give rise to a separate state; then the number of states for the filled level would be 16 (regarding the spin orientation), and g would be $1/16 = 0.063$, close to the deduced value. Once determined for the present sample, the same value of g (0.07) will be used for all the other samples.

In Fig. 2, the $n(T)$ curve for a sample cut from the seed-end of the same crystal is shown. In the seed-end, the nitrogen concentration is somewhat lower, close to $1.1 \times 10^{15} \text{ cm}^{-3}$, and accordingly the produced STD concentration (by annealing at 600 °C for 3 h) is smaller: it is almost equal to N_{B} which gives a remarkably low value for the room-temperature plateau, n_0 . The deduced acceptor level position is now $E_{\text{c}} - 33 \text{ meV}$, somewhat different from the previous level at $E_{\text{c}} - 27 \text{ meV}$. It was already pointed out that in the seed-end part the dominant dimeric species is expected to be N_2O instead of N_2 . Accordingly, we attribute the presently deduced level at $E_{\text{c}} - 33 \text{ meV}$ to “oxidized dimers” N_2O .

This distinction between the levels due to N_2 and to N_2O implies that during anneal at 600 °C the grown-in ratio between these two species does not change much. If the $\text{N}_2 + \text{O}$ reaction were limited by oxygen diffusion then the characteristic time of converting N_2 into N_2O would be $1/(4\pi RDC)$ where D is the oxygen diffusivity, C is the oxygen concentration and R is the capture radius. At 600 °C, this time is close to 2 h which would mean a fast equilibration in favour of N_2O . Therefore we should assume that the $\text{N}_2 + \text{O}$ reaction rate at 600 °C is essentially slower than the diffusion-limited value.

3. Acceptor levels traced in phosphorus- and nitrogen-doped samples

In case of boron-doped samples converted into n-type by annealing, the ultra-shallow electron traps (N_2 or N_2O) compete for trapped electrons with the shallow donor level of STDs. The trapping by STD is easier since their level is a bit deeper. Yet the acceptor level gives a significant contribution (thus affecting the curve shape) due to a higher concentration and a smaller g -factor, in comparison to STDs.

In case of phosphorus donors, instead of STDs, the donor level is deeper, $E_{\text{c}} - 45.6 \text{ meV}$, and it is much harder for the ultra-shallow traps to compete in trapping electrons. Nevertheless, even in phosphorus-doped sample, it is possible to detect the effect of the

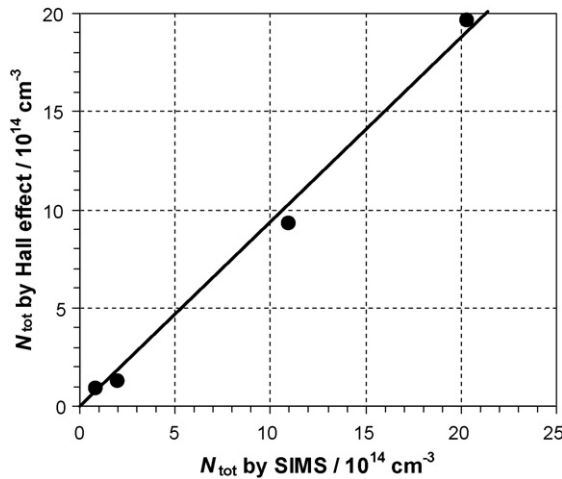


Fig. 3. Correlation between the nitrogen concentration deduced from the $n(T)$ curve as a sum of the two contributions, Eq. (1), and the total nitrogen concentration obtained by SIMS (or calculated using the segregation coefficient of nitrogen).

ultra-shallow traps, and to extract their concentration and the level position by fitting the $n(T)$ curve. For that, we introduce STDs by the same annealing at 600 °C; such an anneal is anyway necessary to eliminate grown-in double TDs. In effect, upon lowering T , the Fermi level passes the electronic level of phosphorus and becomes locked close to the STD level, since N_{std} is higher than the residual concentration of boron, N_{B} . The phosphorus donors are then almost all in the neutral state, and have little effect on the low-temperature portion of the $n(T)$ curve that is controlled, just like before, by STDs and the ultra-shallow traps. The phosphorus concentration, N_{P} , (or rather the phosphorus–boron difference $N_{\text{P}} - N_{\text{B}}$) is known by measuring a sister sample annealed at 900 °C. The STD concentration N_{std} is known by the plateau electron concentration in annealed sample, $n_0 = N_{\text{std}} + N_{\text{P}} - N_{\text{B}}$. The $n(T)$ curve is thus fitted using only three parameters: the level position and concentration of the ultra-shallow traps, and N_{B} .

In one example of phosphorus-doped sample, annealed at 600 °C for 8 h, the nitrogen concentration is as low as $8.5 \times 10^{13} \text{ cm}^{-3}$, and yet the contribution of ultra-shallow traps (acceptors) is felt. Here we have no information on the sample location within the crystal, and accordingly deal with some mixed population of N_2 and N_2O of an unknown proportion. The data accuracy does not allow to deduce the concentrations of these two species separately, and we have to deal with an average level position, and with the effective total concentration N_{dim} of the two dimeric species. The deduced level is $E_{\text{c}} - 32 \text{ meV}$ indicating to the dominance of N_2O in the $\text{N}_2/\text{N}_2\text{O}$ population.

4. A new technique to obtain the total nitrogen concentration in CZ silicon by electrical measurements

From the Hall-effect-based (or resistivity-based) $n(T)$ curve, monitored down to the liquid He temperature, we can deduce the two major contributions into the total nitrogen concentration. The dimeric contribution N_{dim} (generally composed of both N_2

and N_2O) is found as the concentration N_{ust} of the ultra-shallow electron traps extracted by fitting the whole $n(T)$ curve. The concentration of one-nitrogen species, N_{std} , is known just from the room-temperature plateau value of electron concentration. Hence the total nitrogen concentration is calculated as

$$N_{\text{tot}} = N_{\text{std}} + 2N_{\text{ust}}. \quad (1)$$

The concentration calculated by this equation is plotted in Fig. 3 in dependence of the total nitrogen concentration measured by SIMS (or computed using the segregation coefficient of nitrogen). There is a good agreement between the Hall-effect-based value and the actual total concentration.

In the past, another technique to determine N_{tot} was proposed [9]—based on the saturated value of N_{std} achieved after some sufficiently long annealing. This value of N_{std} is related to N_{tot} by a calibration curve that depends on the oxygen concentration. In the new technique, we do not need to reach the saturated state in the course of annealing, neither we need to know the oxygen content. The Eq. (1) applies to any moment of annealing. A complicating feature of the new technique is that we need not just a room-temperature value for the carrier concentration but the whole $n(T)$ curve.

5. Summary

The main result of the present study is that the dimeric nitrogen species, N_2 and N_2O , are not, strictly speaking, electrically inactive defects, as was thought in the past. At very low T , such a species traps an electron, with a very low binding energy, 27 meV for N_2 and 33 meV for N_2O . In other words, they possess acceptor levels extremely close to the bottom of the conduction band, $E_{\text{c}} - 27 \text{ meV}$ and $E_{\text{c}} - 33 \text{ meV}$, respectively. By monitoring the temperature dependence of the electron concentration, down to the liquid He temperature, it is possible to deduce separately the concentration of the dimeric species and the concentration of STDs (one-nitrogen species), and thus to determine the total nitrogen concentration. To be more precise, only the interstitial nitrogen component is determined in this way, but it is likely that substitutional nitrogen plays an insignificant role in CZ material.

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