Out-diffusion of deep donors in nitrogen-doped silicon and the diffusivity of vacancies

V. V. Voronkov and R. Falster
MEMC Electronic Materials, via Nazionale 59, Merano BZ, Italy

(Received 7 February 2012; accepted 30 May 2012; published online 9 July 2012)

A strong resistivity increase in annealed nitrogen-doped silicon samples was reported long ago—but has remained not fully understood. It is now shown that the complicated evolution of the resistivity depth profiles observed can be reproduced by a simple model based on the out-diffusion of some relevant species. Two versions of such an approach were analyzed: (A) out-diffusion of deep donors treated as VN (off-centre substitutional nitrogen), (B) out-diffusion of vacancies (V) and interstitial trimers (N_3) produced by dissociation of VN_3. Version B, although more complicated, is attractive due to a coincidence of the deduced vacancy diffusivity D_V at 1000 °C with the value extrapolated from low-temperature data by Watkins. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4731796]

I. INTRODUCTION

Nitrogen doping is widely used to control microdefects in Czochralski (CZ) and float-zoned (FZ) crystals and yet the behaviour of nitrogen-related point defects is not quite clear.[1] One puzzling feature is the electrical activity of nitrogen: it is absent in as-grown state but becomes strongly pronounced[2] after annealing at 900 or 1000 °C. The FZ samples studied in Ref. 2 had, in the as-grown state, a boron-controlled resistivity $\rho_0 = 150$ Ohm cm (corresponding to a hole concentration $p_0 = 8.9 \times 10^{13}\,cm^{-3}$). After annealing, ρ jumped to 20 kOhm cm (a factor of 125) implying that some deep donors were generated in a concentration larger than p_0 resulting in a pinning the Fermi level to a deep donor energy level.

At high temperatures, nitrogen is mostly in the interstitial dimeric (N_2) and monomeric (N_1) states with the minor species N_1 being responsible for nitrogen transport.[3] Upon lowering T, monomeric nitrogen is almost completely paired into N_2. The dimeric state N_2—observed optically[2,4]—can be concluded to be electrically inactive. At high T, there is also a substitutional (off-centre) nitrogen species[5] denoted VN which is a deep centre.[6] The fraction of this defect at the melting point was estimated[7] as about 10%. In the samples of Ref. 2, the nitrogen concentration was about $3 \times 10^{15}\,cm^{-3}$ and thus the expected concentration of VN is about $3 \times 10^{14}\,cm^{-3}$—well above p_0. Hence, the VN defect is the primary suspect for being the deep donor responsible for the anneal-induced jump in ρ. Apparently, initial VN defects were transformed, during crystal cooling, into some electrically inactive state—most likely by attaching more nitrogen atoms and becoming VN_m species containing m nitrogen atoms. One example of such an inactive defect[6,8] is VN_2. It may be expected that other even-sized species VN_4, VN_6, etc., are also electrically inactive since they are combined of electrically inactive defects VN_2 and N_2.

During subsequent annealing, the grown-in VN_m species (of even m) are expected to convert back into the high-temperature dominant form VN—deep donors. So far so good. However, this concept is very hard to reconcile[9] with the observed evolution of the resistivity depth profile $\rho(z)$ (which was monitored[2] by spreading resistance profiling (SRP)). The measured profiles after 1000 °C annealing are shown in Fig. 1 by circles. There is a donor-depleted region close to the sample surface—narrow after 1 min but much wider after 4 min. After 8 min, the donors disappear completely (the resistivity ρ returns to its initial value ρ_0). To account for these profiles, an extremely complicated model has been developed.[9] In it, in the first place, it should be assumed that the grown-in inactive VN_m species are transformed not directly to the stable form VN but rather to a metastable forms like VN_3. The VN_3 donors are annihilated by in-diffusing self-interstitials (I) by $I + VN_3$ reaction. This produces mobile interstitial trimers N_3 which then out-diffuse and precipitate at the surface—resulting in the emission of I by the nitride precipitates. Each of the two mobile species, I and N_3, is thus created by the other one. An obtained fit was satisfactory but involved a very large number of fitting parameters.

In the present study, a much simpler model of the deep donor loss—entirely based on out-diffusion process—was tried. Before specifying the details, the simulated profiles are shown in Fig. 1 by solid curves, to make it clear that the computed profiles inevitably show a smooth variation in $\rho(z)$ through the whole depth. This is in contrast to the reported plateau in the central sample portion which had a fixed value $\rho_{max} = 20$ kOhm cm (found also after 900 °C anneal). This persistent plateau was actually the main difficulty that necessitated the complicated model of self-interstitial in-diffusion[9] in order to annihilate the donors only up to some limited depth. This difficulty is however removed if ρ_{max} is not the true resistivity but rather simply the upper limit of the SRP instrument used in Ref. 2. In this case, only the profile parts with $\rho(z) < \rho_{max}$ are meaningful, and only these parts are to be fitted—as was done in Fig. 1. The fit is better than that achieved before.[9]

Two qualitatively different models of the out-diffusion process were tried as outlined below.

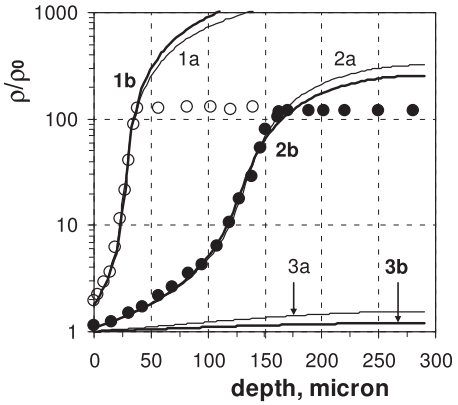

FIG. 1. Resistivity depth profiles[2] measured in nitrogen-doped FZ samples annealed at 1000 °C for 1 and 4 min (open and closed circles). The solid curves numbered 1 to 3 are computed for 1, 4, and 8 min anneal, respectively, within two different out-diffusion models (thin curves 1a to 3a are for model A, and the thick curves 1b to 3b—for model B).

II. MODEL A: OUT-DIFFUSION LOSS OF VN

In this version of an out-diffusion concept, the grown-in neutral species (VN_m) are instantaneously converted—at 1000 °C—back into the original state VN. At the start of anneal, these donors have a uniform concentration N_0 expected to be $\approx 3 \times 10^{14}\,cm^{-3}$.

The loss of VN may then proceed through dissociation into $V + N_1$, with subsequent out-diffusion of vacancies. This process is a trap-limited vacancy out-diffusion, with N_1 atoms as traps of a concentration maintained by the major interstitial species N_2 through a fast dissociation/pairing reaction $N_2 \leftrightarrow 2\,N_1$. The concentration of N_2/N_1 is strongly reduced (by the out-diffusion of N_1) within a narrow near-surface region of about 20 μm after an anneal of several minutes.[10] Accordingly, [VN] would be also reduced in this narrow region in comparison to a deeper part where N_2 is not yet lost. The resistivity profile however shows no such a peculiarity: it decreases steadily towards the surface "not noticing" a narrow near-surface nitrogen-depleted region (Fig. 1).

Therefore, the VN loss cannot be attributed to trap-limited vacancy out-diffusion. This conclusion is consistent with a negligible rate of the dissociation reaction $VN \rightarrow V + N_1$ inferred from the nitrogen effect on the grown-in microdefects.[1]

The remaining loss mechanism of VN is then out-diffusion of VN themselves. There is an analogous species VO (substitutional off-centre oxygen) that is mobile as evidenced by its reaction with oxygen to produce VO_2 at relatively low T—when oxygen itself is practically immobile.[11] The deduced diffusivity of VO, when extrapolated to 1000 °C, equals $\approx 2.5 \times 10^{-8}\,cm^2/s$. The diffusivity of VN deduced below, $2 \times 10^{-6}\,cm^2/s$, is not dramatically higher. Hence an assumption of a mobile VN species does not seem to be unrealistic.

The donor depth profile $N(z, t)$ then evolves by simple diffusion equation, with a diffusivity D. The computed donor concentration should be converted into the measured quantity, the resistivity ρ, which is inversely proportional to the hole concentration p—since the hole mobility, for lightly doped p-Si, has a fixed value. Hence $\rho/\rho_0 = p_0/p$. The hole concentration p is expressed through p_0 and N by the neutrality equation

$$p + N^+ = p_0. \tag{1}$$

The concentration of charged donors N^+ is controlled by the Fermi level position with respect to the donor level E or equivalently[12] by the equation

$$N^+ = Np/(p + p_d), \tag{2}$$

where p_d is the characteristic hole concentration for the Fermi level coincident with the energy level E (referenced from the top of the valence band)

$$p_d = g\,N_v \exp(-E/kT). \tag{3}$$

Here N_v is the state density in the valence band (at T_{room}) and g is the degeneracy factor, on the order of 1. The parameter deduced by fitting is p_d. The energy level E can then be estimated by Eq. (3).

The near-surface resistivity is somewhat larger than the as-grown value (Fig. 1) which can be attributed to a time-dependent boundary condition. For the sake of simplicity, an exponential decay in the boundary donor concentration $N_s(t)$ is assumed

$$N_s(t) = N_{s0} \exp(-t/\tau). \tag{4}$$

By the two values of the near-surface resistivity (after 1 and 4 min in Fig. 1), the parameters in Eq. (1) are: $\tau = 1.7$ min, $N_{s0} = 7 \times 10^{13}\,cm^{-3}$.

The computed profiles of Fig. 1 (thin curves 1a to 3a) are obtained with the following best-fit parameters: $N_0 = 4 \times 10^{14}\,cm^{-3}$ (quite close to the expected value), $D = 2.1 \times 10^{-6}\,cm^2/s$ and $p_d = 1.7 \times 10^{11}\,cm^{-3}$ (which corresponds to the donor level at $\approx E_v + 0.45$ eV). It is also informative to show the depth profiles of VN donors (Fig. 2). The apparent depth of the donor-depleted region is defined by intersection of $N(z, t)$ with horizontal (dashed) line showing the value of p_0. Due to a relatively high D, the VN concentration is reduced through the whole wafer depth already

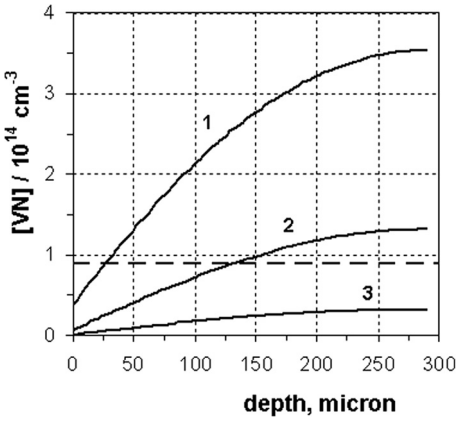

FIG. 2. Computed depth profiles of deep donors VN (model A). The curves 1, 2, and 3 correspond to annealing at 1000 °C for 1, 4, and 8 min, respectively.

after 4 min. This accounts for a propagation of the depleted region at a far faster velocity than that by a normal diffusion law $t^{1,2}$. After 8 min (the curve 3 in Fig. 2), the donor concentration is reduced severely, and the corresponding resistivity (curve 3a in Fig. 1) becomes close to the initial value ρ_0. Yet ρ/ρ_0 is still somewhat larger than 1, in a slight discrepancy with the experiment[2] that shows complete coincidence of ρ with ρ_0 after 8 min anneal at 1000 °C.

III. MODEL B: DISSOCIATION LOSS OF VN_3

The model described above is attractive because of its simplicity but nonetheless leaves an uneasy feeling ascribing a high diffusivity to the off-centre substitutional nitrogen VN. An alternative model can be based on the peculiar shape of nitrogen out-diffusion profile:[13] apart from the major slow-diffusing N_2/N_1 component, there is also a fast-diffusing component. The latter was attributed to a fast out-diffusion of nitrogen trimers N_3 that exist independent of the major N_2/N_1 component and originate from the annihilation reaction of VN_3 defects with in-diffusing self-interstitials. Now, within the out-diffusion concept, the trimers N_3 are supposed to be produced by the dissociation reaction $VN_3 \rightarrow V + N_3$. This leads to an appreciable vacancy supersaturation. The self-interstitial concentration is accordingly undersaturated—which makes a self-interstitial contribution into defect transport inessential. The source defects for the trimers, VN_3, originate from the grown-in VN_m neutral species which means that these species, upon heating, do not return to the stable high-temperature form VN but rather transform into metastable species VN_3.

The first question is: which of the three species involved (VN_3, V, and N_3) is the deep donor responsible for a resistivity jump?

The vacancy is either neutral or negative[14] in p-Si at T_{room}. During a post-anneal quench, V can be trapped by N_2 (the major defect in nitrogen-doped FZ samples). The stable VN_2 complex is electrically inactive[6,8] but there could be a metastable configuration VN_2* produced during a quench. Yet it is highly unlikely that this hypothetical defect—combined of a neutral N_2 and a neutral (or negative) V is a donor.

The next tentative identification of the deep donors is with VN_3. This however does not allow a quantitative fitting of the resistivity profiles. The VN_3 concentration, in equilibrium with V and N_3, is specified by a mass-action law

$$[V][N_3]/[VN_3] = K_3, \tag{5}$$

where K_3 is the equilibrium dissociation constant. Both [V] and [N_3] decrease towards the sample surface linearly, due to out-diffusion. Thus, [VN_3] decreases by a parabolic law—inconsistent with the quasi-linear near-surface portions of the resistivity profiles in Fig. 1.

Therefore, the only suitable identification of the deep donors is N_3. The VN_3 species are also treated as donors but of an energy level essentially below that of N_3 and thus having only a slight impact on ρ. The out-diffusion process is now described by 3 parameters: two diffusivities (D_V of V and D_3 of N_3) and the dissociation constant K_3. The computed profiles are very sensitive to all the three parameters, and therefore all of them were unambiguously deduced by the fitting of the measured curves in Fig. 1: $D_V = 2.3 \times 10^{-5}$ cm^2/s, $D_3 = 3.2 \times 10^{-6}$ cm^2/s, $K_3 = 10^{14}$ cm^{-3}. Remarkably, the deduced value of D_V is very close to the value of 2×10^{-5} cm^2/s extrapolated to 1000 °C from low-temperature radiation data.[15] The best-fit value of the concentration p_d for the deep donor N_3 is about 1.3×10^{11} cm^{-3} (corresponding to the donor level at $\approx E_v + 0.46$ eV).

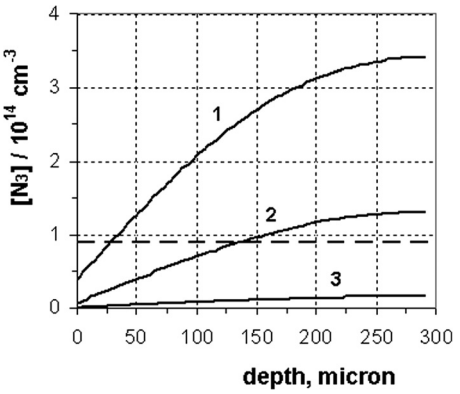

FIG. 3. Computed depth profiles of deep donors N_3 (model B) for annealing at 1000 °C. The curves 1, 2, and 3 correspond to the anneals of 1, 4, and 8 min, respectively.

The best-fit resistivity profiles at 1000 °C for 1 and 4 min (the thick curves 1b and 2b in Fig. 1) are practically indistinguishable from those obtained within the previous model for the meaningful curve portions, $\rho < \rho_{max}$. However, after 8 min, the resistivity (curve 3b in Fig. 1) is somewhat lower and more consistent with the experimental results[2] that give a value of unity for ρ/ρ_0 after 8 min. The computed depth profiles of N_3 are shown in Fig. 3. Initially the VN_3, V, and N_3 species are present in a proportion 0.65:0.35:0.35. The initial amount of N_3 is essentially smaller than N_0 and yet higher than p_0 and thus enough to pin the Fermi level at the deep level of N_3. Upon annealing, the [V]/[N_3] ratio decreases due to a higher diffusivity of V. Accordingly, the ratio of the two donors, [VN_3]/[N_3]—specified by Eq. (5)—is reduced; it becomes <1 already after 1 min, and $\ll 1$ after 4 min. A contribution of VN_3 into the resistivity is insignificant even at the shortest time of 1 min. For this reason, the value of p_d for VN_3 can be estimated only roughly: it is on the order of 10^{15} cm^{-3}. The corresponding level is at $E_v + 0.23$ eV.

IV. GENERATION AND LOSS OF DEEP DONORS AT 900 °C

The reported resistivity depth profiles induced by annealing at 900 °C are much more complicated (Fig. 4). Clearly, transformation of grown-in VN_m species into VN (for model A) or into VN_3 (for model B) is no longer instantaneous but takes several minutes. Only after 8 min anneal, the resistivity reaches a high value, the same as that produced immediately at 1000 °C. To account for the profiles, it is necessary to assume that some intermediate donor species—different from those discussed above—are produced

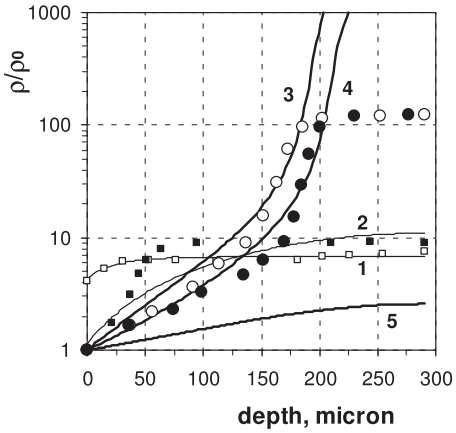

FIG. 4. Resistivity depth profiles[2] produced by annealing at 900 °C for 1 min (open squares), 4 min (filled squares), 8 min (open circles), and 16 min (filled circles). The solid curves 1 to 5 (for annealing time of 1, 4, 8, 16, and 32 min, respectively) are computed within a modified version of model B that includes transient formation of donor species that later transform into VN_3.

within this transient time. It means that additional—and highly speculative—assumptions on the kinetics of VN_m conversion have to be made to describe the profiles. An example, for the model B, is shown by the solid curves in Fig. 4; the fit quality is not yet quite satisfactory for the shorter times of 1 and 4 min. For this reason, the model parameters deduced by the fitting procedure are not as reliable as for 1000 °C case, and they will not be discussed in detail. It is only worth noting that the profiles for 8 and 16 min, can be qualitatively explained by the model B as follows. The dissociation constant K_3 at 900 °C is essentially smaller than at 1000 °C, and hence the concentration of deep donors N_3 is initially low—less than p_0—and insufficient to induce a strong rise in ρ. Only later, due to a reduction in [V] by a fast vacancy out-diffusion does the fraction of N_3 increase—by Eq. (5)—becoming sufficient for a resistivity jump as was observed after 8 and 16 min. In the interval between 8 and 16 min, a loss of $[VN_3]$ is accompanied by an increase in the $[N_3]/[VN_3]$ ratio, and the concentration $[N_3]$ of the major deep donors is not changed much, which accounts for almost identical resistivity profiles after 8 and 16 min. Only for longer anneals, the model predicts an essential reduction in $[N_3]$ and hence in the resistivity (Fig. 4, curve 5). The vacancy diffusivity required to reproduce the profiles at 900 °C is about 3.8×10^{-6} cm^2/s—remarkably smaller than the extrapolated value of Watkins. This may be attributed to vacancy trapping by the major nitrogen species N_2—well pronounced at lower T. The deduced vacancy diffusivity is then an effective value equal to the true diffusivity multiplied by a fraction of free mobile vacancies in the $V + VN_2$ community. Roughly, this fraction is estimated as 0.3 at 900 °C.

V. SUMMARY

The reported resistivity profiles in annealed nitrogen-doped samples[2] include a plateau of a high resistivity, ρ_{max}. Such a shape is very hard to reproduce by simulations. However, once ρ_{max} is treated as an instrumental limit rather than the true resistivity, the genuine parts of the profiles (with $\rho < \rho_{max}$) are successfully fitted by a simple model based on an out-diffusion process. Two versions of this process were considered:

a. The deep donors are VN (substitutional off-centre nitrogen), and they are mobile. There is a known example of an analogous species—substitutional off-centre oxygen, VO—that is mobile too, although its diffusivity is lower by two orders of magnitude (in the same temperature range).
b. The species produced by annealing are VN_3 rather than VN and they are lost through dissociation into two mobile species: vacancies V and interstitial nitrogen trimers N_3. The deep donors are identified as N_3.

The version A is attractive by its simplicity while B is by virtue of a remarkable coincidence of the deduced vacancy diffusivity with the Watkins value[15] extrapolated from cryogenic temperatures. A marginal advantage of the model B is that it predicts a stronger loss of donors after 8 min anneal at 1000 °C.

An apparent next step is to use the out-diffusion models to simulate quantitatively the available nitrogen out-diffusion profiles.

[1]V. V. Voronkov and R. Falster, Solid State Phenom. **131–133**, 219 (2008).
[2]T. Abe, H. Harada, N. Ozawa, and K. Adomi, Mater. Sci. Res. Symp. Proc. **59**, 537 (1986).
[3]V. V. Voronkov and R. Falster, Solid State Phenom. **95–96**, 83 (2004).
[4]H. J. Stein, Mater. Sci. Res. Symp. Proc. **59**, 523 (1986).
[5]K. L. Brower, Phys. Rev. B **28**, 6040 (1982).
[6]J. P. Goss, J. Hahn, R. Jones, P. R. Briddon, and S. Oberg, Phys. Rev. B **67**, 045206 (2003).
[7]V. V. Voronkov and R. Falster, J. Cryst. Growth **273**, 412 (2005).
[8]H. Sawada and K. Kawakami, Phys. Rev. B **62**, 1851 (2000).
[9]V. V. Voronkov and R. Falster, Thin Solid Films **518**, 2346 (2010).
[10]T. Itoh and T. Abe, Appl. Phys. Lett. **53**, 39 (1988).
[11]B. G. Swensson and J. L. Lindstrom, Phys. Rev. B **34**, 8709 (1986).
[12]J. S. Blackmore, *Semiconductor Statistics* (Pergamon, NY, 1962).
[13]V. V. Voronkov and R. Falster, ECS Trans. **3**, 113 (2006).
[14]G. D. Watkins, ECS Proc. **99–1**, 38 (1999).
[15]G. D. Watkins, J. Appl. Phys. **103**, 106106 (2008).