

Nitrogen in Silicon: Properties and Impact on Grown-in Microdefects

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Nitrogen doping is a recognized tool to modify structural properties of silicon materials. In particular, the grown-in microdefects - voids or dislocation loops (A-swirls) - can be controlled efficiently already at a low (around 10^{14} cm^{-3}) doping level with nitrogen [1,2]. To understand this effect one should know what are the basic nitrogen species in silicon lattice.

The dominant species at the room temperature is known to be the dimeric interstitial N_2 [3]. Evolution of implanted profiles upon annealing shows [4] that the dimers are of a very low mobility; the nitrogen transport occurs by dissociation of N_2 into fast-diffusing single interstitials N_1 . This analysis produces the parameter $D_1K^{1/2}$ (where D_1 is the diffusivity of N_1 and K is the dissociation constant) in a range of T , as well as the dissociation time τ of N_2 . A remarkable result is that τ is reduced in the presence of oxygen which accounts for a difference between nitrogen transport in CZ on the one hand and epitaxial and FZ silicon on the other [4].

With extrapolated parameters $D_1K^{1/2}$ and τ , the nitrogen incorporation from the melt can be analyzed. Even if the initially incorporated species are only N_1 , subsequent formation of dimers does not deplete the N_1 concentration due to a fast supply of N_1 by diffusion from the interface. The incorporated concentration of nitrogen (of $N_1 + N_2$) is then in equilibrium with the melt. The experimental segregation law suggests that the dominant nitrogen state at the melting point is N_1 and not N_2 . However, already below 1200°C , the dimeric species becomes dominant. The nitrogen interstitial species N_1 and N_2 can trap vacancies giving rise to substitutional nitrogen (denoted by a symbol VN) and other species like VN_2 and V_2N_2 . Using the reported first-principle formation energies [5,6], it can be concluded that VN far prevails over the two other species at the void formation stage (around 1100°C in CZ crystals). The V_2N_2 species is expected to become favored below 1000°C while VN_2 is always of a negligible contribution.

This scenario of vacancy-nitrogen interaction was shown [7] to be quantitatively consistent with the experimental data on voids in CZ crystals. Nitrogen doping results in a strong vacancy trapping into VN state, which in turn leads to a strong increase in the void density and to a moderate reduction in the void nucleation temperature. Another important effect of nitrogen is to expand the vacancy region of a crystal (where voids are formed) and to shrink the interstitial region (where A-swirls are formed). If a single wafer (of a mixed vacancy/interstitial type in the absence of nitrogen) is inspected, an apparent effect is 'suppression' of A-swirls by nitrogen. Actually, nitrogen simply reduces the interstitial region - not affecting the formation of A-swirls within this region at all. On the contrary, void formation within an expanded vacancy region is strongly affected by the presence of nitrogen, due to the vacancy trapping effect.

In FZ crystals the nitrogen effect on voids is quite different: in spite of a predicted very strong increase in the void density (and accordingly, a very strong reduction in the void size) the voids are completely suppressed. It is

manifested by the presence of frozen-in vacancy-nitrogen point defects, in a concentration $\sim 10^{14} \text{ cm}^{-3}$ which is an expected concentration of incorporated vacancies. These frozen-in 'vacancies' (vacancies trapped by nitrogen) can be detected by a Pt diffusion test [8]. They can be also 'activated' into deep donor centers by a short anneal at 900 or 1000°C [9]. A clear interpretation of the latter result is that the frozen-in species are electrically-inactive but they are converted by anneal into a high-temperature form VN which is known to be a deep center. The grown-in species can not be V_2N_2 since this form is expected to be a stable at 900°C . The conclusion is that although V_2N_2 is a thermodynamically favored form below 1000°C , it is not actually produced during crystal growth for kinetic reasons. On the other hand, VN_2 was concluded to be always a minor species.

A way out of this apparent contradiction is to assume that the single interstitial N_1 is a bistable defect represented by two atomic configurations N_{1A} and N_{1B} . The former is responsible for the nitrogen transport and exists in equilibrium with N_2 ; however it can not trap vacancies. The latter is of a negligible pairing rate but it is a major vacancy trap. In oxygen-rich (CZ) crystals the two forms N_{1A} and N_{1B} are assumed to be in the equilibrium ratio, due to a catalytic effect of oxygen; here one does not need to distinguish between the two forms. On the contrary, in FZ crystals the N_{1A} and N_{1B} species exist independent one of the other. Then the vacancy traps N_{1B} are inherited from a high- T stage in a non-equilibrium (with respect to N_2) concentration. Vacancy trapping is accordingly far stronger than that in CZ crystals which accounts for void suppression and for frozen-in 'vacancies' found in FZ nitrogen-doped samples. In the presence of a high non-equilibrium concentration of N_{1B} species, the initially frozen VN 'vacancy' will be converted into VN_2 upon lowering T , by attaching an abundant N_{1B} species. It was also reported that although Pt test reveals a high 'vacancy' concentration in as-grown nitrogen-doped FZ samples, almost no 'vacancies' are found after a short 1000°C (or similar) anneal. It can be thus concluded that the grown-in species VN_2 are easily 'counted' (converted into Pt_s) by a reaction $Pt_i + VN_2 \rightarrow Pt_s + N_2$ while VN is essentially an uncountable species (the $Pt_i + VN$ reaction is very slow).

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