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A secondary-ion mass spectrometry analysis of the coimplantation of nitrogen, carbon, and oxygen into float-zone silicon followed by rapid thermal annealing for 10 s at different temperatures is used to study the anomalous diffusion behavior of nitrogen in silicon. The results may be only partially explained by a model of paired nitrogen atom diffusion. The complexity of the diffusion of nitrogen in ion-implanted samples, with and without coimplants, and the expectation that the nitrogen after annealing may be in many different forms, suggest that studies which use nitrogen implantation for basic understanding of nitrogen-related defects may be misleading.

Nitrogen from a nitrogen ambient has been shown to incorporate into oxygen precipitates in Czochralski (CZ) silicon as a result of thermal processing.¹ The undoped (by nitrogen) CZ silicon was thermally processed at 1050 °C for 24 h in nitrogen. Secondary-ion mass spectrometry (SIMS) depth profiles of the nitrogen and oxygen concentrations revealed a correlation between the nitrogen and oxygen fluctuations representative of oxygen precipitation, and SIMS images demonstrated even more directly the coaggregation, similar to that found earlier for carbon and oxygen coaggregation.² The puzzle in this recent finding was the obvious requirement for nitrogen to diffuse at least 60 μm deep (the final depth of the SIMS profile) during this thermal processing, while the published diffusion coefficients^{3,4} suggested the nitrogen diffusion length would be between 1 and 4 μm under these conditions.

Recently, it was shown that the diffusion coefficient of a pair of nitrogen atoms in float-zone (FZ) silicon was four to five orders of magnitude greater than the diffusion coefficients reported earlier.⁵ The explanation presented was the earlier work^{3,4} represented the diffusion coefficient of elemental nitrogen accompanied by the lattice. In particular, the diffusion measurements which used ion implants³ depended upon the formation of nitrogen donors, and the donor formation rate of implanted nitrogen atoms is not known. However, it has also been shown⁶ that nitrogen is predominantly incorporated in pairs under ion implantation and annealing. This is also consistent with earlier Rutherford backscattering spectrometry (RBS) studies⁷ of ion-implanted nitrogen and annealing. Since nitrogen pairs diffuse so fast and since ion implantation results in nitrogen pairs, it seemed appropriate to more closely study the diffusion of ion-implanted nitrogen under annealing. Even though nitrogen implants followed by annealing have been used extensively for the study of nitrogen interactions in silicon, to our knowledge the diffusion behavior as determined by SIMS has not been reported.

The samples were prepared by implanting the rare isotopes ¹⁵N, ¹³C, and ¹⁸O into lightly doped FZ silicon, both

$\langle 100 \rangle$ and $\langle 111 \rangle$ orientation, at 200 keV and $1 \times 10^{14}/\text{cm}^2$ doses. Single-element, dual-element, and triple-element implants were made. The annealing was performed using a flashlamp rapid thermal annealer (RTA) for 10 s in argon ambient at different temperatures. The procedure was to cleave each implanted wafer into four pieces, one for no anneal and the other three pieces for annealing at 800, 950, and 1050 °C.

The SIMS measurements were made at Charles Evans & Associates using a CAMECA IMS-3f ion microanalyzer equipped with a cesium primary beam. The cesium beam was rastered over an area of $250 \times 250 \mu\text{m}$ with secondary ions of ²⁸Si¹⁵N⁻, ¹³C⁻, and ¹⁸O⁻ originating from a central area of 85 μm in diameter. The secondary-ion signals were quantitated using ion implants into silicon; this is effective for the molecular ²⁸Si¹⁵N⁻ detection scheme as well.¹ The depth scales were obtained by measuring the sputtered crater depth with a Sloan-Dektak profilometer.

Figure 1 illustrates one of the puzzles about nitrogen diffusion from ion implantation followed by RTA. The figure is a composite of the nitrogen profiles after implantation into $\langle 100 \rangle$ silicon and followed by the three RTA temperatures. The unannealed implant peaks at about 0.6 μm . After 800 °C for 10 s we see a small drop ($\times 1/2$) in the implant peak height and a diffusion tail to about 3 μm at which depth we reach instrumental background conditions. After 950 °C,

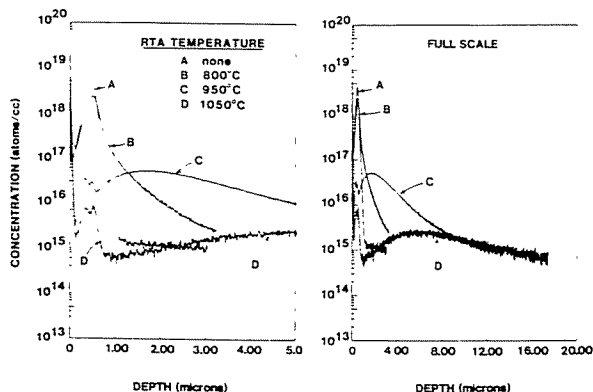


FIG. 1. SIMS depth profiles of [¹⁵N] in $\langle 100 \rangle$ FZ silicon implanted with ¹⁵N at 200 keV and dose of $10^{14}/\text{cm}^2$ followed by RTA (10 s in argon).

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however, we see a large drop ($\times 1/100$) in the implant peak height and a diffusion tail which rises to a level higher than the nearer surface peak and then slowly drops to instrumental background level at about $12 \mu\text{m}$ deep. Furthermore, after 1050°C we see the main peak drops $\times 1/600$ and the diffusion tail again rises and then drops to instrumental background level at about $16 \mu\text{m}$ deep. The same effect shows up for $\langle 111 \rangle$ silicon. The effects are similar although not as dramatic for higher doses of nitrogen.

It appears that the nitrogen at the main peak (R_p) is bound in the damage regions from the ion implantation and that as the annealing temperature is increased more of the bound nitrogen is released, some of which diffuse deeper into the crystal rather than out of the crystal. The diffusion lengths at the three temperatures (800 , 950 , and 1050°C) for paired nitrogen atoms⁵ are ~ 0.3 , 3 , and $7 \mu\text{m}$, respectively, which appear too small to explain the results, although they are far more explanatory than the diffusion lengths from the earlier reports of diffusion coefficients. It is, however, obvious from the formation of the deep broad peak in the nitrogen distribution after 950 and 1050°C anneals that the diffusion of the nitrogen is influenced by something other than simple outdiffusion from an implant. If the annealing process is changing the defect depth distribution caused by the implant in such a way as to form a broad peak of defects below the implant R_p , then paired nitrogen atoms coupled with interstitial diffusion from the implant may diffuse rapidly to the deeper defect distribution. No transmission electron microscopy analysis was performed on the samples to determine the defect distributions.

A comparison of the behavior of nitrogen and carbon diffusion under a 950°C anneal in coimplanted (N and C) $\langle 100 \rangle$ silicon is shown in Fig. 2. More of the nitrogen remains at the original implant peak location after the RTA than when nitrogen is implanted alone, but the rise in the nitrogen tail still occurs. In contrast, the carbon diffusion gives a small broadening in the carbon implant distribution, but no rise in the tail. The nitrogen diffuses to depths greater than $7 \mu\text{m}$, while the carbon tail reaches instrumental background level at about $1.5 \mu\text{m}$. A calculation of the areal den-

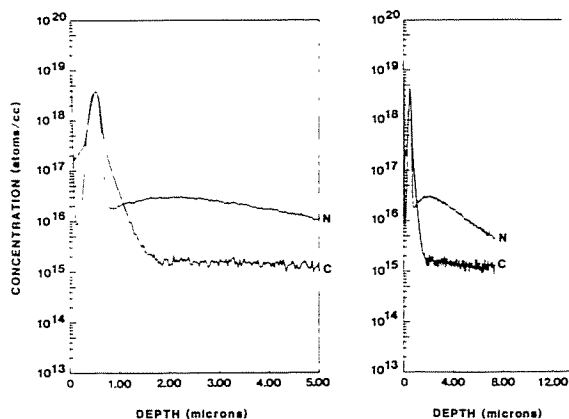


FIG. 2. SIMS depth profiles of [^{15}N] and [^{13}C] in $\langle 100 \rangle$ FZ silicon implanted with ^{15}N and ^{13}C at 200 keV and doses of $10^{14}/\text{cm}^2$ each, followed by RTA at 950°C (10 s in argon).

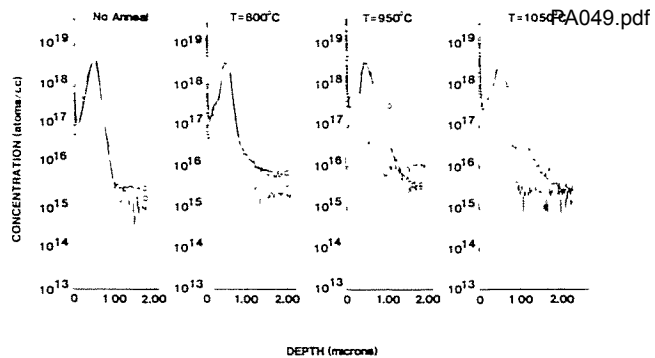


FIG. 3. SIMS depth profiles of [^{15}N], [^{13}C], and [^{18}O] in $\langle 100 \rangle$ FZ silicon implanted with ^{15}N , ^{13}C , and ^{18}O at 200 keV and doses of $10^{14}/\text{cm}^2$ each, followed by RTA (10 s in argon).

sity of the remaining carbon and nitrogen above instrumental background reveals all of the carbon is still present and about half of the original nitrogen is detectable in the first $7 \mu\text{m}$. A similar effect shows up for $\langle 111 \rangle$ silicon. A similar comparison of the behavior of nitrogen and oxygen diffusion results in the same finding as with nitrogen and carbon.

If nitrogen, carbon, and oxygen are all coimplanted and annealed, the result is shown in Fig. 3. In this case the movement of nitrogen as a function of temperature is much more limited than in the single- or dual-implant cases. Integrating the profiles to calculate areal densities shows all the carbon and oxygen are accounted for and most of the nitrogen is accounted for even at 1050°C . The effect is the same for $\langle 111 \rangle$. The calculated ion yields for nitrogen, carbon, and oxygen are the same as for the individual implants, so these different results are not due to some ion yield changes. The difference in nitrogen diffusion here may be due to: the combined presence of oxygen and carbon with the nitrogen forms slowly diffusing nitrogen-related complexes; the nitrogen pairing is broken; or the triple-implant creates more damage-related sites which somehow bond the nitrogen more tightly. However, since higher dose nitrogen implants also show the effect, the latter reason (triple implant at $10^{14}/\text{cm}^2$) seems less likely.

The complexity of the diffusion of nitrogen in ion-implanted samples, with and without coimplants, and the expectation that the nitrogen after annealing may be in many different forms, suggests that studies which use nitrogen implantation for basic understanding of nitrogen-related defects may be misleading.

In summary, the SIMS analysis of coimplanted N, C, and O in FZ silicon followed by very short RTA reveals anomalous diffusion of the nitrogen which may be only partly explained by paired nitrogen diffusion. The anomalous diffusion appears independent of the FZ silicon orientation.

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