

MEIS study of As implantation in O or N pre-implanted Si(001)

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Abstract

We have used medium energy ion scattering (MEIS) to study dopant (arsenic, As) behavior in vacancy-rich layers on Si(100). The vacancy-rich layers were generated by implantation at 400 °C of 240 keV O₂⁺ or N₂⁺ ions and a dose of $2.5 \times 10^{16} \text{ cm}^{-2}$. The As dopant was introduced by implanting at 20 keV at room temperature to a dose of $5 \times 10^{14} \text{ cm}^{-2}$, followed by either rapid thermal annealing (RTA) or furnace annealing (FA). The results showed very good Si crystal quality after both thermal treatments, especially when compared to otherwise identical samples without pre-implanted O or N. Differences between the O and N pre-implanted samples were also observed, suggesting the occurrence of chemical effects in the crystal recovery and dopant diffusion processes.

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1. Introduction

As electronic devices reach ever higher performance and smaller power consumption, their decreasing dimensions require a better understanding of dopant behavior during the various fabrication processes. Ion implantation is still widely used for introducing dopants into single-crystal substrates, despite the fact that this process introduces many crystal defects. It is therefore necessary to use some crystal recovery process, such as thermal annealing, to eliminate defects and to allow dopants to occupy substitutional positions in the lattice so that they can become electrically active. This is also the case for ultra-shallow junction fabrication, where highly doped, highly activated and low sheet resistance films must be obtained [1]. Dopant diffusion and interaction with defects can have drastic effects on device performance [2,3].

It is well known that As strongly interacts with vacancies (V), creating As_nV complexes. When bonded to a

vacancy, As becomes electrically inactive. The presence of vacancies also influences the diffusion of As atoms not directly bonded to the vacancy [4–6]. Vacancies also play a significant role in the annihilation of ion implantation-generated interstitials.

We have previously studied the differences between As behavior in bulk-Si and Separation by IMplantation of OXYgen (SIMOX) wafers [7]. We showed that excess vacancies in SIMOX are responsible for better crystal quality, lower dopant loss and improved electrical characteristics after thermal annealing in SIMOX compared to bulk-Si. We now present results on the effects of vacancies on the As redistribution caused by high temperature co-implantation. To do this, we have created a 150 nm deep vacancy-rich layer by O₂⁺ or N₂⁺ ion implantation prior to As implantation.

2. Experiment

The experiments were performed on (100) oriented p-type Si substrates with resistivity of 8–12 Ω cm. The native SiO₂ layer was removed in diluted HF just before

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implantation. A 150 nm deep vacancy-rich layer was first formed by O_2^+ or N_2^+ ion implantation at 240 keV using a dose of $2.5 \times 10^{16} \text{ cm}^{-2}$ at 400 °C [8,9]. Following this pre-implantation, As^+ was implanted at 20 keV and a dose of $5 \times 10^{14} \text{ cm}^{-2}$ at room temperature. The low As ion implantation energy guarantees that the As profile is fully contained in the vacancy-rich layer. The samples were then processed by rapid thermal annealing (RTA) at 1000 °C for 10 s or by furnace annealing (FA) at 1000 °C for 15 min in a nitrogen atmosphere. Since *all* samples were implanted with As, they will be labeled according to the pre-implantation ion and the thermal treatment, for example, O RTA refers to the sample pre-implanted with oxygen, implanted with As and annealed in RTA. In the same sense, N as-implanted means that the sample was pre-implanted with N, implanted with As and was not annealed.

A H^+ beam with an energy of 130.5 keV was used for the medium energy ion scattering (MEIS) measurements. Backscattered ion energies were analyzed with a high-resolution ($\Delta E/E \sim 0.1\%$) toroidal electrostatic energy detector resulting in a depth resolution of $\sim 0.9 \text{ nm}$ at a depth of 50 nm. In all channeling measurements, the beam was aligned in the [100] channeling direction and the detector was in the [111] blocking direction. For the random geometry measurements, slightly different sample orientations were used, but the angle between the beam and the detector remained constant. These alignment effects were taken into account via simulation with the software MEIS [10] and were used in the normalization of the spectra.

3. Results and discussion

Fig. 1 shows the MEIS spectra in the Si peak energy region for the O or N as-implanted samples. We see that both the channeling and the random spectra coincide to a depth of $\sim 34 \text{ nm}$ (the depth scale was determined from the simulations), which means that the samples were amorphized by the As implantation to that depth. There is a small difference between the yields from the O and N pre-implanted samples. This is most likely associated with

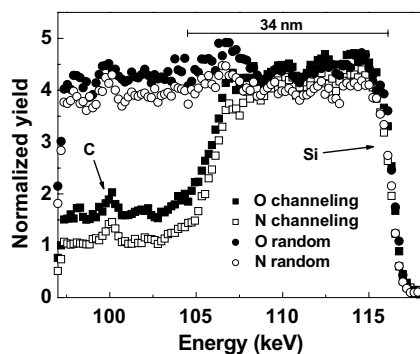


Fig. 1. MEIS spectra of as-implanted samples in channeling and random orientations. The experimental data are shown in the energy region corresponding to the $\sim 34 \text{ nm}$ amorphous region created by the As implantation.

different vacancy concentrations induced by a chemically specific mechanism of N and O interaction with vacancies, as shown previously [8,9]. More studies are necessary to confirm this hypothesis.

Fig. 2 compares the channeling spectra of the samples after RTA and FA. The same energy range was used as in Fig. 1. Clearly, the yield is very low for energies below the Si surface peak ($\sim 115 \text{ keV}$) in all samples. This indicates that the amorphous regions created by the As implantation have been fully re-crystallized and that the remaining crystal has excellent quality (a very low concentration of interstitial defects). A small peak of non-substitutional N appears in the N FA sample. This peak occurs at a depth corresponding to the interface between Si and the surface SiO_2 (the native oxide was removed prior to the ion implantations and anneals. The surface oxide that appears in the spectra was formed during the anneals and/or due to air exposure after the anneals). This means that the N atoms diffused towards the surface and accumulated at the interface with the oxide. In the N RTA sample this peak is very small and almost not detectable. A similar effect is observed indirectly with oxygen in the O FA sample, as it shows a larger O areal density than the O RTA and both N samples corresponding to additional 13 \AA of SiO_2 . MEIS cannot distinguish between oxygen in the surface oxide and implanted oxygen that might have diffused from deeper layers of the sample.

Fig. 3(a) shows the As profiles of the as-implanted samples. No observable differences are seen between the O and N samples nor between the random and channeling alignments, indicating that the As atoms are not substitutional. This is a trivial conclusion as the crystal has been amorphized.

Comparing the As random geometry spectra in Fig. 3(b), we can notice that the dopant profiles after annealing depend both on the nature of the pre-implanted ion and the duration of the annealing, with significant differences between short diffusion processes (RTA, 10 s) and long processes (FA, 15 min). In all the samples As accumulates close to the Si/ SiO_2 interface. The O FA samples present a slightly higher accumulation of As in this region and the N FA sample shows the lowest. The two RTA samples show similar degrees of interface As segregation. Comparison of

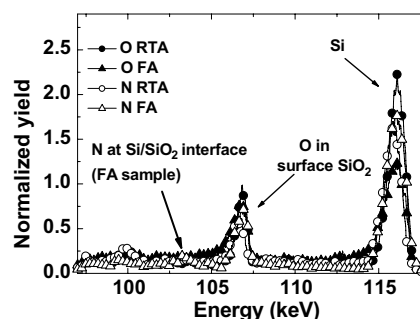


Fig. 2. MEIS spectra of the Si, O and N peaks region of the annealed samples in channeling alignment.

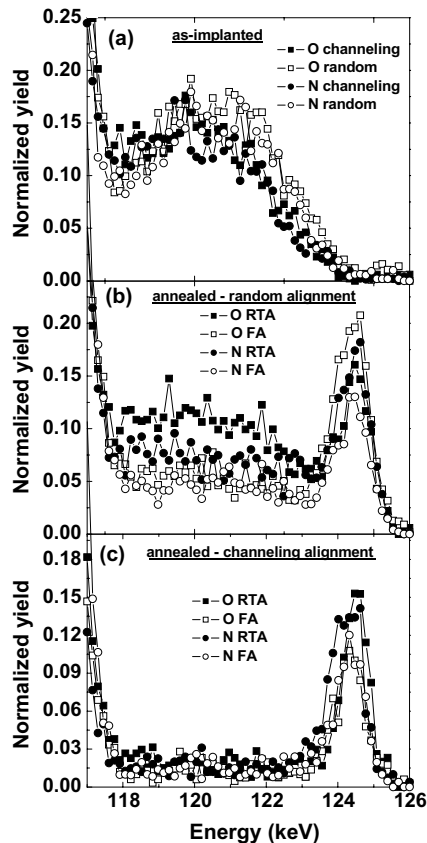


Fig. 3. MEIS spectra of the As peak region: (a) random and channeling spectra of as-implanted As, (b) random MEIS spectra of As after RTA and FA and (c) channeling spectra of annealed As.

the As profiles for the bulk region (between 117 and 123 keV) shows that the O RTA sample presents the highest concentration of As, followed by the N RTA and then by both FA samples, with similar As profiles. A larger amount of As in the N RTA and both FA samples must have out diffused (or diffused deeper into the samples; the latter cannot be positively excluded as a possible As signal is not visible due to the Si background at energies below 117 keV) compared to the O RTA one. It is possible to infer from these data that the As diffuses faster in the first stages of anneal in the N RTA samples in comparison with the O RTA sample, since the As profile in the N RTA sample is more similar to the As profiles in the FA samples. This difference vanishes after a longer annealing (no difference between O FA and N FA), which indicates that the diffusion enhancement mechanism is only important during an initial brief period at the temperature we used for our annealing experiments. In other words, the transient enhanced diffusion (TED) [11] of As is stronger in the N samples than in the O ones (by TED we understand a large increase in the dopant diffusivity usually generated by the interaction of the dopant atoms with the ion implantation damage during the first stages of annealing).

It has been shown elsewhere [12,13] that the presence of N in Si decreases the size of the vacancy agglomerates, but increases their density due to nitrogen–vacancy complex

formation, and that Si crystals doped with N during growth have an excess vacancy concentration [10]. Also, in other studies done on N and O implantation in Si [9], it has been demonstrated that for the same implantation parameters, N implanted samples presented higher negative strain than O ones. This negative strain was related to the presence of vacancies in the crystal lattice. As the implantation conditions used in that study [9] and in our work are comparable, we can postulate that the amount of vacancies in the N pre-implanted samples in our work is larger than in the O pre-implanted ones. Since it is known that As diffusion occurs via interaction with vacancies, higher As diffusion is expected to occur in the N samples in the initial stages (during RTA), when a large amount of vacancies are available to enhance As diffusivity. In the next stages of annealing (FA), since N has higher tendency to capture vacancies than O, the number of vacancies available for As in the N samples is reduced faster, which would explain the faster reduction of As diffusivity in the N samples compared to the O ones.

The channeling spectra of these samples (Fig. 3(c)) show excellent As substitutionality in the Si lattice, except at the Si/SiO₂ interface. A close examination of the As spectra at that interface shows that the O FA samples present the best substitutionality of all (considering that it has the highest amount of As in that region). This is in agreement with the fact that O is less effective in capturing vacancies than N, i.e. the vacancies survive and are able to participate in the crystal recovery process for longer times in the O pre-implanted samples. This is the opposite behavior observed in the SIMOX samples [7]. In SIMOX, the vacancies were responsible for better crystal quality and better As substitutionality in the initial stages of anneal, but after longer annealing times, the amount of Si interstitials and electrically deactivated non-substitutional As atoms increased. The main difference between SIMOX and the samples studied in the present work is that the vacancies in SIMOX have already passed through a very long, very high temperature anneal that allows them to form stable complexes. In the O and N pre-implanted samples studied here, the vacancies have not been annealed prior to the dopant anneal, so they are present as scattered point defects, compared to the vacancies found in SIMOX. Due to the fact that the vacancies in the present case have point defect character, it is easier for the ion implantation-generated interstitials and the As atoms to interact with them. In the N samples, the crystal quality and dopant substitutionality improvement rates are reduced after the initial anneal stages, which is the reason why the difference between the spectra for the N RTA and N FA samples is smaller than the difference between the O RTA and O FA ones (Fig. 3(b)). One possible explanation is the formation of nitrogen–vacancy complexes. These complexes slow down vacancy diffusion and the void formation rate [12,14,15]. In other words, nitrogen–vacancy complexes are less reactive than single vacancies. These complexes make the interaction of vacancies with As more difficult and slows down the dopant diffusion.

4. Conclusions

The effect of a vacancy-rich layer on Si crystal recovery and As anneal behavior was studied by MEIS. The results showed that the amorphized crystal was fully re-crystallized ending up with excellent crystal quality (very low interstitial concentration) independent of the annealing procedure or the nature of the pre-implanted ions. The final crystal quality of the samples studied in the present work was better than in Si(001) without pre-implantation and similar to the SIMOX samples studied previously [7].

We have observed several effects related to the chemical nature of pre-implanted ions. These include differences in the As diffusion mechanism: In the initial stages of annealing, As diffused faster in the N samples than in the O ones. After long annealing times, the dopant profile was similar in the N and O samples. This suggests that the formation of nitrogen–vacancy complexes makes the interaction between vacancies and As more difficult in the N samples than in the O samples right after the initial annealing stages. This effect slows down the dopant diffusion. It should also be the reason why the difference between the As concentration profile in the N RTA and N FA samples is smaller than between O RTA and O FA. Accumulation of N at the Si/SiO₂ interface (mainly in the FA sample) was also observed. It is possible that oxygen also accumulated in the same region in the O samples, but with MEIS we cannot distinguish between the oxygen of the surface oxide and the implanted oxygen that might have diffused from deeper layers of the sample.

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