Formation and growth of nanocavities and cavities induced by He\textsuperscript{+} implantation in silicon

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Abstract
Nanocavities and cavities are known to be efficient gettering sites for metallic impurities in silicon. Here, we report results from implanted \langle\textsuperscript{100}\rangle silicon at room temperature with 50 keV helium ions at a dose of $3 \times 10^{16}$ cm\textsuperscript{-2}. Due to its low solubility, He segregates in gas-vacancy complexes and forms nanobubbles. Then, during an N\textsubscript{2} ambient annealing at 800 $^\circ$C using either rapid thermal annealing (RTA) or conventional furnace annealing, nanobubbles grow and He is released from the nanobubbles by gas exodiffusion, leading to (nano)cavities’ formation. (Nano)cavities and residual defects were observed by transmission electron microscopy (TEM). The fraction of retained helium was shown to decrease with annealing time according to the first-order gas release model. Two nucleation-growth mechanisms involved in the growth of these (nano)cavities have been studied. A remarkable result shows evidence about the balance-time dependence of the two mechanisms involved in the growth process of (nano)cavities. At the very beginning (30 s) of the annealing, the main mechanism is the migration-coalescence including nanobubbles and vacancy-helium complexes leading to the cavities’ formation. Then, the Ostwald ripening mechanism, related to the helium exodiffusion, between the nanocavities and cavities appeared.

Keywords: He ion implantation, nanobubbles, nanocavities, He desorption

Classification numbers: 4.05, 5.01, 6.04

1. Introduction
(Nano)cavities induced by hydrogen or helium implantation are known to be very efficient traps for unwanted metallic impurities in silicon [1–8]. The widely accepted mechanism of trapping (or gettering) is the chemisorption at the internal surface of the (nano)cavities [4]. The gettering procedure is a method of removing impurities from the active device region. Hence it has the most potential to satisfy the requirements on the predicted device layer [9]. Griffioen et al [10] were the first to show that helium, when implanted into silicon may form small bubbles and then outdiffuse during annealing, leaving empty cavities. However, the helium desorption kinetics generally observed at the temperature used to form cavities (higher than 700 $^\circ$C) is not completely understood. In this paper, we show the results of the evolution of (nano)cavities formed at 800 $^\circ$C as a function of the annealing time. The latter allows us to understand the role of the helium desorption in the formation of (nano)cavities.

2. Experimental
Czochralski (CZ), (100) oriented, n-type silicon wafers, 500 $\mu$m thick, were used in this study. They were implanted at room temperature with 50 keV helium ions by means of a Bereas-Nier source-type implanter at a dose of $3 \times 10^{16}$ He m\textsuperscript{-2}. According to the simulation program, named the stopping and range of ions in matter (SRIM08 or TRIM08) [11], the mean projected range ($R_p$) of these ions is $\sim$450 nm.
Figure 1. TEM image of nanobubbles in the as-implanted silicon sample with helium at $3 \times 10^{16}$ cm$^{-2}$ and 50 keV.

Figure 2. TEM cross section of an as-implanted sample with 50 keV and $3 \times 10^{16}$ He cm$^{-2}$. The depth profiles of He and vacancy distribution as obtained by a SRIM08 calculation is reported for comparison.

The implantation of helium ions into the samples was followed by the heat treatment in N$_2$ atmosphere, using either a rapid thermal annealing (RTA) system or a conventional furnace annealing (CFA). The annealing times range was from 30 s to 4 min for RTA and 60 min for CFA at 800 $^\circ$C. This temperature is expected to form a cavity layer. The morphology of the cavity layer was observed by transmission electron microscopy (TEM) using a FEI Tecnai G² F20 microscope. To avoid any electron irradiation we performed TEM observations at 150 kV. The thinned samples in cross section were prepared by mechanical thinning. TEM analyses were performed along the $\langle 110 \rangle$ direction, for cross view analyses.

3. Results and discussion

Helium implants in silicon, at a concentration equal to or higher than the critical value of $3 \times 10^{20}$ cm$^{-3}$ [12], induce nanobubble formation. Nanobubbles can be observed directly by TEM analyses (e.g. figure 1). Figure 2 shows a TEM micrograph of an as-implanted sample with 50 keV He ions at a fluence of $3 \times 10^{16}$ He cm$^{-2}$. Also reported in this figure are the depth profiles of vacancies and He as obtained by SRIM08 calculations.

Nanobubbles of 2–3 nm in diameter are present from sample surface to 700 nm, corresponding to the end of the depth profile of He and vacancy distribution (figures 2–4). The peak of nanobubble concentration is localized at the depth shallower than the one of the He projected range, in a region where the radiation damage peak is located according to SRIM08 calculations.

TEM observations have been performed as well on wafers annealed for various times at 800 $^\circ$C. Figure 5 is a TEM micrograph of a 50 keV—$3 \times 10^{16}$ He cm$^{-2}$ implanted sample annealed for 30 s at 800 $^\circ$C.

We will show below that the main part of He has been removed from the sample after annealing. So, for clarity, we design as (nano)cavities the nanostructures observed after nanobubble evolution during annealing.

It can be seen that, even for this short annealing time, the large cavities (with diameter up to 10 nm) at the region II in...
After annealing time $>2$ min: compared to the nanobubbles we note a significant decrease of the nanocavity concentration at both sides of the cavity band. This confirms the predominance of a diffusion mechanism of vacancies in the second stage.

(iii) Considering the experimental uncertainties, we observe an almost constant concentration of all the cavities between 5 and 30 nm during annealing of 30 s to 4 min. This point is verified by the evaluation of free volumes involved in the band of cavities.

(iv) After 4 min of annealing and even after a furnace annealing during 1 h (figure 9), in front of the band of cavities, the decrease of the distribution is even stronger as we approach either the free surface, or the band of cavities. This leads to the distribution with a peak of 300 nm. This effect may be attributed to the variation of helium exodiffusion rate during annealing.

We estimated the theoretical variation of He from the equation used by Griffioen et al [10] for the helium desorption of the first order:

$$\frac{dN_{He}}{dt} = -\frac{3N_{He}P}{R_{b}} \exp\left(-\frac{E_{p}}{kT}\right).$$

where $N_{He}$ is the number of He atoms in the bubble, being a function of annealing time, $dN_{He}/dt$ is also known as the evolution of the residual fractions of He as a function of annealing time, $P$ is the permeation rate of He in Si, $R$ is the distance from the surface, $r_b$ is a bubble radius, $E_p$ is the activation energy of permeability, $T$ is annealing temperature and $k$ is Boltzmann constant ($\sim 8.6 \times 10^{-5}$ eV K$^{-1}$). Integrating this equation gives a rate of helium remaining in a cavity:

$$\frac{N_{He}}{N_0} = \exp(-At),$$

with

$$A = \frac{3P}{R_{b}} \exp\left(-\frac{1.7}{kT}\right),$$

where $R = 450$ nm, $r_b = 2$–20 nm and $T = 800$ °C.

From the expression (2), we calculated the average number of the helium atoms remaining in the (nano)cavities from their detailed distributions in size.

For the energy of $50$ keV, these calculations show that there are still $97$–$80$% of helium atoms in large cavities for an annealing time varying from $30$ s to $4$ min. For the nanocavities, the amount of remaining helium decreases with depth. It is practically zero at depth lower than or equal to $100$ nm from an annealing time of $4$ min.

For an annealing time of $1$ h, there is almost no more helium in the nanocavities, whatever their position.

The kinetic evolution of ‘nanocavities’, through the evolution of vacancies during annealing at $800$ °C for energy of $50$ keV is summarized in table 1 below.
Figure 8. Implanted samples \((E = 50 \text{ keV}, D = 3 \times 10^{16} \text{ He cm}^{-2})\). Comparison of the nanobubble distribution before annealing with the series of observed (nano)cavities after a rapid annealing of (a) 30 s, (b) 2 min, (c) 4 min.

Table 1. Concentration of vacancies estimated in the cavities and ‘nanocavities’ after annealing at 800 \(^\circ\)C as a function of the annealing time for implantation at 50 keV. All observed (nano)cavity regions have the same thickness.

| Time (s) | Average volume of cavities \((\text{cm}^3 \text{ cm}^{-2}) \times 10^{-14}\) | Vacancy concentration of cavities \((\text{cm}^{-2}) \times 10^{-16}\) | Vacancy concentration of nanocavities zone I \((<400 \text{ nm}) (\text{cm}^{-2}) \times 10^{-14}\) | Vacancy concentration of nanocavities zone III \((>500 \text{ nm}) (\text{cm}^{-2}) \times 10^{-13}\) |
|---------|-------------------|-----------------|----------------------|-----------------------|
| 30      | 6.8               | 3.4             | 3.1                  | 21                    |
| 120     | 7.7               | 5.4             | 2.1                  | 8.8                   |
| 240     | 1.2               | 5.7             | 1.5                  | 8.5                   |

Figure 9. Implanted samples \((E = 50 \text{ keV}, D = 3 \times 10^{16} \text{ He cm}^{-2})\). Comparison of the nanobubble distribution before annealing with conventional annealing for 1 h.

We have shown in table 1:

(i) For the annealing time from 30 s to 4 min, the volume growth of cavities in the band leads logically to an increase in the concentration of vacancies in this band.

(ii) Similarly, for annealing time from 30 s to 4 min, the concentration of nanocavities in the area in front (zone I) and back (zone III) of cavity band (zone II) decreases progressively and also leads to a decrease of the number of vacancies in zones I and III. Then it parallely leads to a decrease of the loss of helium in the nanocavities in zones I and III. This confirms that the loss of helium favors the diffusion of vacancies out of nanocavities.

(iii) However, the decrease of the vacancy concentration of nanocavities in zone I (in the order of \(10^{14} \text{ vacancies cm}^{-2}\)) added to that in zone III (in the order about \(10^{14} \cdot 10^{13} \text{ vacancies cm}^{-2}\)) is two orders of magnitude smaller than the increase of the vacancy concentration in the cavities (in the order of \(1 \cdot 2 \times 10^{16} \text{ vacancies cm}^{-2}\)). The very probable diffusion of the vacancies (zone II) from the nanocavities (part of zone I near the cavity band and zone III) to the cavities (Ostwald ripening mechanism) cannot, anyway, explain the increase of the vacancy concentration of cavities. The most likely hypothesis is the contribution of vacancies with the distance from ‘nanocavities’ \(\leq 1.5 \text{ nm}\) and vacancy-He complexes remained stable in the first stage of annealing. This hypothesis is in agreement with the result obtained for the nanobubble concentration compared to the results obtained by other authors in high resolution.

(iv) In the case of annealing of 1 h, we observe a strong decrease in the vacancy concentration of the nanocavities in zone I and particularly we observe the presence of a hollow between the nanocavity and cavity region (see in figure 9). It is therefore likely that after annealing of 4 min, an Ostwald ripening mechanism becomes significant and increases with time.

4. Conclusion

This study has allowed us to show that:

The evolution during the annealing of nanobubble system created by helium implantation is separated into two stages: (i) at the beginning of annealing (\(\leq 30 \text{s}\)), in the center of the nanobubble band with the high density, there is formation
of a cavity band by migration coalescence. (ii) Secondly, for higher annealing times, the study on (nano)cavities as a function of the annealing time (in particular with RTA) showed that the concentration of cavities is practically constant. The growth mechanism by diffusion of the vacancies predominates.

At the first stage, the nanobubbles which do not participate in the formation of cavities are found to be almost unchangeable (size, density and distribution in depth). This confirms that only the migration coalescence process occurs at this stage.

At the second stage, all our observations and calculations have shown that the evolution of ‘nanocavity’ and cavity system were most likely controlled by a diffusion process of ‘nanocavities’ to the free surface and to cavities (Ostwald ripening mechanism).

The relationship between the rates of helium desorption and the disappearance of the nanocavities has been clearly demonstrated. The phenomenon of vacancy diffusion outside of nanocavities is accelerated by helium exodiffusion. In other words, the activation energy of the vacancies in the nanocavities is lower when the helium exodiffuses [10].

The desorption of helium, especially fast when the system of (nano)cavities is near the free surface, is accompanied by a disappearance of ‘nanocavities’ located near the free surface.

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