Temperature Dependence of Defects in Hydrogen-Implanted Silicon Characterized by Positron and Ion-Beam Analyses

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Abstract

Nanometer-sized voids formed in Si after H implantation to a dose of $3 \times 10^{16} \text{cm}^{-2}$ and annealing at 600 or 800 °C were characterized by slow-positron and ion-beam analyses. Depth profiles of defects were calculated from the S parameter curves of Doppler broadening and from Rutherford backscattering/channeling spectra. Concentrations of gettering sites were also calculated from the Rutherford backscattering spectra of the samples after Au gettering. Defect profiles by Doppler broadening measurements were found to be shallower than the projected range of implanted H, while profiles of defects and gettering sites detected by the backscattering measurements were close to the projected range. The peak concentrations of defects and gettering-sites were dependent on annealing temperature and analytical techniques. The observed annealing behaviors can be explained by the evolution of vacancy clusters and the interaction of H with defects.

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Key words: H implantation; Si; nanocavities; gettering; slow positron; ion channeling

1. Introduction

High-dose H implantation in Si has been extensively studied, as stable nanometer-sized voids (nanocavities) can be formed after thermal annealing near the projected ranges of implanted H ions [1,2]. Previous studies have shown that such nanocavities are very efficient sinks for fast-diffusing metals in Si and suitable for gettering sites to trap and/or remove unwanted metal impurities introduced during device processing. The gettering to nanocavities was found to be effective not only in single-crystalline Si but also in multicrystalline Si used for solar cells [3]. H-implanted Si has been studied from the side of fundamental materials research in terms of thermal evolution of radiation damage and formation of vacancy-hydrogen complexes by using traditional defect probes such as infrared

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absorption, Raman scattering and electron spin resonance methods [4, 5]. Such techniques are very effective to identify different types of defects but essentially they don’t give the depth information of defects. In order to understand complex annealing behaviors of H-implanted Si and to determine optimal conditions of gettering, positron annihilation spectroscopy with slow positron beams and ion-beam analysis with MeV ion beams have been used as depth-sensitive analytical techniques [6-12]. Note that these two techniques are essentially complementary where positrons and MeV ions are sensitive to vacancy- and interstitial-type defects, respectively. There have been reports using the slow positrons and the MeV ions for H doses ≤ 2×10^{16} cm^{-2} or ≥ 4×10^{16} cm^{-2}. However, the previous gettering studies were mostly performed at a H dose of 3×10^{16} cm^{-2}. This dose was chosen to enhance the nanocavity formation as much as possible and yet to avoid unwanted surface blistering. The annealing behaviors of H-implanted Si are strongly dose-dependent in this dose range. Therefore, this study concentrates on the H dose of 3×10^{16} cm^{-2} corresponding to the previous gettering experiments.

2. Experimental

Czochralski (Cz)-grown Si wafers (B-doped, p-type, 8-12 Ωcm) of (100) orientation were used in this study. Implantation of 50 keV H^+ was performed at room temperature to a dose of 3×10^{16} cm^{-2}. The samples were tilted about 7° off the beam direction to avoid channeling. The samples were cut into about 1.5×1.5 cm^2 pieces and subsequently annealed for 1h at 600 or 800 °C. A conventional quartz-tube furnace with flowing Ar atmosphere was used for annealing. Selected samples were further implanted with 100 keV Au^+ to a dose of 1×10^{14} cm^{-2}, followed by annealing at 600 or 800 °C for 1-10h for the Au labeling of gettering sites. Doppler broadening of annihilation radiation (DBAR) was performed at the slow-positron beamline of the electron linear accelerator at AIST. Before the positron measurements, the surface of the samples was cleaned with acid (H_2SO_4 with H_2O_2) at 50-70 °C and diluted HF to remove contaminations and native oxide layers on the surface. S-E curves obtained by DBAR measurements were analyzed by the VEPFIT code [13]. Rutherford backscattering/channeling (RBS/C) was performed with a 2 MeV He^+ beam from a single-end Pelletron accelerator at AIST. The Au implanted samples were analyzed by RBS without channeling. A projected range and a defect profile of H^+ in Si were calculated by the TRIM code [14]. It should be noted that the analytical data were taken from our previous study [12] but additional data analysis was performed for this study.

3. Results and discussion

Figure 1(a) shows the Doppler broadening S parameters as a function of positron energy for the as-implanted and annealed samples. Solid lines are fits obtained by the VEPFIT code. In the VEPFIT calculation, a bulk S parameter

![Fig. 1 Dopper broadening measurements for the as-implanted sample and the samples annealed at 600 or 800 °C. (a) S-E curves for each sample. (b) Trapping rates calculated from the S-E curves.](image-url)
was determined by the DBAR measurement of the unirradiated Si sample and the bulk diffusion length of 250 nm was assumed [15]. The parameters of the Makhovian function to calculate positron implantation depths were chosen from the report by Vehanen et al. [16]. The S parameter curve of the as-implanted sample has a peak at 4 keV. At this energy, the S parameter increased after the irradiation and decreased after annealing at 600 °C. After annealing at 800 °C, the S parameter increased again. On the other hand, the S parameter curves of the samples annealed at 600 or 800 °C have peaks at 7 keV. This difference in peak energies will be discussed later in this section. Figure 1(b) shows the trapping rates obtained by the VEPFIT calculation assuming two layers to describe the implantation-induced damage. Trapping rates were calculated from positron diffusion lengths [15]. A thin solid line in Fig. 1(b) indicates the projected range of 50 keV H⁺ in Si. The shallow damage layer (first layer from the surface) showed lower trapping rates than the deep damage layer (the second layer from the surface). This trend is consistent with the TRIM calculation, where electronic energy deposition is dominant (i.e., lower damage formation) near the surface but nuclear energy deposition is dominant (i.e., higher damage formation) around the projected range. In the case of the as-implanted sample, the deep damage layer was exactly at the projected range. In the case of the annealed sample, however, the deep damage layers were found to be shallower than the projected range. In addition, the trapping rate at 600 °C was higher than that at 800 °C.

Figure 2 shows the defect (scattering center) concentrations as a function of depth for the as-implanted and annealed samples. The defect profiles were obtained from the RBS/C spectra (shown as the inset of Fig. 2) after the subtraction of dechanneling fraction of aligned spectra. To calculate the depth scale of the horizontal axis in Fig. 2, the energy loss of channeled He ions [17] was taken into account. Defect levels were close to the background in the range from the surface to 300 nm. Defect peaks were detected around the projected range. The peak position of the as-implanted sample was slightly deeper than those of the annealed samples but the differences among them are small in contrast to the DBAR results in Fig. 1(b). The peak defect levels were in order of (600 °C) > (as-implanted) > (800 °C), indicating a different behavior from DBAR results.

Table 1. Peak defect (gettering site) concentrations calculated from three analytical methods used in this study.

|                  | DBAR  | RBS/C | RBS (Au gettering) |
|------------------|-------|-------|--------------------|
|                  | (defects/cm³) | (defects/cm³) | (sites/cm³)       |
| as-implanted     | 2.9×10¹⁷ | 3.5×10²¹ | -                 |
| 600 °C 1h        | 1.8×10²⁰ | 1.3×10²² | 7.1×10¹⁸          |
| 800 °C 1h        | 1.1×10²⁰ | 1.4×10²¹ | 1.5×10¹⁹          |
Figure 3 shows the Au profiles measured by RBS of the samples after Au implantation. Each sample was H-implanted and annealed at 600 or 800 °C for 1h to form nanocavities. Then, the samples were Au-implanted, followed by annealing at 600 °C for 10h or 800 °C for 1h. Since the diffusion of Au at 600 °C is slower than that at 800 °C, the longer annealing time of 10 h was chosen for 600 °C. The second annealing induced the Au diffusion (gettering) to nanocavities and indicate gettering sites through Au decoration of the defects. The Au profiles were plotted only in the range of >100 nm in Fig. 3. The projected range of 100 keV Au in Si was calculated to be 45 nm and thus the damage layer of <100 nm should be related to the Au implantation rather than the H implantation. The Au peak of the sample annealed at 800 °C was detected at the projected range, while the peak position of the sample annealed at 600 °C appears to be shallower. However, in this case, we believe that the diffusion of Au was still in progress even after the annealing for 10h and sufficient gettering sites also exist around the projected range.

Table 1 summarizes the peak concentration of defects calculated from Figs. 1 – 3. The concentrations of defects of DBAR measurements in Fig 1 were calculated using the specific trapping rate for divacancies (1×10¹⁵ s⁻¹) [18] as a measure of defect concentration. As revealed in positron lifetime measurements in our previous study [12], the as-implanted sample has mainly divacancies and the annealed samples have vacancy clusters with temperature dependent sizes. The lifetimes longer than 400 ps were detected in the samples annealed at 600 °C or 800 °C. Such positron lifetimes correspond to vacancy clusters with more than 10 monovacancies. Since specific trapping rates of vacancy clusters increases with increasing vacancy number [19], higher specific trapping rates, that is, lower defect concentrations are expected for the annealed samples in Fig. 1. However, it is difficult to estimate exact cluster sizes of the measured samples as well as corresponding specific trapping rates. Thus, we showed the results in Table 1 just as upper limits of defect concentrations using the specific trapping rate of divacancies. The defects detected by RBS/C correspond to interstitial-type defects as well as dislocations and lattice strain rather than vacancy-type defects. The gettering experiments with the RBS essentially do not give the information on defect types (i.e., vacancy or interstitial type) as Au atoms are trapped at nanocavities and dislocations. Wong-Leung et al. showed that approximately 96% of the 1×10¹⁵ cm⁻² Au atoms was trapped to the nanocavities after annealing for 1h at 850 °C under a similar experimental condition [2]. In this study, we introduced only one tenth the Au atoms (1×10¹⁴ cm⁻²) of their report and hence we expect much more gettering sites than the value of Table 1 at least in the case of 800 °C.

To interpret the data shown in this study, it is worth mentioning about positron lifetimes and H release. The positron lifetime measurements of the same type of samples showed a constant increase in the positron lifetime, corresponding to vacancy clusters, with increasing annealing temperature from 400 to 900 °C [12]. The observed increase in positron lifetime is consistent with the increase in S parameters from 600 °C to 800 °C in Fig. 1(a). On the other hand, H release can be detected up to the annealing temperature of about 700 °C according to thermal desorption spectroscopy and secondary ion mass spectroscopy [1, 9, 10]. The effect of H on defects must be taken into account for the sample annealed at 800 °C, while there should be no effect of H for the sample annealed at 600 °C. In view of these results including Figs. 1 – 3, a possible origin which accounts for the observed annealing behaviors might be embryonic microcracks decorated with H atoms [20, 21] rather than dislocations, H-vacancy complex (e.g., VHₓ), H-induced lattice strain and dechanneling at nanocavities [12]. Since vacancies or vacancy clusters are favorable trapping sites for positrons, possibly vacancy clusters (i.e., nanocavities) were selectively detected in positron lifetime measurements regardless of the existence of other defects such as microcracks.

In the S-parameter plot of Fig. 1(a), the peak energy of the as-implanted sample was lower than those of the annealed samples. This difference can be explained as the H-induced decrease in S parameters [9-11] around the projected range. The annealing induced the H release and the nanocavity growth, eventually leading to the increase in S parameters around the projected range. In Figs. 1(b), 2 and 3, defect peaks were always detected around the projected range but their depths are slightly different. In the DBAR measurements [Fig. 1(b)], in particular, the damage layers of the annealed samples were clearly shallower than that of the as-implanted sample. Williams et al. pointed out about the difference between implanted-ion and nanocavity profiles [1]. The depth of He-induced nanocavities is shallower than the projected ranges, while the depth of H-induced nanocavities is very close to the projected range. Indeed, the peaks of the annealed samples were found to be very close to the projected range in the case of the RBS/C (Fig. 2) and Au gettering (Fig. 3) results. We believe that a strong gettering centers are formed at the projected range but the vacancy clusters widely distribute from the projected range to shallower regions. In other word, large nanocavities with strong gettering ability are formed around the projected range and small nanocavities with less gettering ability are also formed at shallower regions. It is interesting to note that the trapping
rate in the range of 0 – 300 nm was not zero in the case of the 800 °C annealing (Fig. 1). The defect level in the range of 0 – 300 nm was close to the background in the RBS/C measurement (Fig. 2). The DBAR measurements suggested the existence of the small vacancy clusters, which do not contribute gettering strongly. The transient Au profiles detected in the range of 100 – 400 nm at 600 °C in Fig. 3 can be attributed to such defects.

In terms of the peak defect levels, three analytical methods gave different values as shown in Table 1. It is an acceptable result as each method gives different information on implantation-induced damage. The balance of sizes and concentrations of vacancy clusters can explain the change in trapping rates of Fig. 1. The size of vacancy clusters (nanocavities) increased from the as-implanted state to 600 °C with increasing temperature, leading to the increase in the trapping rate. However, with increasing annealing temperature from 600 to 800 °C, the growth of the vacancy clusters significantly decreased the concentration of vacancy clusters, leading to the decrease in the trapping rate. On the other hand, the defect peak in the RBS/C was highest at 600 °C. This annealing behavior can be ascribed to the increased dechanneling at the microcracks incorporated with H atoms. At 800 °C, H atoms were fully released from the sample and the microcracks would be annealed out at this H dose, leading to the much lower defect peak. With respect to the Au gettering results in Fig. 3, the lower Au peak of the sample annealed at 600 °C is ascribed to slower diffusion of Au atoms as written previously in this paper.

4. Conclusion

Nanocavities formed by 50 keV H⁺ implantation in Si were characterized by Doppler broadening, RBS/channeling and RBS measurements. Peak concentrations and depth profiles of defects (gettering sites) were evaluated for the as-implanted sample and the samples annealed at 600 °C or 800 °C. The defect profiles detected by Doppler broadening measurements were shallower than those of defect profiles detected by RBS/channeling or RBS (Au gettering). The concentrations of defects or gettering sites were temperature dependent and showed different annealing behaviors depending on analytical techniques. The observed annealing behaviors can be explained by the growth of vacancy clusters and the interaction of H with defects.

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