In-situ Heating Experiments of Proton-implanted Silicon

プロトン注入シリコンの加熱その場観察

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Abstract: It is known that silicon wafers implanted at adequate conditions (such as room temperature, 80keV, $5\times10^{16}\,\mathrm{H\cdot cm^{-2}}$) induce exfoliation phenomena after 500℃ heating. However, we found that the samples implanted at –150℃ did not induce exfoliation even at above 500℃ heating.

In this study, for making of the influence of implantation temperature clear, the damaged layer in the hydrogen-implanted silicon was observed with cross sectional transmission electron microscopy. The behaviors of three types of specimens (implanted at –150℃, at room temperature and at +100℃, respectively) were compared by carrying out in-situ heating experiment. In the case of –150℃ implantation, the defects-distribution became wider. This wider defects-distribution assists the preservation of much hydrogen gas and this phenomenon impedes the exfoliation by suppressing the growing pressure of hydrogen in the sample implanted at –150℃.

In the in-situ heating experiments, the quantities of damages showed a tendency to decrease above 300℃. Although, the damages in the sample implanted at –150℃ vanished by heating of around 750℃, the damages of the sample implanted at room temperature tended to vanish at the heating of above 900℃. The damages of the sample implanted at +100℃ remained even at above 1100℃ heating. These results showed that the recovery temperature of the damage caused by high-dose hydrogen-implantation had the relation with the implantation temperature.

1. Introduction

Both the diffusion and the reactivity of hydrogen in solid materials remain a matter of lasting interest in material engineering. Hydrogen in silicon plays an important role in the technological applications such as passivation of the defects and suppression of carrier traps. On the other hand, silicon on insulator (SOI) material technology has become attractive for low power, low voltage and high-speed electronics. Though several methods of manufacturing SOI material have been developed during the last two decades, the hydrogen exfoliation method introduced by Bruel [1,2] has advantages of greater uniformity of thickness of the surface layer and crystal quality than other techniques. This method involves a micro slicing process of silicon by high dose hydrogen implantation. This slicing process is usable as a valuable new micro slicing tool for such hard materials as SiC or diamond, and has also been used to obtain the transfer of thin layers from thick substrates on to different substrates [3,4]. Although this unique and useful process has been extensively developed in industrial applications during the past few years, the fundamental phenomenon and the underlying mechanism are still not completely understood. Generally, silicon wafers implanted at room temperature (80keV, $5\times10^{16}\,\mathrm{H\cdot cm^{-2}}$) induce exfoliation phenomena after 500℃ heating. However, silicon wafers processed in some certain conditions do not induce exfoliation even at above 500℃ heating. Example for, n-type silicon [5], co-implantation [6], etc.

In this study, for making clear the influence of implantation temperature, the damaged-layer induced in hydrogen-implanted silicon was observed with cross sectional transmission electron microscopy (XTEM). The behaviors of three types of specimens (implanted at –150℃, at room tem-

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perature and at +150℃, respectively) were compared by carrying out in in-situ heating experiment.

2. Experiments

All studies were performed on p-type CZ-grown silicon (100) wafers. Hydrogen implantations were carried out with 80keV H$^+$ ions at three implantation temperatures (–150℃, room temperature and +100℃). These temperatures were measured on the wafer holder in the chamber of ion-implanter before the implantations. The wafers were oriented 7° off normal to the incident ion beam in order to minimize channeling effects. The hydrogen dose was 5.0×10^{16} ions/cm^2, this dose is high enough dose quantity required to cause blistering on the surface of a wafer or exfoliation in the bonded wafer. In order to confirm the appearance of blistering or exfoliation, the furnace annealing was carried out under N$_2$ gas at 500℃ for 30 minutes. The damaged layers induced by hydrogen implantations were examined by XTEM using a JEOL JEM-2010 with a [110] 200kV electron beam. The cross-sectional specimens were prepared by a combination of mechanical polishing and ion thinning with 3keV Ar$^+$ ions. These preparation processes involved gluing small pieces from a single sample face-to-face using epoxy cement and mounting into a ϕ3mm brass pipe to strengthen the specimen. In-situ heating experiments were carried out using a Gatan Model 628 heating specimen holder. The furnace-temperature of the holder was measured with thermocouple, and all high temperature metal parts of the holder were made of the refractory metal tantalum. The heating rate was almost 1000 [℃/hour].

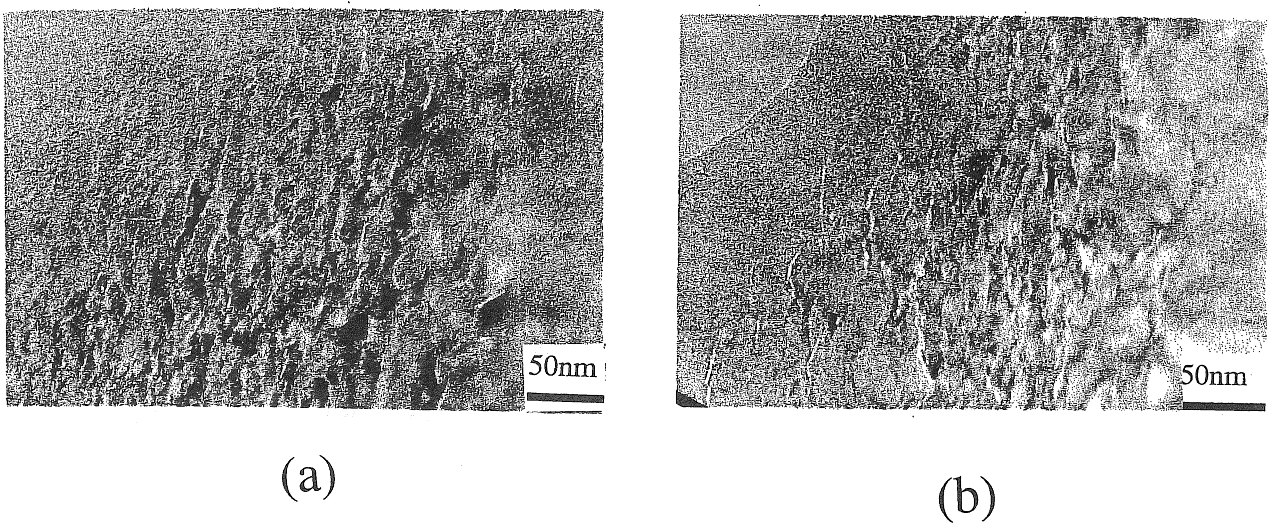


Fig. 1 (a) XTEM micrograph of the damaged layer induced by room temperature implantation with the 5.0×10^{16} Hcm^{-2} doses. (b) XTEM micrograph of the damaged layer induced by –150℃ implantation with the 5.0×10^{16} Hcm^{-2} doses. Left side is surface. In (b), the defects was apparent long in the shallower (left) part of defects layer..

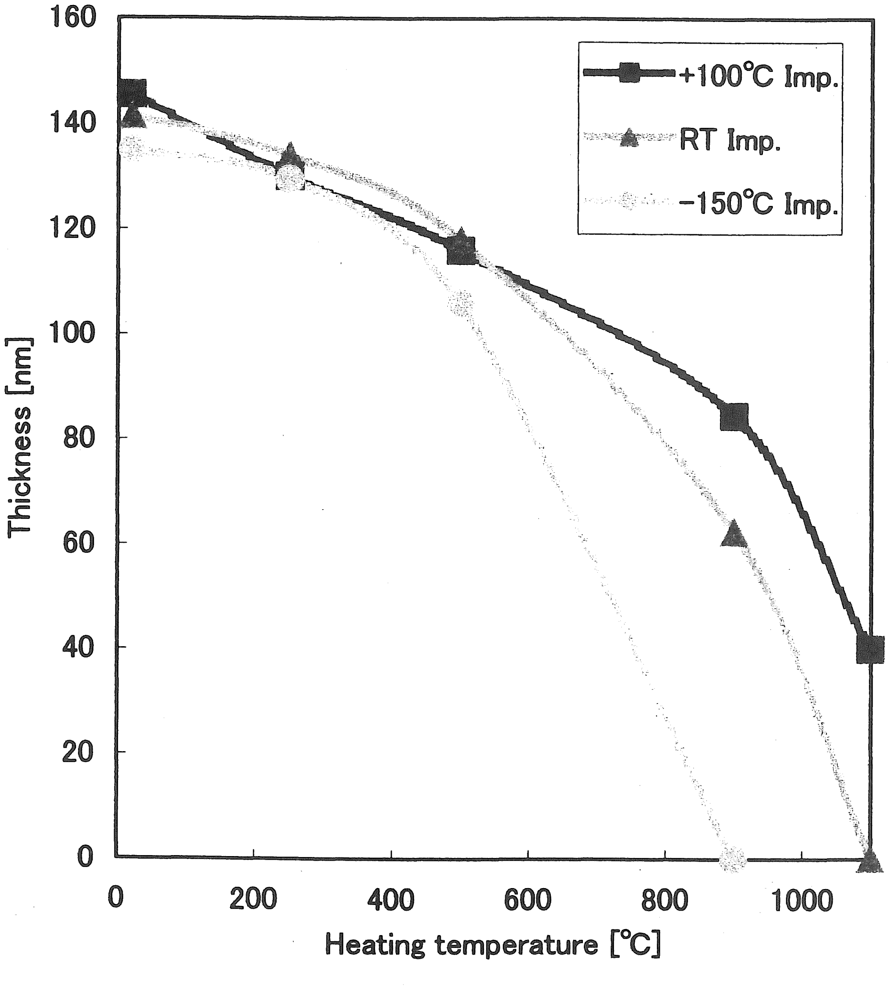
3. Results

3.1 Furnace annealing

Three types (implanted at –150℃, room temperature and +100℃) of as-implanted wafers were given a furnace annealing at 500℃ for 30minutes in N_2 gas ambient. Exfoliation or blistering were observed in the wafers which were implanted at room temperature and +100℃; however, exfoliation or blistering had not appeared in the wafers implanted at –150℃.

3.2 Defects Distribution observed by high resolution XTEM

In the specimen made from the wafer implanted at room temperature, the defects layer was observed and had a sharp peak defects-distribution in the depth of projection range. Figure 1 (a) shows the XTEM micrograph of the damaged layer induced by room temperature implantation with the 5.0×10^{16} Hcm^{-2} doses. The layer located approximately 0.7μm below the surface; the depth of the layer was in agreement with the depth of theoretical projection range (Rp). However, in the case of –150℃ implantation, the thickness of damaged layer becomes a little thicker than the case of room



Average thickness of the damaged layer

Fig. 2 Average thickness of the damaged layer. The thickness obtained from XTEM micrograph taken at in-situ heating experiments.

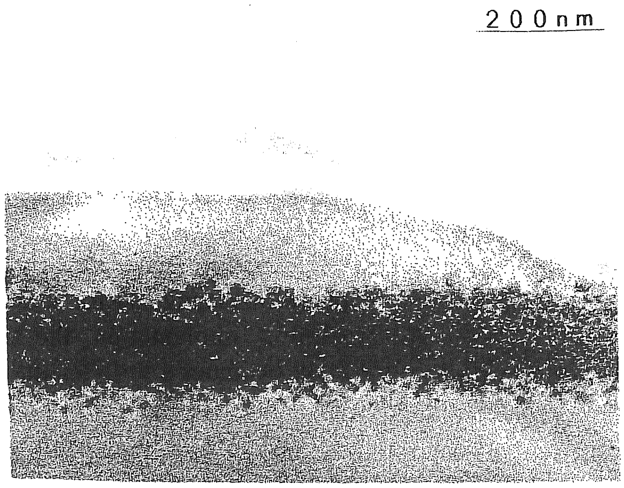


Fig. 3 XTEM micrograph obtained in in-situ heating experiments. Sample implanted at −150℃ and observed at room temperature.

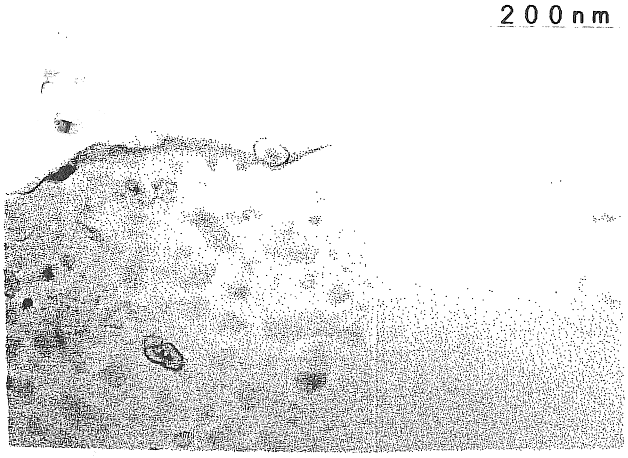


Fig. 4 XTEM micrograph obtained in in-situ heating experiments. Sample implanted at −150℃ and heated till 900℃.

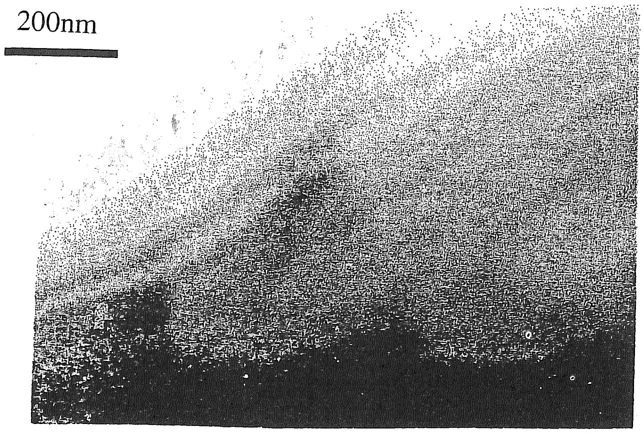


Fig. 5 XTEM micrograph obtained in in-situ heating experiments. Sample as implanted at room temperature.

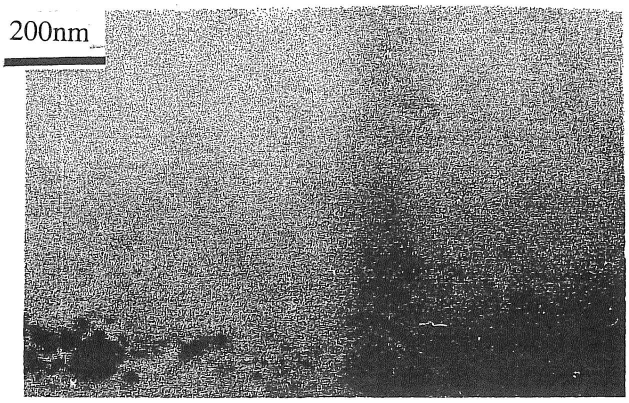


Fig. 6 XTEM micrograph obtained in in-situ heating experiments. Sample implanted at room temperature and heated till 900℃.

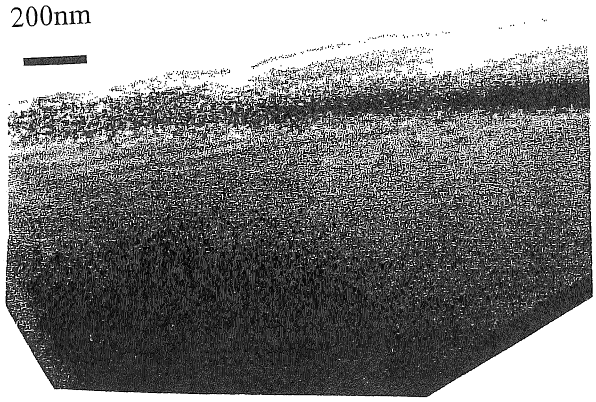


Fig. 7 XTEM micrograph obtained in in-situ heating experiments. Sample implanted at +100℃ and observed at room temperature.

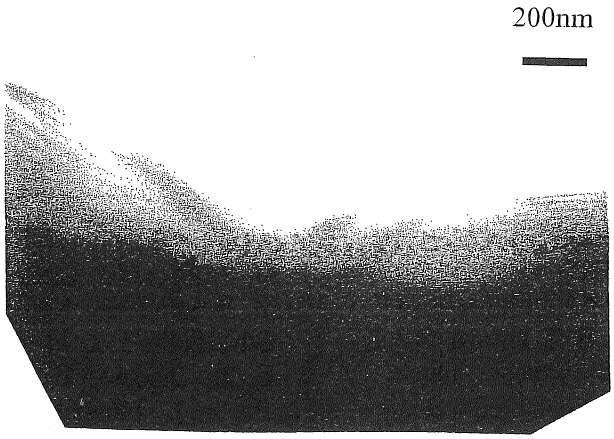


Fig. 8 XTEM micrograph obtained in in-situ heating experiments. Sample implanted at +100℃ and heated till 1100℃. Topside is surface.

temperature, as it were, the density of defects in the shallow part of the damaged layer almost equals the density in the depth of the projection range as shown in Fig.1 (b). On the other hand, the thickness of damaged layer of the +100℃ implantation was little thinner than the case of room temperature and no apparent difference was observed in the distribution of defects.

3.3 In-situ heating experiment

In the heating experiments, the quantities of damages in the above mentioned three samples showed a tendency to decrease above 300℃. Consequently, the thickness of damaged layer became thinner above 300℃heating as shown in Fig.2. Although the damages in the sample implanted at –150℃ vanished by heating of around 750℃ as shown in Figs.3 and 4, the damages in the sample implanted at room temperature tend to vanish at the heating of above 900℃ as shown in Fig.5 and 6. The damages of the sample implanted at +100℃ remained even at above 1100℃ heating as shown in Fig.7 and 8. On the other hand, exfoliation or blistering was not observed in all samples through these in-situ heating experiments.

4. Discussion

After the above a critical dose ($3\sim\times10^{16}$ H/cm^2) hydrogen implantation, the trapped hydrogen atoms combine with silicon atoms to form a Si-H complex [7,8]. During thermal annealing (~500℃), the trapped hydrogen atoms dissociate and segregate near the peak implantation region, forming microcavities filled with H_2 molecules. The high pressure inside the microcavity becomes the driving force for its expansion and growth. These microcavities grow along the plane of parallel to the surface during annealing. Afterward, all the microcavities are linked together, blistering or exfoliation is obtained in the Si wafer.

In our experiment, no exfoliation occurred in –150℃ implanted wafers. From secondary ion mass spectroscopy, effective difference was not detected in hydrogen concentration between the sample as implanted at –150℃ and the sample as implanted at room temperature. It is known that lower-temperature implantation causes much defects [9,10]. In the case of –150℃ implanted wafer, the density of defects in the shallow part of the damaged layer was high, or the defects had much capacitance for preserving much hydrogen atoms. Therefore, it is conceivable that inside pressure of the microcavity can not be high enough to cause exfoliation. In the case of in-situ heating experiments, no exfoliation occurred in the all samples. This reason is considered that hydrogen gas is slipped out from cross sections, because the TEM specimen is too thin to fill high-pressure hydrogen. The differences of the recovering temperature of the damaged layers can be explained as following. Generally, amorphousized defects is formed by high dose ion implantation [10], and the lower temperature implantation causes much amorphous region. The recovering temperature from amorphous to crystal is in lower temperature as almost 600℃ [11]. Therefore, the recovering temperature had the relation with the implantation temperature.

5. Concluding remarks

The samples implanted at –150℃ did not induce exfoliation even above 500℃ heating because of wide defects-distribution. The damaged layer in the hydrogen-implanted silicon was observed with XTEM. Three types of specimens (implanted at –150℃, at room temperature and at +100℃, respectively) were compared by carrying out in-situ heating experiment. In the case of –150℃ implantation, the defects-distribution became wider than others. In the in-situ heating experiments, results showed that the recovery temperature of the damage had the relation with the implantation temperature. The reason of these results could be explained with that the much amorphousuzed defects is obtained by lower temperature implantation.

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