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Thermal Behavior of MCZ-NTD Silicon

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Thermal behavior of MCZ-NTD silicon has been investigated by PL, TEM and so on. The NTD radiation damage has been recovered by an anneal at 700°C or higher. When the annealing time become longer, however, the MCZ-NTD silicon induces oxygen related defects even in such a low oxygen wafer as 5.3×10^{17} cm^{-3}. From the PL measurement, D1 , D2 and new peaks, which are considered to be correlated with precipitates, have been observed.

1. Introduction

Neutron transmutation doping (NTD) is an advantageous method to make highly homogeneous crystal. The NTD has been conventionally applied to a float zone (FZ) Si crystal for a power device.

Recently a magnetic-field applied Czochralski-grown (MCZ) Si crystal has been adopted for the NTD, because of an easy method to grow a large diameter crystal with both low oxygen content and high resistivity . The MCZ-NTD wafers are strongly interested in advanced large scale integrated circuits (LSI) because these wafers can be expected to have superior resistivity uniformity without fluctuation. For example, an image device manfactured by using MCZ-NTD wafers can be expected to keep highly uniform contrast on a screen. The MCZ Si contains oxygen, however, so that many defects could be introduced during thermal annealing to recover the neutron radiation damage.

In the present study, thermal behavior of the MCZ-NTD silicon wafer was investigated by resistivity measurement, photoluminescence (PL), transmission electron microscope (TEM), and so on. The PL is a powreful method to characterize both dopant concentrations and defect formation. For the MCZ-NTD wafer, it has been found that many defects correlated with oxygen can be introduced during thermal annealing even in such a low oxygen as 5.3×10^{17} cm^{-3}.

2. Experiment

2.1. sample wafer

Sample wafers were three kinds of MCZ-Si with different oxygen concentration and a FZ-Si with 5 inch in diameter. Table 1 shows the characteristics of the sample wafers. The NTD was carried out in the nuclear reactor with light water (Cd ratio ≒ 10).

2.2. Themal anneal

The MCZ-NTD wafers with different oxygen concentration and the FZ-NTD wafer were subjected to thermal annealings at temperature between 600 and 900 °C in dry O_2 ambient. Annealing time was changed from 0.5 to 64 hr.

2.3. Characterization

After annealing, resistivity and dopant concentration were measured by four point prove and photoluminescence (PL) method, respectively. The PL measurement was carried out at liquid herium temperature. The each dopant concentration was determined by the PL method

sample		resistivity (Ωcm)		oxygen	NTD
		as-grown	aimed val.	(cm^{-3})	dose (cm^{-2})
I	MCZ	440	42-49	1.9×10^{17}	5.85×10^{17}
II	MCZ	3550	54-66	2.8	5.08
III	MCZ	470	42-49	5.3	5.76
IV	FZ	90	>1000	$<1 \times 10^{17}$	

Table 1. Characteristics of used each wafer.

deveroped by Tajima(1). That uses calibration curve between the dopant concentration and the PL peak height normalized to intrinsic peak height. Carrier concentration deduced from the PL method was compaired to that converted from resistivity by using ASTM, F723-81. Moreover, in order to investigate a defect generation, PL peaks relating deep levels were measured by using a Ge detector. The detail characterization of each defect was carried out by TEM observation.

3. Result

Figure 1 and Fig. 2 show the carrier concentration obtained from PL and resistivity measurement in the FZ and the MCZ wafers, respectively. Carrier concentration from resistivity measurement agrees well with that obtained from PL measurement in the FZ wafer, however, that does not meet well in the MCZ wafers. The resistivity does not change in MCZ wafer like FZ wafer during anneal at 700℃ or higher. In the case of 600℃ anneal, the resistivity is gradually recovered and gets to the aimed value after the anneal over 16 hr. The dopant concentration estimated by PL method in the MCZ wafer, however, changed depending on annealing temperature and time as shown in Fig.2. This value does not agree with that obtained from resistivity measurement.

Figure 3 shows the change of P_{NP} PL peak height as a function of annealing time. The P_{NP} peak height in the FZ wafer is nearly constant. In the MCZ wafer the P_{NP} peak height varies from sample to sample. As the annealing time is longer, the P_{NP} peak height increases at 600℃ and decreases at 800℃. In the relatively high oxygen MCZ wafer (sample Ⅲ), the change of the peak height is different from other MCZ wafer with low oxygen content. These behaviors are considered to be due to the recovery of radiation damage and the defect generation in MCZ wafer during the thermal anneal.

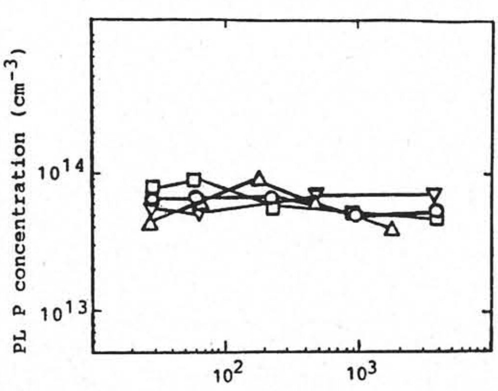

Fig.1. P concentration of FZ-NTD wafer decided by PL method as a function of annealing time.
▽:600℃, ○:700℃, □:800℃, △:900℃

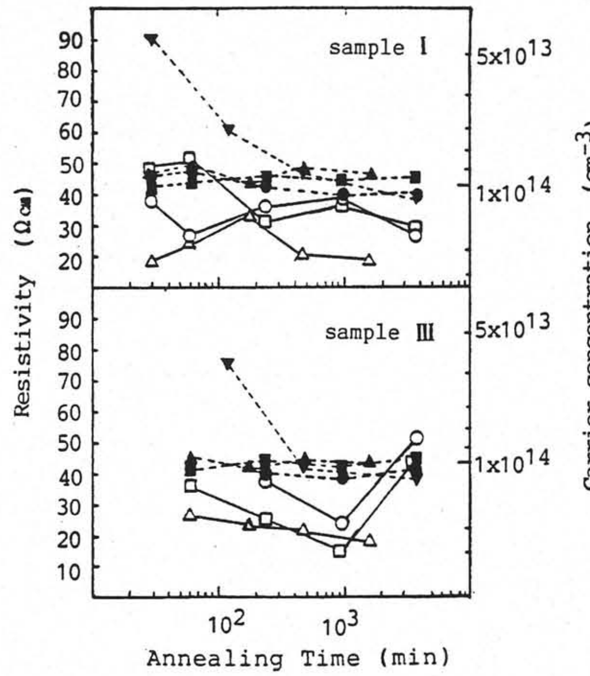

Fig.2. Resistivity and carreir concentration decided by PL method as a function of annealing time.

	600℃	700℃	800℃	900℃
resistivity	▼	●	■	▲
concentration	▽	○	□	△

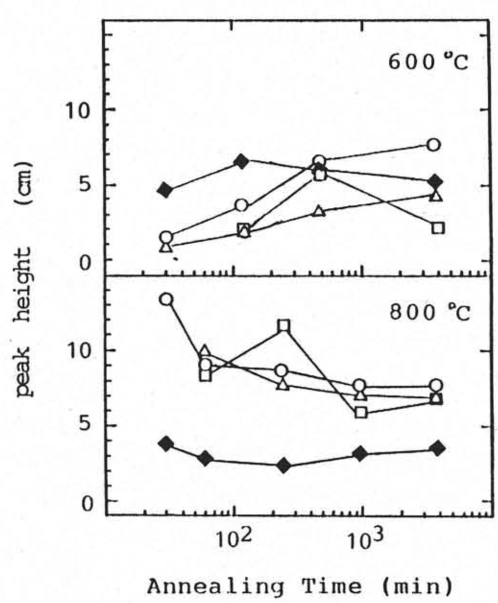

Fig.3. Peak height of P_{NP} change due to annealing time.
○:sample Ⅰ, △:sample Ⅱ, □:sample Ⅲ, ◆: FZ

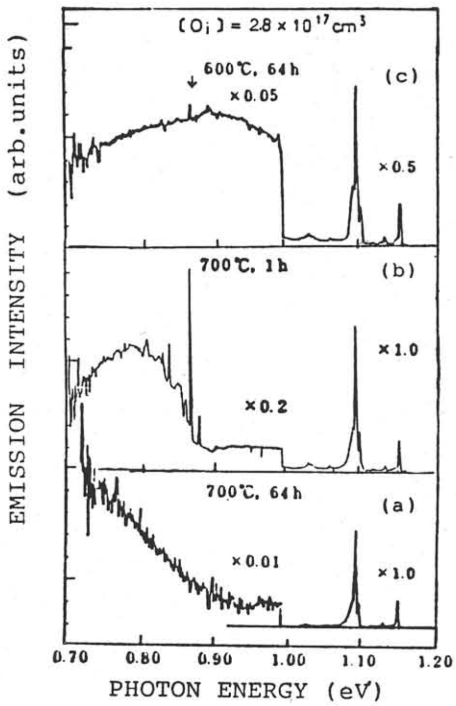

Fig.4. PL spectrum change in MCZ-NTD sample annealed at 600℃ and 700℃.
(a) 700℃,64hr. (b) 700℃,1hr (c) 600℃,64hr.

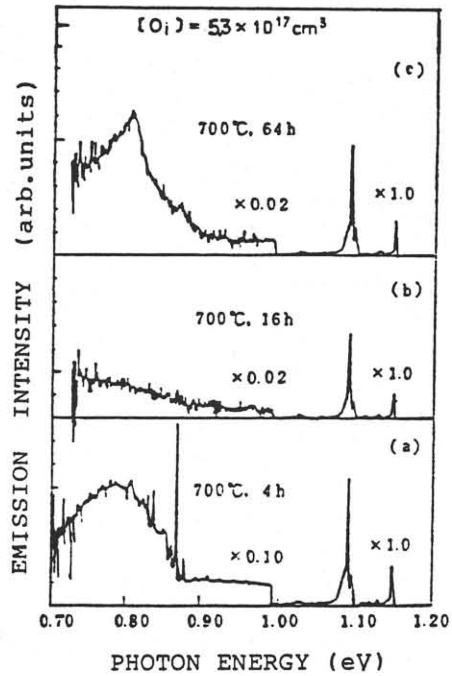

Fig.5. PL spectrum change in MCZ-NTD sample annealed at 700℃.
(a) 4hr. (b) 16hr. (c) 64hr.

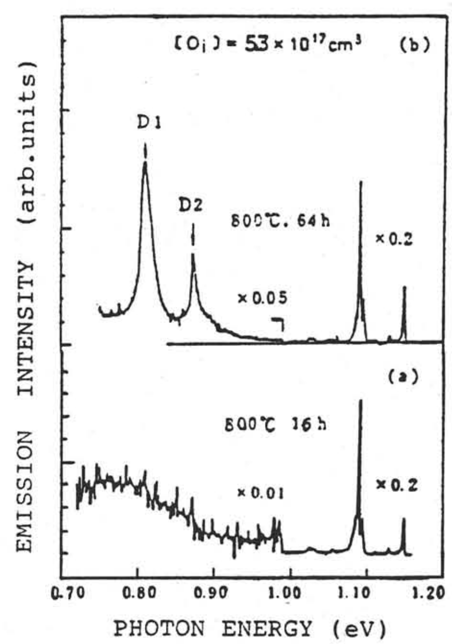

Fig.6. PL spectrum change in MCZ-NTD sample annealed at 800℃.
(a) 800℃,16hr.(b) 800℃,64hr.

The PL spectrum between 0.7 and 1.2 eV shows in the annealed MCZ-NTD wafers, as shown in Fig.4-Fig.7. Figure 4 shows the PL spectrum in the low oxygen MCZ-NTD wafer. The broad PL peak around 0.7-0.9 eV was observed in the sample annealed at 600℃ (Fig.4 (a)) and 700℃ for 4 hr.

In addition, some sharp peaks, which are due to the residual radiation damage, appeared around 0.84 to 0.88 eV. The radiation damage was not perfectly recorvered in the sample annealed at 600℃ for the time at least 64 hr. This may be why the PL peak height is gradually increased by 600℃ annealing as shown in Fig.3. When the annealing time was longer at 700℃, the sharp peaks around 0.84 to 0.88 eV perfectly disappeared and the radiation damage was recovered.

On the other hand, in the relatively high oxygen sample 3, the radiation damage was recovered by 700℃ annealing for 16 hr. But the broad PL peak relating to deep level was observed again after 700℃ annealing for 64 hr, as shown in Fig.5 (c). This broad peak is probably correlated with oxygen related defects. When the annealing temperature was higher, it was clearly found that the oxygen related defects would be formed in the sample Ⅲ. The strong D1 and D2 peaks, which are assigned as the PL peaks correlated with dislocation loops induced from oxygen precipitate(2),(3), were observed after the anneal at 800℃ for long time (Fig.6 (b)). The D1 and D2 peaks were also observed in the sample annealed at 900℃ and the peak intensity became stronger with the increase of annealing time. When the annealing time became over 8 hr

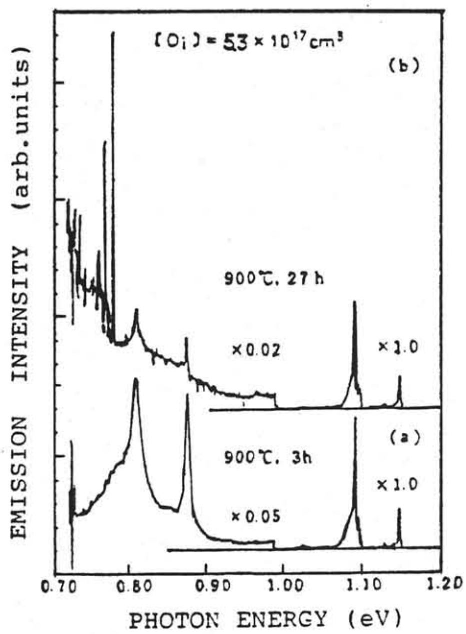

Fig.7. PL spectrum change in MCZ-NTD sample annealed at 900°C. (a) 3hr. (b) 27hr.

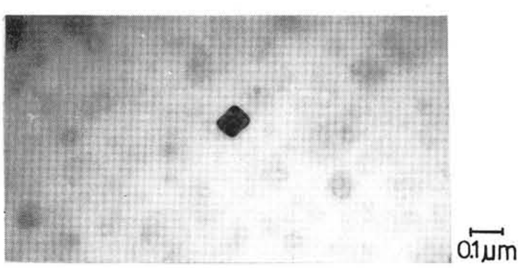

Fig.8. TEM phothgraph of sample III at 900℃ for 3 hr, (220) excitation.

at 900℃, new sharp peaks, which have not been identified yet, appeared at 0.77 and 0.78 eV (Fig.7(b)) in addition to the D1 and D2. These new peaks increased as D1 and D2 decreased, then the origin of these peaks may come from the same kind of defects.

In order to investigate the defect generation, the annealed MCZ-NTD samples were observed by Wright etching/microscopy and TEM. In the sample annealed at 900℃, any defects did not appeared for 1 hr but many shallow pits were observed for 3 hr or longer by Wright etching/microscopy. From the TEM observation, the micro precipitate as shown Fig.8 was observed. From the TEM observation, it was found that no dislocation loops but micro precipitates were induced in the sample annealed at 900℃, as shown in Fig.8. Therefore, it is considered that the D1 and D2 peaks could not correspond to the dislocation loops but to the micro percipitate.

4. Discussion

According to the PL method, the dopant concentration is calibrated from the ratio between the dopant peak height and the intrinsic peak height. When the PL centers exist in the deep levels, however, the luminescences correlated with shallow levels are influenced. Therefore, it may be impossible to determine the dopant concentration in the sample with deep levels originated from defects. This is reason why the dopant concentration from the PL method did not meet with that converted from the resistivity. Moreover, it can not judge whether the radiation damage has recovered or not from only the resistivity measurement, because the radiation damage is observed in the PL spectrum of the wafer, whose resistivity gets to the constant value, as stated in Fig.4.

Generally, the oxygen related microdefects are hardly generated in a conventional CZ silicon with oxygen content lower than 7.5×10^{17} cm^{-3}. In the case of NTD silicon, however, the oxygen related microdefects can be induced even in such a low oxygen as 5×10^{17} cm^{-3}. This may be because point defects, which are introduced during the neutron radiation, act as nuclei to oxygen precipitation.

5. Summary

In order to recover the neutron radiation damage perfectly, thermal annealing must be carried out at 700℃ or higher in the low oxygen wafer ($[Oi]\leq2.8\times10^{17}$ cm^{-3}). When the oxygen concentration in the wafer is over 5×10^{17} cm^{-3}, the oxygen related microdefects could be induced during thermal annealing at 700 ℃ or higher. Moreover, the deep levels D1, D2 and the new levels at 0.77 and 0.78 eV were observed in MCZ-NTD wafer after thermal annealing at 800℃ or 900℃ and these levels may be correlated with the precipitate induced by thermal annealing.

6. Acknowledgment

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7. Reference

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