

Oxygen Precipitation Control by Hydrogen and Preannealing at 425°C in Czochralski Silicon Crystals

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The depth profile of oxygen precipitation is controlled and oxygen precipitation enhanced by using hydrogen and preannealing below 450°C (425°C in our case) before precipitation annealing. Oxygen precipitation density in the shallow region, less than 80 μm from the surface, is controlled to 1/3 to that of the deep region, greater than 150μm from the surface.

1. Introduction

Oxygen precipitation control is vital to intrinsic gettering in Czochralski (CZ) silicon (Si) crystals. We propose a new method to control the amount and depth distribution of oxygen precipitates.

2. Experiment

We used (100) oriented 1.0mm thick wafers. We introduced hydrogen by annealing CZ Si wafers in nitrogen with about 5% hydrogen between 1000 and 1270°C for 25 to 60 minutes. We then quenched or slowly cooled the samples. In quenching, samples are pull from the hot-wall furnace at 4 cm/s. In slow cooling, samples were cooled at 7°C/min in the furnace. We used hydrogen-undoped CZ Si, too. Hydrogen is present in quenched CZ Si crystals for two reasons. One is the formation of a boron-hydrogen complex [1][2], which produces local vibrational mode (LVM) at 1905cm⁻¹. We observed this LVM at liquid He temperature in heavily-boron (~2x10¹⁷cm⁻³) and hydrogen-doped crystals.[3] The other is the enhancement of thermal donor (TD) formation. Two groups have reported hydrogen-enhanced TD formation.[4,5] Newman et al. reported that an increase in the oxygen diffusion coefficient, measured by the stress-induced dichromatic method, enhanced TD formation in hydrogen-doped CZ Si crystals.[6]

3. Results and discussion.

Figure 1 shows TD concentration generated in CZ

Si crystals with and without hydrogen doping. Hydrogen was doped by annealing at 1150°C for 60 minutes followed by quenching. The TD concentration was obtained by four-point probe resistivity measurement. The TD concentration of samples containing hydrogen (A) was very large compared to the undoped samples (B) due to hydrogen-enhanced oxygen diffusion.

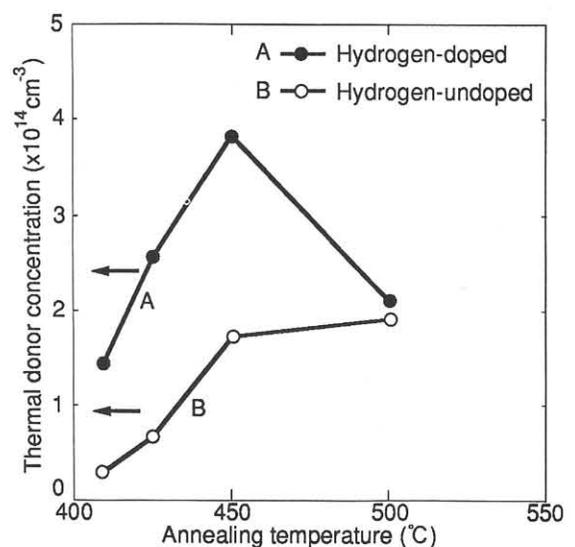


Fig.1. Thermal donor (TD) concentration generated in crystals with and without hydrogen doping.

Figure 2 shows the amount of oxygen precipitation of hydrogen-doped (A) and hydrogen-undoped (B) after annealing at 410, 425, 450, and 500°C for 60

minutes (preannealing), followed by annealing at 700°C for 13 hours and then annealing at 1000°C for 10 hours to precipitate oxygen (precipitation annealing). Hydrogen was doped by annealing at 1150°C for 60 minutes followed by quenching. The amount of oxygen precipitation without hydrogen and preannealing is also shown (B').

Oxygen precipitation of hydrogen-undoped samples with preannealing (B) was large compared to sample B'. Increase of oxygen precipitation by preannealing at 450–500°C before precipitation annealing (at 700°C for 13 hours and then at 1000°C for 10 hours in our case) is due to formation of small oxygen aggregates so called oxygen-related embryos. This is widely known phenomenon.

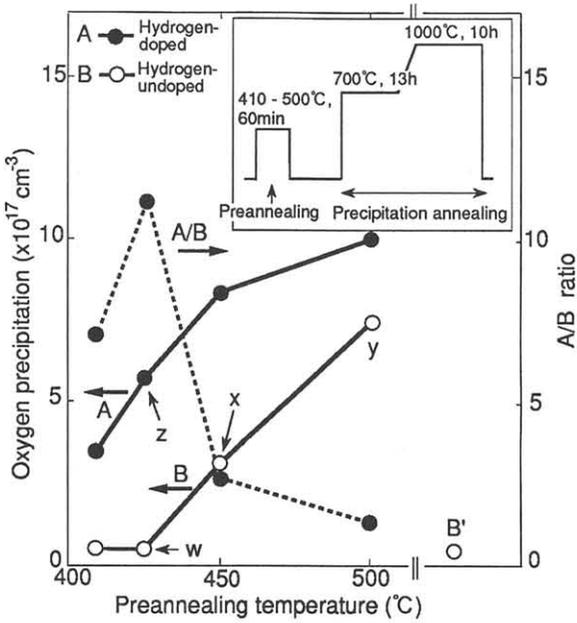


Fig. 2. Oxygen precipitation in crystals with and without hydrogen doping. The A/B ratio for the oxygen precipitation is also shown.

Oxygen precipitation of hydrogen-doped samples with preannealing (A) was very large compared to hydrogen-undoped samples (B). Since the diffusion coefficient of hydrogen is very large, supersaturated hydrogen change into aggregates quickly at low temperature. We observed such microdefects by transmission electron microscope (TEM) and selective etching. Hydrogen-related aggregates will act as nucleation sites for oxygen precipitates. Hydrogen causes the formation of many oxygen-related embryos, by enhanced oxygen diffusion, as well as formation of many hydrogen-related aggregates. Moreover, hydrogen also enhances growth of oxygen precipitates by enhanced oxygen diffusion. Enhanced oxygen precipitation in hydrogen-doped crystals (Fig. 2, A) is caused by the above effects.

The ratio A/B of oxygen precipitation is also shown in Fig. 2. Oxygen precipitation ratio A/B is small at 450°C and 500°C, because many oxygen-related embryos are formed at 450°C and 500°C even in the absence of hydrogen as shown by points x, y in Fig. 2. Oxygen precipitation ratio A/B is largest at 425°C, because enhanced oxygen precipitation occurs in hydrogen-doped sample (Fig. 2, z) and oxygen-related embryos are not formed in hydrogen-undoped samples (Fig. 2, w).

Figure 3 shows resistance depth profiles after annealing at 510°C for 60 minutes and 425°C for 30 minutes for slowly-cooled (C) and quenched (D) samples after hydrogen doping at 1200°C for 30 minutes. Since we used highly resistive samples (>3000ohm-cm), low resistance indicates high TD concentration. The profile of the slowly-cooled sample C is related to the oxygen depth profile by following reason. Hydrogen concentration in sample C must be small due to hydrogen out-diffusion during slow-cooling. The profile shows that the concentration of oxygen is constant except at the oxygen out-diffusion region near the surface.

The wide and negative resistance slope profile of sample D differs from that of sample C. Most of hydrogen introduced by annealing at 1200°C are frozen

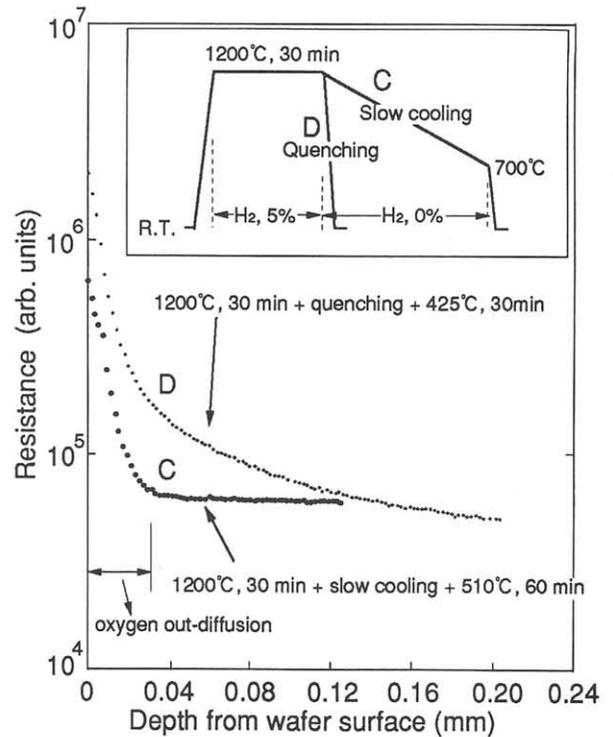


Fig. 3. Resistance depth profiles for samples C and D (insert). Hydrogen doping was at 1200°C for 30 minutes. Sample C was cooled to 700°C at 7°C/min in a nitrogen (hydrogen 0%) ambient. Sample D was quenched after hydrogen doping.

in crystal by quenching, but hydrogen diffusion coefficient is very large and hydrogen evaporate from surface, then hydrogen deficient region are formed near surface during rapid cooling. The wide and negative resistance slope of D was formed by profile of hydrogen and hydrogen-enhanced TD formation at 425°C.

Figure 4 shows the oxygen precipitates. Hydrogen was doped by annealing at 1200°C for 60 minutes and then quenching. Hydrogen-doped and hydrogen-undoped samples were annealed at 425°C for 60 minutes (preannealing) and then annealed between 700°C and 1100°C to precipitate oxygen (precipitation annealing). Figure 4 (a) shows oxygen precipitates at shallow region (50 μm from the surface) and 4 (b) shows the deep region (150 μm from the surface). The amount of oxygen precipitates of hydrogen-undoped sample was less than that of hydrogen-doped due to the absence of hydrogen. This is consistent with results of Fig. 2. The concentration of oxygen precipitates of hydrogen-undoped sample is same between shallow region (a) and deep region (b), whereas that of hydrogen-doped sample differs from hydrogen-undoped sample. The concentration of oxygen precipitates near surface is smaller than in the deep region in hydrogen-doped sample. This difference occurs due to hydrogen rather than oxygen effects,

because the oxygen is uniform except in the DZ region (Fig. 3 C). Since the hydrogen greatly affects oxygen precipitation at 425°C (A/B ratio of Fig. 2), oxygen precipitation is expected to be large in the deep or hydrogen rich regions and small at the surface or hydrogen deficient region.

4. Summary

We proposed a new method to control the amount and depth distribution of oxygen precipitates. The oxygen precipitate density in the shallow region, less than 80μm from the surface, is controlled to 1/3 to the value in deep region, greater than 150μm from surface, by using hydrogen and preannealing at 425°C before precipitation annealing.

References

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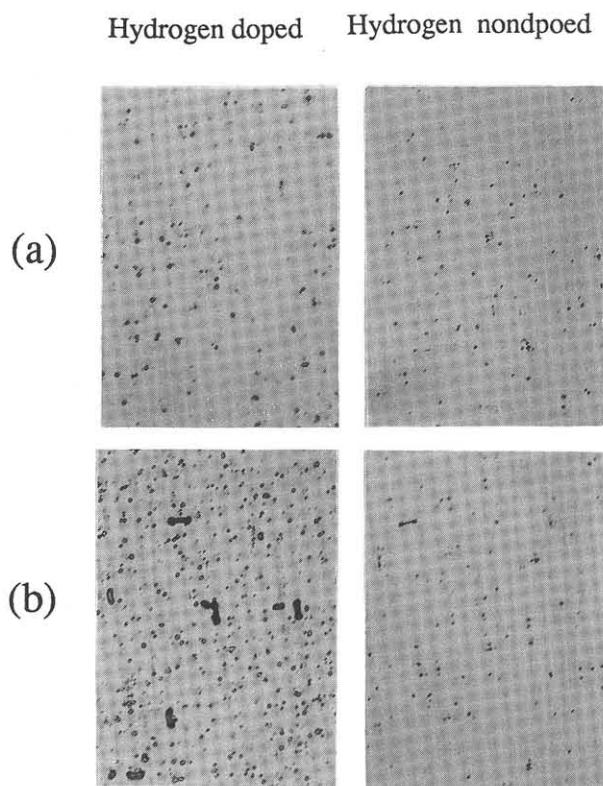


Fig. 4. Oxygen precipitate distribution. (a) Oxygen precipitates near surface (50μm from surface). DZ width is 25 μm. (b) Oxygen precipitates about 150 μm from surface.