Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 1014-1016

C-7-1

Hydrogen in As-Grown Czochralski Silicon Crystals

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Hydrogen enhances thermal donor (TD) formation. This effect is strong by annealing at 425°C but its effect is weak by annealing at 500°C. Bulk crystals 10 mm thick made from commercially available Czochralski (CZ) as-grown silicon (Si) ingot were annealed at 750°C for 5 minutes, then at 425°C or 500°C for 30 minutes to form TDs. The TD concentration increased with depth to 1 mm from the surface for samples annealed at 425°C. No change in depth TD profile was observed in samples annealed at 500°C. These TD depth profiles were explained by out-diffusion of hydrogen in as-grown crystals. Hydrogen in as-grown CZ-Si crystals enhance oxygen precipitation.

1. INTRODUCTION

Oxygen and carbon are the most important residual impurities in Czochralski (CZ) as-grown silicon (Si) crystals, and much research has been done on them. We found hydrogen in commercially available as-grown CZ-Si crystals that enhances oxygen precipitation.

2. EXPERIMENT

Two Si wafer vendors supplied our samples as 4-inch as-grown ingots (Table I). We prepared 8- to 10-mm-thick bulk samples and 1- or 2-mm-thick wafers from the same ingot region. We used enhanced thermal donor (TD) formation by hydrogen to detect grown-in hydrogen. We used the spreading resistance (SR) after angle polishing, four-point resistivity, optical absorption at 8 K, electron spin resonance (ESR), and deep level transient spectroscopy (DLTS) to detect thermal donors (TDs). We used an optical microscope to observe oxygen precipitates after selective etching.

3. RESULTS AND DISCUSSION

3-1. Detection of hydrogen in as-grown CZ-Si crystals

Bulk crystals made from ingot A were annealed in oxygen for 5 minutes at 750°C to completely eliminate TDs formed during crystal growth. We then annealed samples in oxygen for 30 minutes at 425°C or 500°C to form TDs. We then checked how resistance varied with depth. Since we used highly resistive ingot A, a low resistance indicates a high carrier concentration. For samples annealed at 425°C, we found that the resistance is high at the surface and decreases with depth (Fig. 1).

Table I. Samples (old ASTM, ND=non detection)

Vendor	Ingots	Dopant	Resistivity (ohm-cm)	Oxygen (ppma)	Carbon
1	A	Nondoped	>3000	~30	ND
2	B	Phosphorous	2	~30	ND
	C	Boron	20	~30	ND

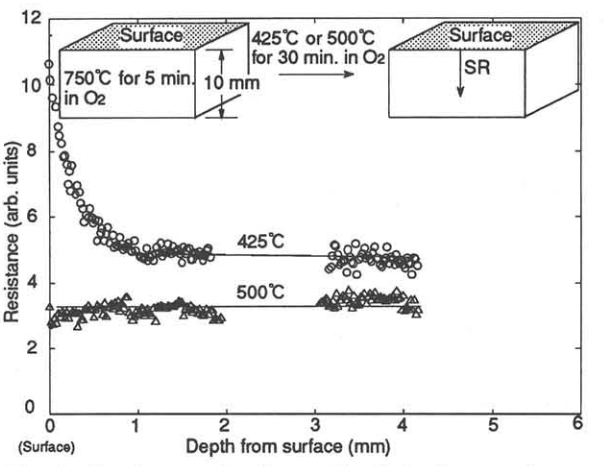

Fig. 1 Resistance depth profiles in bulk crystals. Samples were prepared as shown in the inset. Resistance was measured by SR after angle polishing. Low resistance indicates a high TD concentration.

After studying the relationship between the width of the high-resistance region and annealing time at 700°C, we found that the width spread with increasing annealing time. In contrast, the resistance profiles of samples annealed at 500°C are nearly constant (Fig. 1). Our optical absorption experiment showed that carriers are generated from TDs. Therefore, the TD concentration is

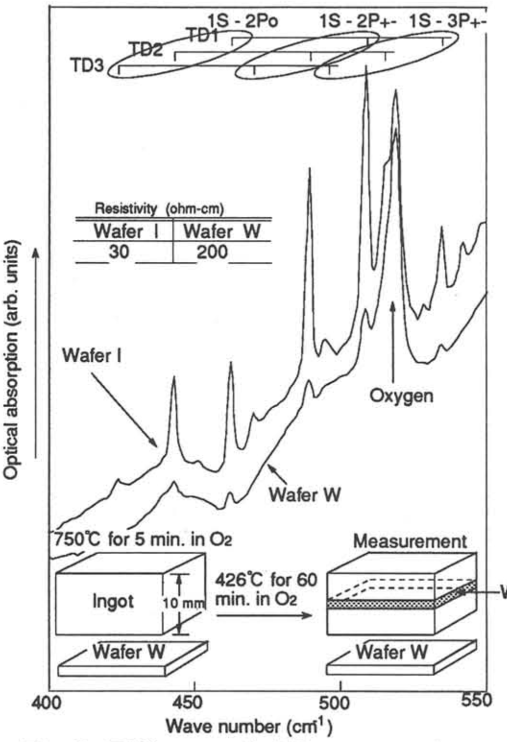

Fig. 2 Differences in TD concentration. Resistivity in wafers W and I is shown in the inset.

low at the surface and high in deep regions. Using DLTS for ingot B and ESR for ingot C, we observed similar TD distribution.

We compared the TD concentration in wafers annealed in oxygen for 5 minutes at 750°C, then for 60 minutes at 426°C (Fig. 2). Sample preparation is shown in inset figure. Wafer W was originally 1.0 mm thick. Wafer I, made from the middle of the bulk crystal after annealing was completed, was 1.0 mm thick. We found that the optical absorption intensity due to TDs is greater in wafer I than wafer W (Fig. 2). Wafers W and I had resistivity of 200 ohm-cm and 30 ohm-cm.

Rapidly diffusing hydrogen atoms enhance oxygen diffusion and TD formation [1], but this effect depends on temperature (Fig. 3). We made hydrogen containing 2.0 mm thick wafers by annealing at 1200°C in nitrogen gas containing hydrogen. Very enhanced TD formation occurs at 422°C, but the effect is small at 507°C. The TD concentration thus follow the hydrogen profile for samples annealed at about 422°C, but becomes independent of the hydrogen profile at about 500°C. To confirm our theory, we did as follows : We prepared bulk crystals doped with hydrogen by annealing at 1150°C for 120 minutes in nitrogen gas containing hydrogen. Since hydrogen diffused 12 mm under this conditions, hydrogen concentration in samples should be uniform. We annealed samples in oxygen at 800°C for 10 minutes to establish the hydrogen profile in bulk crystals, then at 425°C or 500°C for 30 minutes to form TDs. Hydrogen diffuses

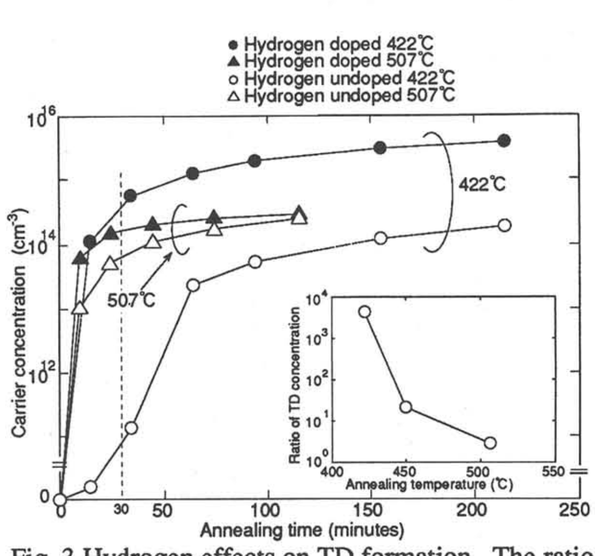

Fig. 3 Hydrogen effects on TD formation. The ratio of TD concentration formed in hydrogen-doped and undoped CZ-Si crystals after annealing at 422,450, and 507 ℃ for 30 minutes is shown in the inset.

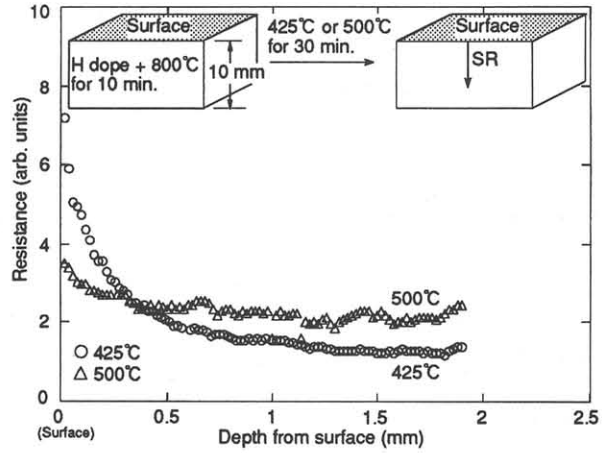

Fig. 4 Resistance depth profile in hydrogen-doped CZ-Si crystals. Low resistance indicates a high TD concentration. Since hydrogen doping was intentional, the resistance at the deep region was low compared to the resistance in Fig. 1.

1.8 mm in annealing for 10 minutes at 800°C. The resistance profile of the sample annealed at 425°C varies significantly with depth, but its profile of sample annealed at 500°C is weak despite the existence of hydrogen depth profile. These results are caused by hydrogen effects mentioned above.

The results shown in Figs. 1 and 2 are explained as follows : Hydrogen exists in commercially available as-grown CZ-Si crystals. Hydrogen in as-grown crystals out-diffuses 1.1 mm in 5 minutes during annealing at 750°C, nearly equaling the width of the high resistivity region in Fig. 1. TDs are formed based on the hydrogen profile by annealing at 425°C, but TD formation becomes independent of hydrogen in annealing at 500°C. The difference in TD concentration in wafers W and I is explained by hydrogen out-diffusion from as-grown crystals. For wafer W, hydrogen out-diffused completely during annealing at 750°C for 5 minutes, but not that in the deep bulk crystal region. Enhanced TD formation thus did not occur in wafer W, but did in the deep region of ingot or wafer I.

3-2. Grown-in hydrogen effect on oxygen precipitation

We studied how hydrogen in as-grown crystal affects oxygen precipitation, preparing 1-mm-thick wafers and 8-mm-thick bulk crystals from ingot A, both from the same ingot region to avoid differences in thermal history during crystal growth and in oxygen and carbon content. We then annealed these samples at 750°C for 5 minutes in nitrogen. Hydrogen out-diffused completely from the wafer sample, but not from the deep region of bulk crystals, since its diffusion length in this annealing is about 1.1 mm. We annealed these samples at 425°C for 20 hours, then at 700°C for 48 hours or at 510°C for 20 hours, then at 700°C for 20 hours to precipitate oxygen. The density of oxygen precipitates in the deep region of bulk crystals is four times that of wafer heat-treated at 425°C for 20 hours, then at 700°C for 48 hours (Fig. 5), but we observed nearly equal oxygen precipitate density in heat treatment at 510°C for 20 hours, then at 700°C for 20 hours, for the deep region of bulk crystal and the wafer. Since hydrogen enhances oxygen diffusion, nucleation and growth of oxygen precipitates will also be enhanced. Such effects did not occur in the wafer due to the lack of hydrogen, but did in deep region of bulk crystal. Oxygen diffusion is very enhanced by hydrogen at 425°C, but its effect is weak at 510°C (Fig. 3). Differences between the bulk crystal and wafer and between annealing at 425°C and 510°C in the amount of

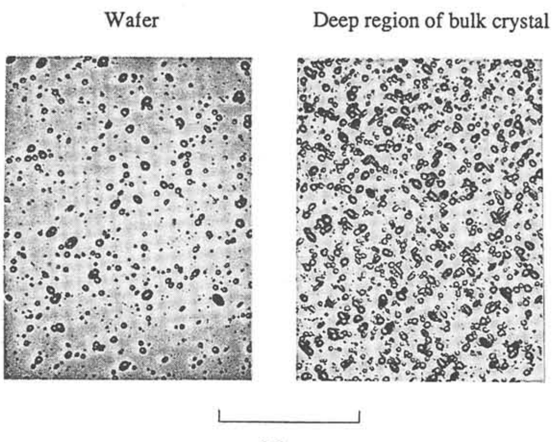

Fig. 5 Oxygen precipitates formed by annealing at 425℃ for 20 hours, then at 700℃ for 48 hours.

oxygen precipitates were due to the above reason, indicating that hydrogen already present enhances oxygen precipitation and that oxygen precipitate formation during crystal growth will be enhanced by the existence of grown-in hydrogen due to long annealing time during crystal growth.

4. CONCLUSION

We found hydrogen in commercially available as-grown CZ-Si crystals that enhanced oxygen precipitation. Many small oxygen precipitates are most likely present in commercially available as-grown crystals due to hydrogen-enhanced oxygen diffusion and long annealing time during crystals growth. Reducing hydrogen contamination during crystal growth is important to growing high-quality CZ-Si crystals.

REFERENCES

1) R. C. Newman,J. H. Tucker, A. R. Brown, and S. A. McQuaid : J. Appl. Phys. 70 (1991) 3061.