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2004 J. Phys.: Condens. Matter 16 1539

(http://iopscience.iop.org/0953-8984/16/9/003)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 1539–1545 PII: S0953-8984(04)68875-8

The effect of the ramping rate on oxygen precipitation and the denuded zone in heavily doped Czochralski silicon

Yiying Zhao, Dongsheng Li, Xiangyang Ma and Deren Yang[1]

State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027,
People's Republic of China

E-mail: mseyang@dial.zju.edu.cn

Received 12 September 2003
Published 20 February 2004
Online at stacks.iop.org/JPhysCM/16/1539 (DOI: 10.1088/0953-8984/16/9/003)

Abstract

The effect of the ramping rate on oxygen precipitation and the denuded zone in heavily doped Czochralski (CZ) silicon has been investigated. Wafers with different dopants (boron, arsenic and antimony) were subjected to a pre-annealing at 1150 °C and then ramping processes with different rates. It was found that along with the decrease of the ramping rates, the density of oxygen precipitates increased in all the heavily doped silicon wafers; however, the width of the denuded zone decreased in heavily boron doped silicon. It is considered that compared with case for lightly doped wafers, the oxygen precipitation was enhanced in the heavily boron doped wafers; but was retarded in the heavily arsenic and antimony doped wafers during the ramping process. The mechanism of the ramping on the oxygen precipitation and the denuded zone was also discussed.

1. Introduction

Recently, heavily doped silicon wafers have been widely used in ultralarge scale integration (ULSI) manufacturing processes. The structure of an epitaxial layer on a heavily doped substrate can avoid the latch-up in metal–oxide–semiconductor devices and the soft failure caused by alpha particle irradiation [1].

Oxygen, the most important impurity in heavily doped CZ silicon, has been extensively investigated [2–15, 23]. Now it is well accepted that dopants influence not only the oxygen incorporation during crystal growth [2–5, 7, 13, 23], but also the precipitation behaviours during subsequent thermal processes in device fabrication [6–13]. Compared with the case for lightly doped silicon, oxygen concentration is higher in heavily boron doped (HB) silicon [2, 4], and is lower in heavily antimony doped (HSb) silicon [3, 5, 7, 13, 23]. It was also reported that oxygen precipitation is enhanced in the HB wafers [4, 7–13], while it is retarded in HSb

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[1] Author to whom any correspondence should be addressed.

0953-8984/04/091539+07$30.00

Table 1. Initial parameters of the samples.

Number	Dopant	Resistivity (Ω cm)	Initial oxygen concentration (10^{18} cm^{-3})
HB1	B	0.020	1.6
HB2	B	0.027	1.2
HAs	As	0.005	1.6
HSb	Sb	0.025	1.6
LB	B	15.9	1.2

wafers [6, 14], and is unchanged in heavily phosphorus doped wafers [6, 15]. But for heavily arsenic doped (HAs) wafers, research on the behaviour of oxygen precipitation is relatively minimal.

The intrinsic gettering (IG) process associated with oxygen precipitation has been widely used to improve the performance of devices [16]. And a ramping annealing procedure was proposed to replace the conventional IG process [17], which can decrease the thermal budget and shorten the annealing time. Furthermore, this procedure is compatible with ULSI fabrication processes. However, it is still unknown whether the ramping processes have an effect on oxygen precipitation and the denuded zone in heavily doped silicon.

In this paper, the effect of the ramping rate on the oxygen precipitation and the denuded zone in heavily doped CZ silicon was investigated. The heavily doped silicon was first annealed at a high temperature. Meanwhile, the lightly doped silicon was used for comparison. And then the samples were ramped to 1050 °C with a different ramping rate. Finally, the bulk microdefects (BMDs) in the samples were checked.

2. Experimental details

The samples used in our experiments were CZ silicon with heavy doping with boron, arsenic and antimony. The initial concentrations of oxygen in the heavily doped silicon were determined with Leco Ro-416 gas fused analysis (GFA) equipment. The initial oxygen concentrations in the samples chosen from the different heavily doped samples were same: 1.6×10^{18} cm^{-3}. Their resistivities were in the range of 0.025–0.005 Ω cm. Lightly boron doped (LB) CZ silicon wafers were used as a control. The initial oxygen concentration of the LB samples was determined by a Bruker V66 Fourier transform infrared spectrometer (FTIR). The calibration factor of oxygen is 3.14×10^{17} cm^{-2}. The parameters of the samples are shown in table 1.

All the samples were pre-annealed at 1150 °C for 2 h for oxygen out-diffusion and cooled in the air. Next, the samples were kept at 650 °C for 1 h and then annealed to 1050 °C with a ramping rate of 2, 1 and 0.5 K min^{-1}, respectively, and then quenched in air. The heat treatments were carried out in a N_2 ambient. After the heat treatments, the (111) cleaved samples were etched in a Sirtl etchant for 5 min. Finally, the BMDs, which are related to oxygen precipitates and their induced defects, were observed with an Olympus MX50 optical microscope.

3. Results and discussion

3.1. The effect of ramping rate on oxygen precipitation in HB silicon

Figure 1 shows optical images of the cross-sections of the annealed HB1 and LB silicon with a ramping rate of 2 K min^{-1}. It can be seen that the BMD density in the HB1 silicon was

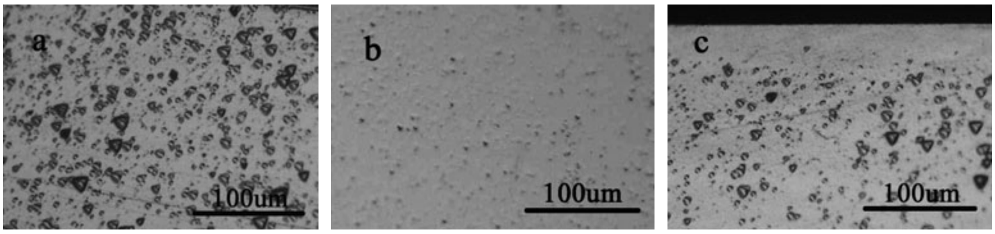

Figure 1. Optical images of the cross-section of the annealed HB1 and LB silicon at a ramping rate of 2 K min^{-1}; (a) BMDs in the centre of the HB1 silicon, (b) BMDs in the centre of the LB silicon, (c) the denuded zone of the HB1 silicon.

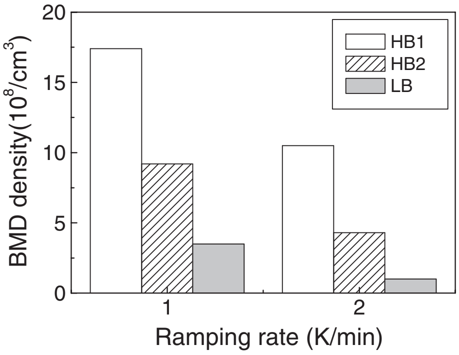

Figure 2. Densities of the BMDs in the HB1, HB2 and LB silicon annealed at ramping rates of 2 and 1 K min^{-1}.

much higher than that in the LB silicon (figures 1(a) and (b)). A well-defined denuded zone in the HB1 silicon was also observed (figure 1(c)). The BMD densities in the HB1, HB2 and LB silicon annealed at ramping rates of 2 and 1 K min^{-1} are shown in figure 2. It also shows that the BMD densities in HB1 and HB2 silicon were higher than that in LB silicon. Compared with LB silicon, HB1 silicon contained higher oxygen and B concentration and HB2 silicon contained a higher B concentration and the same oxygen concentration. Therefore, it is obvious that a high B concentration can enhance the oxygen precipitation during the ramping. Figure 3 shows the density of the BMDs in the annealed HB1 and LB silicon as a function of the ramping rate. It is evident that along with the increase of the ramping rate, the BMD densities in the HB1 and LB silicon wafers decreased substantially, correspondingly. This result indicates that besides the initial oxygen concentration, the B concentration also affects the oxygen precipitation during the ramping; moreover, the ramping rate has a significant influence on oxygen precipitation in HB silicon.

It is well known that oxygen precipitates whose sizes are larger than the critical size at the annealing temperature can grow, whereas the precipitates smaller than the critical size shrink during the annealing [18]. In our experiments, while the annealing temperature rose gradually during the ramping annealing, the critical size for oxygen precipitates enlarged, and the growth speed of oxygen precipitates increased, too. So there is a potential competition between the growth and dissolution of the oxygen precipitates. If the expanding speed of the critical size is lower than the growth rate of the oxygen precipitates, a high density of oxygen precipitates can be obtained; in contrast, the density of oxygen precipitates will be low. Furthermore, in HB wafers there are more as-grown oxygen precipitates, the critical size for oxygen precipitates is

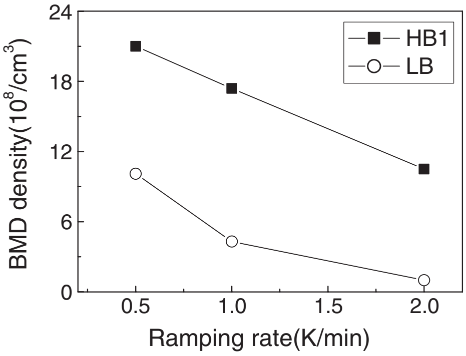

Figure 3. Densities of the BMDs in the annealed HB1 and LB silicon as a function of the ramping rate.

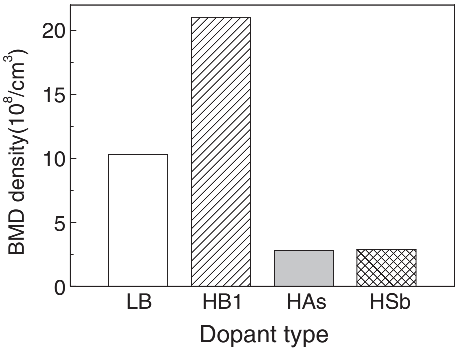

Figure 4. Densities of the BMDs in the HB1, HAs, HSb and LB silicon annealed at a ramping rate of 0.5 K min^{-1}.

smaller [7, 10] and the growth speed of precipitates is higher [12, 19]. In the experiments, the slower the ramping rate, the lower the expanding speed of the critical size, and the higher the density of oxygen precipitates. The size–number distribution of oxygen precipitates largely depends on the ramping rate. Therefore, the density of oxygen precipitates is higher, and increases with decreasing of the ramping rate in HB silicon (figures 1–3).

3.2. The effect of dopant type on oxygen precipitation during ramping

The densities of the BMDs in the HB1, HAs, HSb and LB silicon annealed with a ramping rate of 0.5 K min^{-1} are shown in figure 4. It can be seen that in contrast to the HB1 silicon, the BMD densities in the HAs and HSb silicon wafers were lower than that in the HB silicon, and were only about one fourth of that in the HB1 silicon wafers. Furthermore, while the ramping rate was 2 K min^{-1}, the BMD density was 1.0×10^9 cm^{-3} in the HB1 silicon wafers (figures 2 and 3), but could not be observed in the HAs and HSb silicon wafers. Accordingly, it can be concluded that oxygen precipitation was retarded in the HAs and HSb wafers during the ramping process.

As in the one-step or multistep annealing [6–14], in the ramping processes the oxygen precipitation in ramping processes is enhanced in HB wafers, and is retarded in HSb wafers. Since the critical size for oxygen precipitation is larger and the growth speed of precipitates

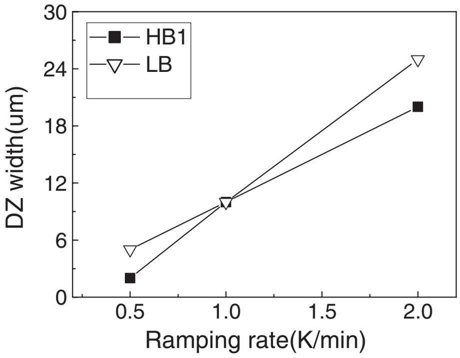

Figure 5. The width of the denuded zone of the HB1 and LB silicon as a function of the ramping rate.

is lower in HSb wafers [6, 14], the oxygen precipitates in HB wafers are easier to nucleate and grow than those in HSb wafers. Under the same heat treatments, the BMD density in HB wafers was higher than that in HSb wafers with the same oxygen concentration (figure 4).

As for HAs silicon wafers, the oxygen precipitation is also retarded during the ramping. There are some possibilities for the mechanism of the retardation in HAs wafers. Firstly, the results can be explained by the free-electron model [20]. If oxygen precipitates nucleate homogeneously, the oxygen precipitate nucleation rate in n-type silicon is dependent on the electron concentration, having an inverse power dependence between about 3 and 4 at an annealing temperature of ~600 °C. In HAs wafers, the dopant concentration is greater than the intrinsic carrier concentration; thus the higher electron concentration will obviously decrease the formation rate and the equilibrium concentration of the oxygen precipitates. Secondly, it was found that the vacancies tended to be localized near As atoms in HAs wafers [21]. It is well known that the retardation of the vacancy mobility will affect the growth of oxygen precipitates. Thirdly, the heavily doped As could reduce oxygen diffusivity in the temperature range of 500–800 °C [22]. However, the nucleation and growth of oxygen precipitates is the mechanism of diffusion limitation. Therefore, the nucleation and growth of precipitates is retarded in the HAs wafers due to slow diffusion of oxygen.

3.3. The effect of ramping rate on denuded zone in HB wafers

As there are not enough oxygen precipitates in the HAs and HSb silicon wafers, it is meaningless to discuss the width of the denuded zone (DZ) in these wafers. The width of the DZ in the HB1 and LB wafers as a function of ramping rate is shown figure 5. It is noticeable that there is no significant difference between the DZ width in HB1 and LB silicon, though compared with the LB silicon the HB1 silicon contained a higher initial oxygen concentration and B concentration, both of which can enhance oxygen precipitation. Moreover, it can be seen that the DZ width in both HB1 and LB increased with increasing ramping rate. This result is in accord with Kissinger *et al* [24–26]. So the above results indicate that the DZ width depends more on the annealing than the impurity concentration during the ramping.

During the pre-annealing at 1150 °C, oxygen in the near-surface region diffused out, and then the supersaturation of the oxygen concentration decreased from the centre to the surface. The supersaturation is the driving force of oxygen precipitation. Once the oxygen concentration in the near-surface region of silicon wafers is lower than the critical size, a precipitation-free

DZ will be generated during the following heat treatments. Furthermore, since the time for oxygen out-diffusion is very short, the profile of the oxygen concentration is always very steep in the near-surface region and the width of DZ is always no more than 50 μm. So even if the B does enhance the formation of the oxygen precipitation, it is difficult to observe the change of the DZ width. At the same time, while the ramping rate decreased, the HB silicon wafers experienced a relatively long low temperature annealing, and the comparable small oxygen precipitate nuclei can grow, so oxygen precipitates could be generated in the region where the oxygen concentration is relatively low. Accordingly, the DZ in the HB silicon with a small ramping rate was narrow, and did not change with the B concentration (figure 5).

4. Conclusion

The effect of the ramping rate on oxygen precipitation and the denuded zone in heavily doped CZ silicon has been investigated. Wafers with different dopants were subjected to a high temperature pre-annealing and a subsequent ramping at various rates. It was found that compared with that in lightly doped wafers, the oxygen precipitation was enhanced in HB wafers and was retarded in HAs and HSb wafers during the ramping process. With decreasing ramping rate, the precipitate densities increased in the HB, HAs and HSb wafers. For annealing at a ramp rate of 0.5 K min^{-1}, enough oxygen precipitation can occur in HAS and HSb silicon to improve the intrinsic gettering effect. Furthermore, the width of the denuded zone decreased with decrease of the ramping rate, while the B concentration and the initial oxygen concentration have little effect on the width of the DZ.

Acknowledgments

The authors would like to thank the Natural Science Foundation of China (Nos 50032010 and 60225010) and 863 programmes (No 2002AA3Z1111) for financial support.

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