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Denuded zone in Czochralski silicon wafer with high carbon content

Jiahe Chen, Deren Yang¹, Xiangyang Ma and Duanlin Que

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

E-mail: mseyang@zju.edu.cn

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Abstract

The thermal stability of the denuded zone (DZ) created by high–low–high-temperature annealing in high carbon content (H[C]) and low carbon content (L[C]) Czochralski silicon (Cz-Si) has been investigated in a subsequent ramping and isothermal 1050 °C annealing. The tiny oxygen precipitates which might occur in the DZ were checked. It was found in the L[C] Cz-Si that the DZ shrank and the density of bulk micro-defects (BMDs) reduced with the increase of time spent at 1050 °C. Also, the DZs above 15 μm of thickness present in the H[C] Cz-Si wafers continuously and the density and total volume of BMDs first decreased then increased and finally decreased again during the treatments. Moreover, tiny oxygen precipitates were hardly generated inside the DZs, indicating that H[C] Cz-Si wafers could support the fabrication of integrated circuits.

1. Introduction

It has been reported that carbon can affect the behaviour of oxygen [1] and generate swirl defects [2], and even induced carbon precipitates [3], in Czochralski silicon (Cz-Si) crystals, and high carbon content (H[C]) in wafers can increase the leakage current in p–n junctions and therefore reduce device yield [4, 5]. It is widely considered that carbon should be avoided during crystal growth, and thus H[C] Cz-Si crystals have not been used as materials supporting device fabrication [6]. Here, it is worth pointing out that the operating voltages of integrated circuits (ICs) have been declined dramatically and no chained breakdown voltage affected by the carbon presence is requested. Moreover, integration units can be fabricated intensively only in the 2–5 μm thick denuded zone (DZ) near the wafer surfaces and gettering sites can be generated in wafer bulk [7]. In addition, crystal originated particles, the main as-grown defects in fast pulled vacancy-rich Cz-Si crystals, can be impeded by carbon presence [8]. Therefore,

¹ Author to whom any correspondence should be addressed.

whether or not H[C] Cz-Si could support the fabrication of integrated circuits (ICs) needs to be reinspected.

Internal gettering (IG) effects based on defect-free DZs together with high-density bulk micro-defect (BMD) regions are believed to be of potential application in next-generation double-side polished wafers. However, the recent continuous pursuits in obtaining large diameter wafers and shallow-junction devices lead to the reduction of oxygen content in crystals as well as the decline of thermal cycle temperatures in IC device processes, which result in the decrease of oxygen precipitate density and further the softening of gettering capability [9]. Intentional doping with some impurities that can promote oxygen precipitation in silicon, such as nitrogen, is considered to be a feasible solution for maintaining the IG efficiency [10]. Due to the enhancement effect on oxygen precipitation [11] and the larger segregation coefficient (compared with nitrogen) as well as the neutral electrical properties in crystals, carbon doping is therefore considered to be of potential application for IC fabrication.

In our recent work, fairly clean DZs can be generated in H[C] Cz-Si wafers through an appropriate thermal cycle [12]. However, considering the enhancement by carbon of oxygen precipitation, tiny precipitates maybe exist in the zone of oxygen out-diffusion after IG treatment. In this paper, prolonged annealing was used to check the existence of tiny oxygen precipitates in the DZ of H[C] Cz-Si wafers. It was found that their DZs became narrower whereas tiny oxygen precipitates were hardly formed within DZs. Based on the experimental facts, the effects of carbon on shrinkage of the DZ and variation of oxygen precipitate distribution are discussed.

2. Experiments

Sample wafers with 2 mm thickness were sliced from similar positions of two 75 mm diameter phosphorus-doped n-type (111) Cz-Si ingots grown under almost identical conditions except for the carbon content: one was high carbon content (H[C], $\sim 2.0 \times 10^{17} \text{ cm}^{-3}$) and the other was low carbon content (L[C], $\sim 2 \times 10^{16} \text{ cm}^{-3}$). The as-grown interstitial oxygen concentrations ($[O_i]$ s) and the resistivities of both the samples were about $8.7 \times 10^{17} \text{ cm}^{-3}$ and 10–20 $\Omega \text{ cm}$, respectively. Wafers were mirror-polished on both sides and annealed under argon atmosphere: first they were annealed with three-step high–low–high steps (Hi–Lo–Hi, 1200 °C/2 h + 750 °C/16 h + 1050 °C/16 h) to form DZs, then ramped from 450 °C at a rate of 1 °C min^{-1} to 1050 °C, and finally annealed at 1050 °C isothermally for 1–64 h. After the full heat treatments, the specimens were cleaved across their cross-section and etched in Sirtl etchant for 5 min at 30 °C, then observed under an Olympus MX-50 optical microscope. The substitutional carbon concentrations ($[C_s]$ s) and $[O_i]$ s in the wafers before/after annealing were measured with a Bruker IFS 66v/S Fourier transform infrared (FTIR) spectroscope at room temperature according to the 1106 and 605 cm^{-1} absorption bands, respectively. And they were calculated with the conversion coefficients of $1.0 \times 10^{17} \text{ cm}^{-2}$ for $[C_s]$ s following the norms of ASTM F 123-91 standard and $3.14 \times 10^{17} \text{ cm}^{-2}$ for $[O_i]$ s following the norms of ASTM F 121-89 standard, respectively.

3. Results and discussion

Figure 1 illustrates the cross-sectional optical microphotographs for both the L[C] and H[C] Cz-Si wafers annealed with the Hi–Lo–Hi thermal process and the isothermal heating after rigorous ramping. Their DZ widths, BMD densities, average BMD sizes and the $[O_i]$ s and $[C_s]$ s are listed in table 1. As can be seen, similarly to the L[C] Cz-Si wafers, the defect-free DZ near surface and the high-density BMDs in the matrix were both formed in the H[C] Cz-Si

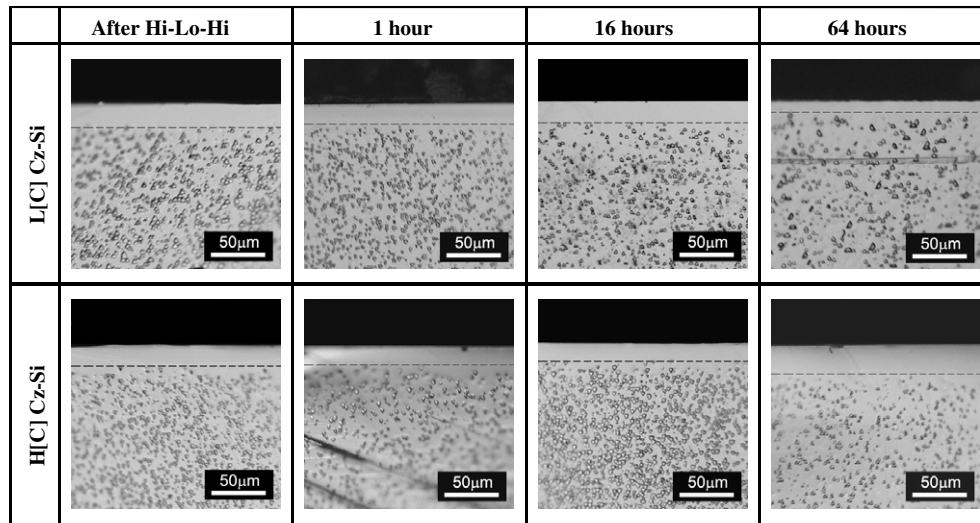


Figure 1. Cross-sectional optical microphotographs for the L[C] and H[C] Cz-Si wafers after the Hi-Lo-Hi annealing and subjected to the rigorous ramping process following by the isothermal annealing at 1050 °C for 1, 16 and 64 h, respectively. The dashed lines on them were drawn to show the DZ width for clarity.

Table 1. DZ widths, BMD densities, average BMD sizes and the concentrations of interstitial oxygen and substitutional carbon atoms in both the L[C] and H[C] Cz-Si wafers during the full thermal cycle.

	DZ width (μm)		BMD density ($\times 10^9 \text{ cm}^{-3}$)		Average BMD size ^a (μm)		[O _i] ($\times 10^{17} \text{ cm}^{-3}$)		[C _s] ($\times 10^{17} \text{ cm}^{-3}$)	
	L[C]	H[C]	L[C]	H[C]	L[C]	H[C]	L[C]	H[C]	L[C]	H[C]
As-grown	—	—	—	—	—	—	8.72	8.67	0.23	2.06
Hi-Lo-Hi cycle	23	20	2.3	3.3	3.5	3.2	3.32	3.07	0.22	1.91
Ramping +										
1050 °C/1 h	19	19	2.6	1.6	3.2	3.3	3.19	2.95	0.14	1.67
1050 °C/16 h	20	15	1.9	3.2	3.1	3.6	2.92	2.46	0.19	1.79
1050 °C/64 h	10	28	1.6	1.3	4.0	2.8	2.67	3.21	0.15	1.80

^a The BMDs in wafers are treated as approximate spheres and their volumes can be calculated through the sphere volume formula from the average sizes. The total volumes can be obtained by considering their densities.

wafers after the Hi-Lo-Hi annealing. The DZ in the H[C] Cz-Si wafer was a little narrower compared with the L[C] Cz-Si wafer; however, its width reached 20 μm , which entirely satisfies the demands of large-scale integrated device fabrication. It can also be seen that, after the isothermal annealing at 1050 °C for various durations between 1–64 h after ramping, high-quality DZs with sufficient width (above 10 μm) were still present near the wafer surfaces for both Cz-Si materials despite the width shrinkage.

Generally, devices are mostly fabricated in the DZs or in the epilayers deposited on wafer surfaces, so the quality of surface/subsurface zones in wafers affects the device yield remarkably. It is considered that, if there are still some tiny oxygen precipitates within DZs formed by the Hi-Lo-Hi thermal cycle, they could obviously be harmful for devices [13]. Researchers have suggested that the oxygen precipitate nucleus could exist to

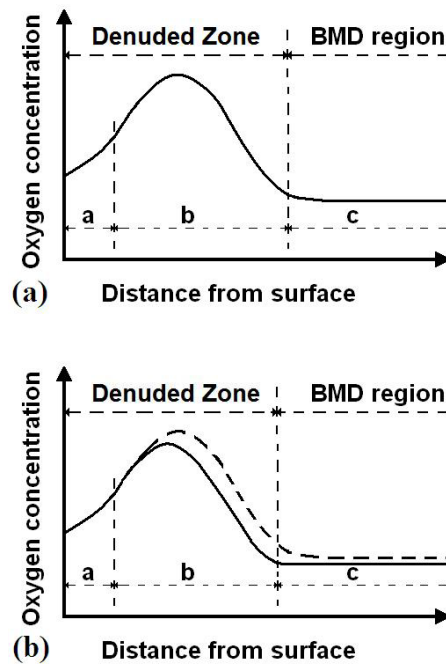


Figure 2. Schematic illustration of $[O_i]$ s near the Cz-Si wafer surfaces (a) after Hi-Lo-Hi annealing and (b) after ramping plus 1050 °C annealing for 16 h. The regions a, b and c represent different levels of interstitial oxygen content.

higher temperatures and then increase in size there when the wafers were ramped from a lower temperature with a controlled rate of 1 °C min^{-1} [14, 15]; thus the defects can be detected by the silicon etching technology [16]. From the optical images shown in figure 1, it is obviously suggested that tiny oxygen precipitates can hardly be present in the DZs for both Cz-Si wafers. Besides, their BMD densities in the matrix remained of the order of 10^9 cm^{-3} , which could supply effective gettering sites sufficiently [7]. Therefore, it is believed that H[C] Cz-Si materials could also support the IG technique used widely in the industry.

It is noted that the DZ widths shrank appreciably in both the L[C] and H[C] Cz-Si wafers when the duration in the final isothermal annealing reached 16 h, which should be probably ascribed to the further precipitation of oxygen atoms in the bulk of the wafer. For clarifying the physics, schematic illustrations of $[O_i]$ s near wafer surfaces after Hi-Lo-Hi annealing and after ramping plus 1050 °C annealing for 16 h are shown in figure 2. During the 1200 °C/2 h annealing, the $[O_i]$ in the subsurface zone (region b, (a)) was higher than that in the surface zone (region a, (a)) due to the out-diffusion of oxygen, while $[O_i]$ in the bulk (region c, (a)) kept close to the grown-in level. And then during the subsequent nuclei stage at 750 °C/16 h and growth stage at 1050 °C/16 h, majority of oxygen atoms in the bulk (region c, (a)) precipitated whereas almost no oxygen precipitate nucleus formed in the surface zone (region a, (a)) due to the low oxygen level. In particular, in the subsurface zone (region b, (a)), some oxygen precipitate nuclei could be generated in the 750 °C/16 h annealing but could hardly grow or even dissolve in 1050 °C/16 h annealing because of there being fewer surrounding oxygen atoms [17]. Actually, the peak-shape depth profile of oxygen in DZs after Hi-Lo-Hi annealing has once been obtained by the spreading resistance measurements [18]. Subsequently, when the

controlled ramping processing was applied, oxygen atoms both in the bulk and the subsurface zone (regions c and b, (b)) precipitated again owing to the surviving seeding sites, and then these precipitates could grow during the final isothermal annealing at 1050 °C. Therefore, some fresh precipitates could be formed in regions c and inner b of figure 2(a) that shift the oxygen profile towards the wafer surface (from the dashed curve to the solid curve, (b)), resulting in the reduction of DZ width in both Cz-Si wafers. Furthermore, it seems that the declines in DZ width in the H[C] Cz-Si wafer were a little larger than that in the L[C] Cz-Si wafer, which is considered to be associated with the weak enhancement effect of carbon on oxygen precipitation.

Concerning the variation in BMD distributions during the full thermal treatments, a distinctive picture was present in H[C] Cz-Si wafers compared with L[C] Cz-Si wafers. For L[C] Cz-Si wafers, as illustrated in table 1, the $[O_i]$ dropped close to the solubility level after the ramping processing and further decreased indistinctively during the subsequent isothermal annealing while the BMD volumes calculated from their densities and average sizes increased slightly when the duration was prolonged, that is, the majority of supersaturated oxygen in the wafers had precipitated. From their images shown in figure 1, with the increase of duration at 1050 °C, the BMDs with larger size increased while those with smaller size dissolved, and therefore the BMD density together with the DZ width in the 64 h case were almost half of that in 1 h case, respectively. That is, the prolonged annealing at 1050 °C leads to the continued growth of larger precipitates and a progressive loss of smaller particles. This process, that is well-known in metallurgy, minimizes the total interface energy of the system and is called *Ostwald ripening*, which has once been observed by Newman *et al* [19] in Cz-Si wafers. From this viewpoint, some precipitates generated in inner DZs could coarsen in this process so that the DZ widths in the L[C] Cz-Si wafer would shrink with the increase of duration of the 1050 °C annealing.

Furthermore, it seems that the conversion of precipitates can be revealed from the FTIR absorption spectra for L[C] Cz-Si wafers during the whole thermal cycle which are given in figure 3. The band at $1225\text{ cm}^{-1}(\nu_P)$, which has been considered to be related to the plate-like oxygen precipitates [20], diminished with the increase of duration at the final 1050 °C annealing (from curves a1 to a4). So it is suggested that the plate-like oxygen precipitates that possess larger interface energy may convert to the polyhedral ones that are associated with smaller interface energy [21, 22], resulting in the reduction of the total system energy during the prolonged isothermal annealing.

For H[C] Cz-Si wafers, in comparison with the Hi-Lo-Hi case, the BMD density decreased evidently in the 1 h case and increased obviously if the duration was prolonged to 16 h, while the average BMD size increased gradually and the $[O_i]$ declined slightly continuously, however, the $[C_s]$ almost remained. Oxygen precipitation retardation, which has been observed widely in low-high annealing applied to high carbon content Cz-Si wafers [23–25], is considered. In general, carbon could enhance oxygen precipitation during low-temperature annealing (such as the ramping processing), so a great number of oxygen precipitate nuclei could form and the majority of them could grow when the samples are ramped to higher temperatures above 1000 °C (such as isothermal annealing at 1050 °C). However, the further growth of these nuclei would be restrained in the subsequent 1050 °C/1 h annealing because a mass of self-interstitial silicon atoms were emitted by the growth of oxygen precipitates and these interstitials were assembled surrounding them. Hence, the oxygen precipitation in bulk was retarded [26] while the density and total volume of BMDs decreased. When the duration was prolonged to 16 h, however, these silicon interstitials diffused sufficiently and the oxygen precipitates were generated in abundance, so that the density and size of BMDs increased dramatically while the $[O_i]$ decreased slightly. Herein,

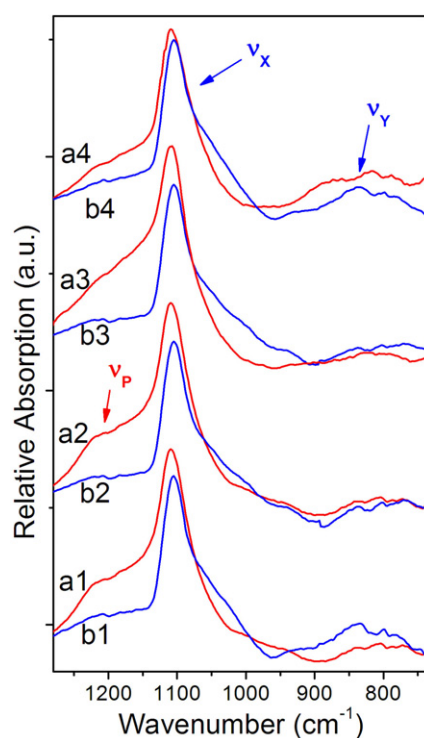


Figure 3. Room-temperature FTIR absorption spectra for both the L[C] (curves a1–a4) and H[C] (curves b1–b4) Cz-Si wafers. (a1, b1) after the Hi–Lo–Hi annealing, (a2, b2) after the final annealing at 1050 °C for 1 h, (a3, b3) after the final annealing at 1050 °C for 16 h, and (a4, b4) after the final annealing at 1050 °C for 64 h.

(This figure is in colour only in the electronic version)

it is worth mentioning that carbon can generate $[C_i-O_i]C(3)$ centres at low temperatures to seed the oxygen precipitates and therefore reduce the critical nucleation radius of the precipitate [27]. However, due to the short duration at low-temperature annealing and ramping, a weak enhancement effect on oxygen precipitation by high content carbon presence has been proposed; the BMD densities as well as their total volumes in H[C] Cz-Si wafers were therefore higher than the L[C] ones that are shown in figure 1 and table 1.

If the duration at 1050 °C increased to 64 h, the density and size of BMDs in H[C] Cz-Si wafers decreased remarkably and the $[O_i]$ increased appreciably as well as the DZ widening, all of which indicates that a portion of oxygen precipitation has dissolved. It is established that the growth and dissolution of precipitates have been suggested to coexist and to be in competition with each other dynamically during the annealing processes, i.e., some oxygen atoms could precipitate due to the limit of solubility, meanwhile, some others could dissolve by obtaining outer energy such as from long-term heating. With the increase of duration, oxygen supersaturation decreased continuously so that the precipitation slowed down while the precipitates formed previously could dissolve straightaway. It is therefore reasonable that the precipitate dissolution would become dominant after annealing for a certain hours, and the DZs would widen due to dissolution of oxygen precipitates in the boundary of DZs and BMD regions.

Besides, it seems that the dissolution of oxygen precipitate in H[C] Cz-Si wafers might be revealed from the FTIR spectra. The $[C_i-O_i]C(3)$ centres generated after 750 °C/16 h of

Hi–Lo–Hi processing have been proposed to be related with the bands at 850 cm^{-1} (ν_Y) and 1100 cm^{-1} (ν_X) [28]. It is considered that these centres might incorporate into the oxygen precipitates during the precipitate growth. As illustrated in figure 3, it is interesting to detect the bands of $[\text{C}_i\text{--O}_i]\text{C}(3)$ centres after the Hi–Lo–Hi and the final $1050^\circ\text{C}/64\text{ h}$ annealing (curves b1 and b4); however, these bands diminished when the wafers were annealed for 1 or 16 h at 1050°C (curves b2 and b3). It is indicated that some of the oxygen precipitates might be dissolved in H[C] Cz-Si wafers and the $[\text{C}_i\text{--O}_i]\text{C}(3)$ centres would be released after the final $1050^\circ\text{C}/64\text{ h}$ annealing.

4. Summary and conclusion

In this paper, the thermal stability of defect-free DZs with adequate width formed near the wafer surfaces in both H[C] and L[C] Cz-Si crystals has been investigated. For the L[C] Cz-Si, the width of DZ shrank and the density of BMDs reduced with the duration at 1050°C after a rigorous ramping treatment, and an *Ostwald ripening* process that minimizes the total interface energy of system was suggested. However, the density and total volume of BMDs in H[C] Cz-Si first decreased then increased and finally decreased again during the full treatments. Oxygen precipitation retardation and dissolution were considered at the early and later stages, respectively. Furthermore, it has been shown that a DZ above $15\ \mu\text{m}$ in thickness was always present in H[C] Cz-Si and no tiny oxygen precipitates were generated in it, indicating that H[C] Cz-Si wafers might be used as a silicon material in IC manufacture.

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