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The effect of germanium doping on oxygen donors in Czochralski-grown silicon

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Abstract

In this paper the effect of germanium doping on oxygen donors in Czochralski (CZ) silicon has been investigated. It is found that germanium suppresses the formation of thermal donors during annealing at 450 °C, as a result of the reaction of Ge with point defects in CZ silicon. Meanwhile, it is clarified that germanium enhances the formation of new donors in CZ silicon, which is proposed to be a process associated with the nucleation enhancement of oxygen precipitation by germanium doping.

1. Introduction

Excess oxygen, incorporated into Czochralski (CZ)-grown silicon, is inclined to agglomerate to form oxygen-related donors and precipitates in CZ silicon during crystal cooling and subsequent thermal cycles. These oxygen donors including thermal donors and new donors can degrade device electrical stability. It is well known that thermal donors (TDs) form at low temperature (350–550 °C) [1, 2], while new donors (NDs) relative to oxygen clusters generally form at 600–700 °C [3, 4]. Impurities in silicon have been reported to have great effect on oxygen donors. Nitrogen can slightly inhibit TD formation [5, 6], and react with oxygen to generate nitrogen–oxygen complexes as shallow thermal donors [7]. Additionally, it has been found that isovalent dopants such as carbon and germanium can retard thermal donor formation. Recently, Hild *et al* [8] have investigated thermal donor formation at 450 °C in oxygen-rich SiGe with more than 1% Ge content by means of Hall measurements and infrared spectroscopy and confirmed the slowing down of thermal donor formation when the Ge content exceeded 1%.

Ge, isovalent to Si, can introduce size strain in the Si lattice because of its bigger atomic radius. It has been reported that Ge atoms can lock dislocations to increase mechanical

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Table 1. Initial data for the samples.

Samples	Ge conc. (cm^{-3})	Oxygen conc. (cm^{-3})	Resistivity (Ω cm)
CZ	0	$1.0–1.1 \times 10^{18}$	13–16
GCZ	$\sim 10^{18}$	$1.0–1.1 \times 10^{18}$	8–10

strength [9] and suppress TD [10–14] and ND [15], suppress void defects [16] and enhance oxygen precipitation [17]. In our previous papers, it has been proved that germanium doping of CZ silicon could affect the formation of voids, which can be easily annihilated by annealing; meanwhile, it has been clarified that germanium can enhance oxygen precipitation and therefore improve the inner gettering ability of wafers. This means that Ge-doped CZ silicon is of benefit in controlling microdefects in CZ Si and can be used in the microelectronics industry.

In this paper, the effect of germanium doping on oxygen donors including thermal donors and new donors in CZ silicon has been investigated by means of four-point probe and FTIR measurements. Some new results were obtained in our comparative experiments. Based on the findings, the mechanism of germanium doping of oxygen donors has been discussed.

2. Experimental details

Two kinds of p-type CZ crystals were grown under almost the same conditions. One is conventional CZ crystal and the other is germanium-doped CZ (GCZ) silicon. According to the segregation coefficient of Ge, the Ge concentration of GCZ samples was calculated to be about 10^{17} cm^{-3} in the seed portion and 10^{18} cm^{-3} in the tail portion in the crystal. Samples from the tail portions of these two crystals were called CZ and GCZ respectively. The detailed data on these samples are given in table 1.

In order to investigate the effect of germanium on TDs, the samples were divided into two groups. Samples in one group were pre-annealed at 650 °C for half an hour to annihilate TDs. Then the samples were annealed at 450 °C for different times. The resistivity of the annealed samples was measured by a four-point probe technique. The donor concentration was converted from resistivity according to ASTM F723-88. Interstitial oxygen concentrations were measured using a Fourier transform infrared spectrometer (FTIR, Bruke 66Vs) at wavenumber 1107 cm^{-1} with a calibrated coefficient of 3.14×10^{17} cm^{-2}.

In addition, the samples were annealed at 650 °C for 128 h to investigate the effect of germanium on NDs. The resistivity and oxygen concentration of the annealed samples were measured as above.

3. Results and discussion

Figure 1 shows the decrease in carrier content along the axial orientation in the CZ silicon and GCZ crystals after 650 °C/2 h annealing. The samples cut from the seed end, middle portion and tail portion of the CZ and GCZ silicon ingots were annealed at 650 °C for half an hour to annihilate the grown-in TDs. According to the variation of resistivity before and after 650 °C/0.5 h, we can obtain the carrier concentrations corresponding to grown-in TDs, which depend on the thermal history of the crystal growth. In the bulk, the distribution trends of decreasing carrier content in the CZ and GCZ silicon along the axial direction are similar; that is, the decrease in carrier concentration in the seed end is higher than those in the middle and tail parts. However, in the middle and tail parts, the decrease in carrier concentration in the CZ wafers is much greater than that in the GCZ wafers. As we know, the segregation coefficient of

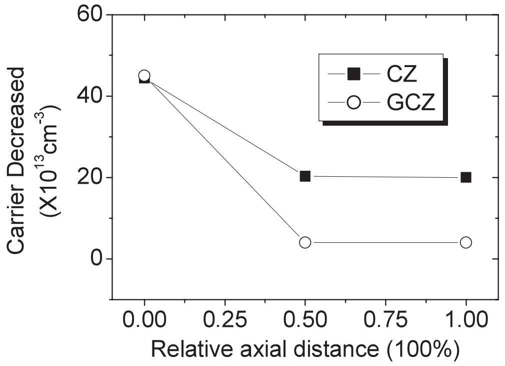

Figure 1. Decreasing grown-in carrier concentration along the axial orientation in CZ and GCZ silicon.

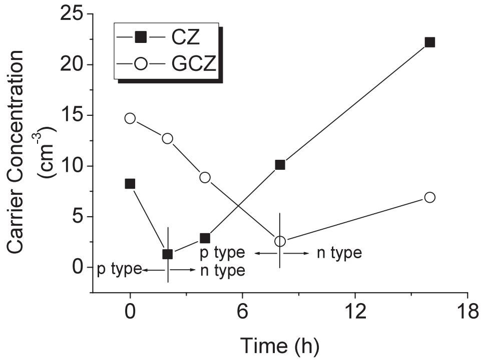

Figure 2. Carrier concentrations of the CZ and GCZ wafers with the annealing time of 450 °C.

Ge in crystal is about 0.33, smaller than 1. This means that the Ge concentration increases from the seed end to the tail portion of the crystal ingot. Therefore, it is concluded that Ge doping suppresses the formation of grown-in TDs during crystal growth, so the decreased carrier concentration corresponding to grown-in TDs is lower in the tail portion of GCZ samples than in that of CZ ones.

In order to further investigate the effect of Ge on the TD formation at 450 °C, the samples with or without 650 °C/1 h pre-annealing were annealed at 450 °C for different times (2–16 h). Figures 2 and 3 show the carrier concentration variations of these two groups of p-type CZ and GCZ wafers as a function of the annealing time at 450 °C. It can be seen that the carrier concentrations varied more rapidly with increasing time in the CZ wafers than in the GCZ wafers, which further confirms that germanium doping suppresses the formation of TDs.

Furthermore, the carrier concentrations in the CZ and GCZ wafers annealed at 650 °C are shown in figure 4. The hole concentration of the CZ wafers decreased with the annealing time due to the formation of NDs. However, the hole concentration of the GCZ silicon decreased more rapidly, so the conductivity type has reversed from p-type to n-type upon annealing for 128 h. This indicates the huge number of the NDs generated due to the enhancement effect of germanium on the formation of NDs. The oxygen concentration variations of the annealed CZ and GCZ silicon are also shown in figure 5. It is found that more oxygen has precipitated in the GCZ wafers than in the CZ silicon, as a result of germanium enhancing oxygen precipitation.

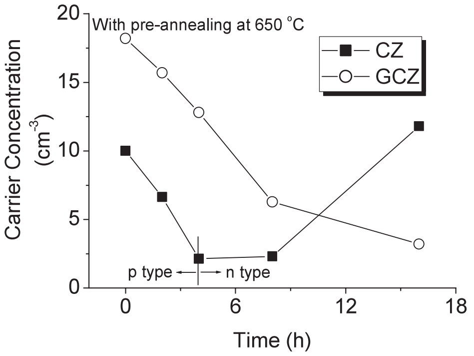

Figure 3. Carrier concentrations of the CZ and GCZ wafers with pre-annealing at 650 °C for 1 h as a function of the annealing time at 450 °C.

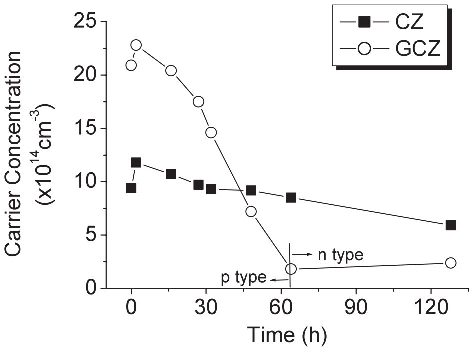

Figure 4. Carrier concentrations in the CZ and GCZ wafers annealed at 650 °C as a function of the annealing time.

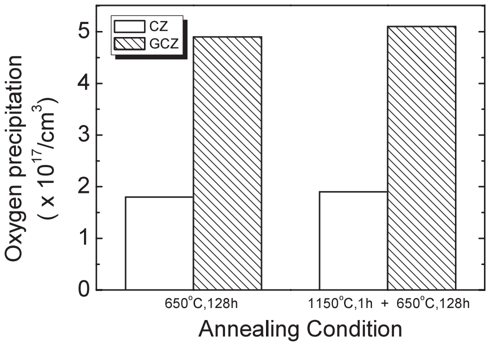

Figure 5. Decreasing oxygen concentration (oxygen precipitation) after annealing at 650 °C for 128 h.

In GCZ silicon, the size effect induced by Ge atoms in the silicon lattice is crucial. Germanium and silicon are isovalent elements with a substantial difference in atomic radius. As isoelectrical impurities, Ge atoms are mostly located in substitutional sites in Si lattices. The radius of the Ge atom is 1.52 Å, which is larger than that of the Si atom. Thus, the incorporation of Ge into silicon will lead to increase of the internal stress. Therefore, during crystal growth, vacancies are inclined to combine with Ge atoms to form complexes Ge–V_n ($n \geqslant 1$), as has been unambiguously identified by DLTS measurements on Ge-doped Si crystals [18]. In our previous work, it has been clarified that germanium can enhance the nucleation of oxygen precipitation in the wide temperature range of 650–1200 °C; this is based on the assumed Ge–O and Ge–O–V complexes. On the other hand, TDs generated around 450 °C are believed to be due to a SiO_4 complex [19]. The molar volume of SiO_4 is about 2.4 times larger than that of Si, so during the TD formation the lattice strain must be released by attracting free vacancies. However, the Ge–V complex formation will decrease the concentration of free vacancies and suppress the formation of TDs. Moreover, the generation of SiO_4 is a process of oxygen clustering, so the Ge–O complex formation and the enhancement of oxygen precipitation will reduce the oxygen flux, leading to the formation of smaller oxygen clusters at lower temperature and therefore suppressing the TD formation.

New donors are considered to be bigger oxygen clusters as compared to TDs, which are generally nuclei of oxygen precipitates during lower temperature annealing [20]. In our present experiment, it is found that Ge could enhance the formation of NDs, which is opposite to the finding of the work of Babitskii [15]. In Babitskii's work, the samples used are from small diameter silicon crystals and the germanium concentration is much higher. However, with much lower Ge concentration and larger crystal diameter, the rate of generation of oxygen precipitation and the formation of new donors were enhanced. The enhancement of ND formation in GCZ silicon is thus considered as a process related to Ge enhancing the oxygen precipitation. A considerable number of these denser small oxygen precipitates are believed to have become NDs with electrical activity.

4. Conclusions

In summary, Ge doping is found to effectively suppress TD formation and enhance ND formation. It is believed that Ge can complex with oxygen and vacancies to form stable complexes, which reduces the oxygen flux leading to smaller oxygen clusters being related to TDs and suppresses the release of stress during TD formation. However, these relative germanium complexes enhance the production of denser oxygen precipitation nuclei at 650 °C and therefore benefit ND formation.

Acknowledgments

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