Impact of silicon substrate germanium doping on diode characteristics and on thermal donor formation

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ABSTRACT

Ge-doped Si is of potential interest for specific microelectronics applications; in particular, it is known that its incorporation can lead to an improvement of the radiation hardness of the Si. However, the role of the introduced Ge in the electrical stability of the material is also of special concern. In this contribution we investigate the effects of thermal anneals on the electrical characteristics of p-on-n diodes fabricated on Czochralski-grown Ge-doped-Si and on control Si wafers. Diodes fabricated on high resistivity (HR) magnetic CZ, as well as standard HR float zone (FZ) and oxygenated FZ are also added for comparison. The results show little differences between the electrical characteristics of the devices fabricated on the CZ Si and CZ SiGe substrates, however, the differences increase after thermal anneals. Interestingly and important for device applications, less thermal donor generation is found for the case of the Ge-doped material. The obtained results should be taken into account when defining potential applications of Ge-doped materials.

1. INTRODUCTION

Ge-doped Si is of potential interest for application in microelectronics. In particular, it has been reported that Si-Ge solid solutions at low Ge contents, as well as $\text{Si}_{1-x}\text{Ge}_x$ epitaxial layers, exhibit higher radiation resistance than Si [1-3]. The improved radiation-hardness is attributed to the role of Ge atoms as centres of annihilation of radiation-induced primary defects [1,3]. Moreover, its higher absorption coefficient than Si makes it suitable for certain radiation detectors and imaging applications [4]. It has also been reported that doping Si with Ge leads to a reduced formation of oxygen-related thermal donors (TDs) [5-7]. This may be of particular interest for processing of Si radiation detectors, where temperatures in the range of 450°C may be reached during back-end and post-metallization annealing. It is believed that Ge can pair with oxygen and vacancies to form stable complexes, while reducing the oxygen flux leading to the small oxygen clusters related to TDs [7]. However, the generation of thermal donors may significantly depend on the involved temperatures and thermal history of the material [8]. With this respect, recently it has been observed that the formation of thermal donors in Ge-doped Czochralski Si may be even higher than in control Si by the application of a rapid thermal annealing pre-treatment [9].

In order to shed some further light on the behavior of Ge-doped Czochralski (CZ) Si material, n-type crystals with (CZ SiGe) and without Ge doping (CZ Si) were studied in the present work. As a difference to previous studies, in which in general unprocessed material was used, in the present study p-on-n diodes were fabricated on polished wafers prepared from both crystals following a well-established diode fabrication process [10]. To our best knowledge, this is the first time that a thermal donor generation comparison between

standard Si and Ge-doped Si is performed on fabricated diodes (not on raw/as-received material). This means that the studied materials have been subjected to all the thermal steps of a typical diode fabrication process, including high temperature steps like field isolation and impurity activation anneal. Such thermal donor generation study is of particular interest for back-end steps, as the final metal annealing, which is performed at temperatures and ambient in the range of the thermal treatments studied in the present work. Moreover, such a device-level approach is currently especially opportune, since opposite results for thermal donor generation in standard and Ge-doped Czochralski Si have been published recently [8,9], indicating that the thermal history of the material can have an important impact on the thermal donor generation in Ge-doped Si compared to control standard Si. For comparison, devices processed on other types of Si materials with different oxygen contents, i.e. high resistivity (HR) standard and oxygenated float zone (FZ), as well as HR magnetic CZ (MCZ) Si, were also included in the study. The effects of thermal anneals in the range of 250°C to 450°C on the electrical characteristics of the fabricated p-on-n diodes were investigated.

2. EXPERIMENTAL DETAILS

Two n-type CZ crystals were pulled by QL electronics, in collaboration with State Key Laboratory of Silicon Materials (Hangzhou, P. R. China). One of the crystals was doped with a Ge concentration of about $1 \cdot 10^{19} \text{ cm}^{-3}$, whereas the second did not receive any Ge doping. Both crystals were grown under the same pulling conditions, giving rise to similar thermal histories, final resistivities and interstitial oxygen contents ($[O_i]$) (Tables 1 and 2). The

fabricated p-on-n diodes, with an active area of 0.25 cm^2 , were subjected to a anneals at temperatures ranging between 250°C and 450°C , for times between 0.5 h and 5h and using N_2/H_2 or N_2 ambients. The impact of Si substrate Ge doping on diode characteristics and on thermal donor formation has been analyzed by means of capacitance-voltage (C-V), current-voltage ($I_{\text{leak}}\text{-V}$) and exploratory microwave photoconductance decay ($\mu\text{W-PCD}$) recombination lifetime measurements using a Semilab WT1000 setup [11].

3. RESULTS AND DISCUSSION

Fig. 1 shows typical current-voltage characteristics ($J_{\text{leak}} = I_{\text{leak}}/\text{Area}$) measured for two sets of 10 CZ Si and CZ SiGe diodes. From the figure, and also from wafer mapping of the $I_{\text{leak}}-V$ measurements, a clear homogeneity in the characteristics was observed. Slightly higher reverse current levels have been observed for the CZ SiGe diodes compared to their CZ Si counterparts (Fig. 1). Although a somewhat higher free carrier concentration was extracted for the CZ SiGe diodes ($2.20 \cdot 10^{14} \text{ cm}^{-3}$) compared to the control CZ Si ones ($2.05 \cdot 10^{14} \text{ cm}^{-3}$) (Fig. 2), the slightly higher reverse current levels in CZ SiGe diodes could be associated to their lower generation lifetimes (as will be shown later in Fig. 5(a)).

Interestingly, a significant increase of the free carrier concentration is progressively observed when subjecting the CZ Si and CZ SiGe diodes to thermal anneals at 450°C (Fig. 2). Within the assessed depth corresponding to a maximum applied reverse voltage of 100 V, the carrier concentration increases after the 5 h treatment by a factor of four and two for the Si and SiGe substrates, respectively. Such increase in the carrier concentration is attributed to the generation of oxygen-related thermal donors (OTD) [12,13]. This is corroborated by the results shown in Fig. 3, in which the extracted free carrier concentration for the CZ Si and CZ SiGe diodes has been plotted together with the results obtained for devices fabricated on HR MCZ, HR FZ and HR OXFZ substrates. The changes in the free carrier concentration are only observed for the materials with the higher interstitial oxygen contents (CZ Si, CZ SiGe and HR MCZ) (Tables 1 and 2). From Fig. 3(a), the thermal donor (TD) generation rate for CZ SiGe (around $2.6 \cdot 10^{13} \text{ cm}^{-3}/\text{h}$) is found to be nearly 5 times lower than the one extracted for CZ Si (around $1.26 \cdot 10^{14} \text{ cm}^{-3}/\text{h}$, in good agreement with

previous results on CZ Si material with similar oxygen contents [12]). The lower TD generation rate in Ge-doped Si can be attributed to the ability of Ge to pair with oxygen atoms, thus reducing the oxygen flux leading to the small oxygen clusters related to TDs [7]. On the other hand, the TD generation rate for the HR MCZ is estimated to be around $1.5 \cdot 10^{13} \text{ cm}^{-3}/\text{h}$. Furthermore, as could be expected from previous experience with different hydrogenation procedures [13], there is a lower donor formation in N_2 ambient compared to N_2/H_2 ambient. This is explained by the H accelerating the interstitial oxygen diffusion resulting in a faster OTD formation [12,13].

As observed in Fig. 3(b) results, under the limited experimental conditions studied, the changes in the free carrier concentrations are only observed for annealing temperatures above 400°C for the HR MCZ material and 450°C in the case of the CZ Si and CZ SiGe. However, as shown in Fig. 4, significant changes in the current-voltage characteristics are already observed for the diodes subjected to lower temperature annealing. In this way, from Fig. 4, a trend to increased leakage currents is observed for the higher temperature annealing, nevertheless, no significant differences are observed between different annealing times at 450°C . In parallel, a decrease of the generation lifetime (extracted from J_{leak} vs. depletion depth plots [14]) is also observed in Fig. 6(a). Interestingly, the measured μW -PCD recombination lifetimes also decrease for the higher temperature annealing (Fig. 5(b)), but, different to previous irradiation studies [14], no clear correlation has been found with the degradation of the generation lifetime extracted from the J_{leak} versus depletion depth plots.

4. CONCLUSIONS

The effects were investigated of thermal anneals in the range between 250°C and 450°C on the electrical characteristics of p-on-n diodes fabricated on Czochralski-grown Ge-doped-Si (CZ SiGe) (with $[Ge]=1\cdot 10^{19} \text{ cm}^{-3}$) and control CZ Si devices. Diodes fabricated on high resistivity (HR) magnetic CZ, as well as standard HR float zone (FZ) and oxygenated FZ were also included for comparison. The results show little differences between the electrical characteristics of the devices fabricated on the CZ Si and CZ SiGe substrates. Low temperature anneals increase however the differences between the devices on both substrates. Possibly of interest for device applications, is that less thermal donor generation is found for the Ge-doped substrates. The obtained results should be taken into account when defining potential applications of Ge-doped materials.

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TABLE CAPTIONS

Table 1: Main specifications of the Si and SiGe substrates studied.

Table 2: Main specifications of the three high resistivity (HR) Si substrates which were included in the study for comparison.

FIGURE CAPTIONS

Fig. 1: J_{leak} vs. reverse bias for 10 CZ Si and 10 CZ SiGe diodes.

Fig. 2: Free carrier concentration versus depletion depth for (a) CZ Si and (b) CZ SiGe diodes subjected to different thermal annealing conditions.

Fig. 3: Extracted free carrier concentration for CZ Si, CZ SiGe, HR MCZ, HR FZ and HR OXFZ p-on-n diodes subjected to (a) different annealing times at 450°C and (b) different anneal temperatures. For the CZ Si and CZ SiGe diodes, the carrier concentrations correspond to the values for a depletion depth of 16.5 μm while, for the HR materials, they correspond to the assessed flat region of carrier concentration.

Fig. 4: J_{leak} versus depletion depth for CZ SiGe diodes subjected to different thermal annealing conditions.

Fig. 5: (a) Generation lifetime (extracted from J_{leak} versus depletion depth plots [14]) and (b) μW -PCD recombination lifetime [11], for CZ Si and CZ SiGe diodes annealed for 2 hours at different temperatures.

Substrate	CZ Si	CZ SiGe
Supplier	QL	QL
Type	n	n
Orientation	<100>	<100>
Thickness (d) [μm]	525 ± 15	525 ± 15
Resistivity [$\Omega\cdot\text{cm}$]	23.7 ± 2.5	19.4 ± 1.0
Average [O_i] [$\times 10^{17} \text{ cm}^{-3}$]	7.81 ± 0.43	6.82 ± 0.41
Ge conc. [cm^{-3}]	0	1×10^{19}

Table 1

Substrate	HR MCZ	HR FZ	HR DOFZ
Supplier	Okmetic	Topsil	Topsil
Type	n	n	n
Orientation	<100>	<100>	<100>
Thickness (d) [μm]	300 ± 10	280 ± 15	280 ± 15
Resistivity [$\text{k}\Omega\cdot\text{cm}$]	1.0 ± 0.1	4.5 ± 0.6	2.5 ± 0.1
Dopant conc. [$\times 10^{12} \text{ cm}^{-3}$]	3.9 ± 0.4	0.9 ± 0.1	1.6 ± 0.1
Average [O_i] [$\times 10^{17} \text{ cm}^{-3}$]	3.5 ± 1.5	< 0.09	1.7 ± 0.4

Table 2

Fig. 1

Fig. 2(a)

Fig. 2(b)

Fig. 3(a)

Fig. 3(b)

Fig. 4

Fig. 5(a)

Fig. 5(b)