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Stress-dependent transformation of interstitial oxygen in processed Ge-doped Cz-Si

A. Misiuk [a,*], C.A. Londos [b], J. Bak-Misiuk [c], Deren Yang [d], W. Jung [a], M. Prujszczyk [a]

[a] *Institute of Electron Technology, Al. Lotnikow 46, 02-668 Warsaw, Poland*
[b] *University of Athens, Panepistimiopolis Zografos, Athens 157 84, Greece*
[c] *Institute of Physics, PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland*
[d] *State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, PR China*

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Abstract

The effect of stress induced by enhanced hydrostatic pressure (HP, up to 1.2 GPa) applied at processing at up to 1400 K, on the transformation of interstitial oxygen (O_i) in Ge-doped Czochralski silicon (Cz-Si:Ge, $c_{Ge} = 7 \times 10^{17}$ cm^{-3}) was investigated by spectroscopic, X-ray and electrical methods.

While the presence of Ge results in reduced generation of thermal donors (TDs) in Cz-Si:Ge annealed under 10^5 Pa, the same processing under HP at 675–750 K produces TDs in a concentration up to about 10^{15} cm^{-3}. The treatment under HP at 1270–1400 K stimulates agglomeration of interstitial oxygen; the HP-dependent generation of different oxygen-containing defects is observed. The effect of HP on transformation of oxygen in Ge-doped Cz-Si is related, among others, to stress-induced activation of germanium to act as a component of nuclei for precipitation of O_i's.

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1. Introduction

Light doping of single crystalline silicon with germanium has been reported to affect beneficially some its properties [1]. Uniform stress (e.g. exerted by enhanced hydrostatic pressure, HP, of ambient inert gas) applied at processing at up to 1400 K strongly affects clustering of oxygen interstitials (O_i's) and related properties of germanium-enriched Czochralski grown silicon (Cz-Si:Ge) [2].

In comparison to the case of germanium-lean Cz-Si, annealing of Cz-Si:Ge under the conditions of enhanced uniform stress has been reported [2,3] to result, among others, in

- Non-typical increase of the concentration of thermal donors (TDs) with HP (lack of saturation of TDs concentration in effect of processing at 720 K under HP up to 1.2 GPa),
- Decreased stress-induced precipitation of O_i's, and
- Restrained creation of extended defects, such as dislocations.

This work concerns the study of stress-dependent transformation of interstitial oxygen in Cz-Si:Ge subjected to processing at enhanced temperatures (HT).

2. Experimental

Oxygen-containing ($c_{Oi} \approx 6.5 \times 10^{17}$ cm^{-3}) Czochralski grown silicon, of (001) orientation, doped with Ge during

* Corresponding author. Tel.: +48 22 548 7792; fax: +48 22 847 0631.
E-mail address: misiuk@ite.waw.pl (A. Misiuk).

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its growth ($c_{Ge} \approx 7 \times 10^{17}\,cm^{-3}$) was investigated in the present research. The Cz-Si:Ge samples of $10 \times 8 \times 2\,mm^3$ dimensions were annealed for up to 10 h at HT $\leqslant$ 1400 K in Ar atmosphere under HP $\leqslant$ 1.2 GPa; the details of experimental procedure have been reported elsewhere [4].

The effect of HP on the transformation of oxygen and on the resulting microstructure of Cz-Si:Ge was investigated by electrical (four points probe and *C–V*), spectroscopic (IR absorption) and X-ray (to record X-ray Reciprocal Space Maps, XRRSMs, and Rocking Curves, RCs) methods.

3. Results and discussion

The presence of Ge in Cz-Si is known to result in suppression of TDs formation [3]. This has been confirmed in the present study for the case of Cz-Si:Ge annealed for 10 h at 723 K under 10^5 Pa (atmospheric pressure). While conductivity of Cz-Si:Ge was of n type in the case of all investigated samples, the concentration of electrons after annealing at 723 K under 10^5 Pa remained relatively low, of about $0.5 \times 10^{14}\,cm^{-3}$ (Fig. 1). Contrary to this, processing of Cz-Si:Ge under 1.1 GPa within the 675–750 K temperature range results in a distinct HP-induced increase of the TDs concentration (Fig. 1). The highest concentration of electrons has been detected for Cz-Si:Ge treated at 723 K under the highest pressure applied, 1.2 GPa; this increased electron concentration in the conduction band is directly related to the HP-induced creation of TDs [5,6].

Generally, TDs-related enhancement of electron concentration in silicon is considered to be caused by the presence of small oxygen-containing clusters. In the case of Cz-Si, the lattice strain related to the creation of TDs should be released by attracting free vacancies (V) or ejecting oxygen interstitials (Si_i's). In the case of germanium doping, Ge atom, with the radius exceeding that of Si atom, tends to form the Ge–V complex. The creation of such complexes in Cz-Si:Ge should result in the decreased concentration of Si_i's and so in suppressed TDs formation [1].

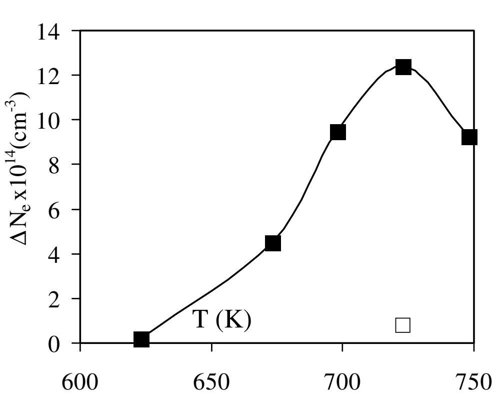

Fig. 1. Dependence of N_e ($N_e = N_{HT\text{-}HP} - N_i$, where $N_{HT\text{-}HP}$ – concentration of electrons after processing at HT–HP and N_i – initial concentration of carriers) on processing temperature for Cz-Si:Ge samples treated for 10 h at 625–750 K under HP = 1.1–1.2 GPa (■). N_e for Cz-Si:Ge processed for 10 h at 723 K under 10^5 Pa is indicated (empty mark, □).

The effect of HP on TDs creation in Cz-Si has been suggested to originate from enhanced oxygen diffusivity [3] or/and HP-induced activation of the nucleation centres for TDs formation [5]. As it has been demonstrated by *C–V* measurements [2,6], the depth profile of TDs in Cz-Si:Ge processed at 723 K is non-uniform and related to the presence of structural non-homogeneities, especially near the Cz-Si:Ge surface. Just these non-homogeneities can be activated under HP to act as the nucleation centres for the creation of oxygen-containing clusters exhibiting electrical activity.

Generation of TDs does not result in a marked decrease of infrared (IR) absorption at about $1106\,cm^{-1}$, being directly related to the presence of O_i's (Fig. 2(a)). Assuming that about 20 oxygen interstitials are involved in a creation of one TD, one can estimate that observed increase of ΔN_e for about $1.2 \times 10^{15}\,cm^{-3}$ corresponds to the removal of about $2.5 \times 10^{16}\,cm^{-3}$ of O_i's from Cz-Si:Ge (this material can be considered as the solid solution of germanium and of oxygen in silicon). This loss of O_i's is, however, just at the detection limit of the used IR absorption method.

Processing of Cz-Si:Ge for 10 h at 923 K under HP results in partial precipitation of oxygen interstitials as follows from observable decrease of the intensity of IR absorption at $1107\,cm^{-1}$. Absorption at about $1081\,cm^{-1}$, observable after deconvolution of the absorption curve (Fig. 2(b)), evidences most probably the presence of needle-like oxygen precipitates formed in the Cz-Si:Ge matrix. Comparing the effects of HP on oxygen precipitation in Cz-Si and in Cz-Si:Ge, it is obvious that in Cz-Si:Ge the HP-induced precipitation of O_i's is distinctly weaker. This is related to numerous nucleation centres (NCs) present in Cz-Si:Ge from the very beginning because of some non-homogeneity of this material, related to the non-uniform Ge distribution [7]. So oxygen precipitation at processing, both under 10^5 Pa and under HP, is dependent mainly on NCs present within the Cz-Si:Ge lattice.

No evident HP-induced electrical activity has been detected after the treatment at 923 K (compare [6]).

The treatment of Cz-Si:Ge for 5 h at 1270 K under 1.1 GPa causes massive precipitation of oxygen [2]. It has been also reported that such processing results in a decreased intensity of the PL lines around 1.1 eV related to the band-to-band transitions while the intensity of emission at about 1.08 eV related to the presence of EHD (electron–hole droplets [8]) increases with HP [2].

This means that some additional non-homogeneities (such as oxygen clusters/precipitates) and interfaces are increasingly formed under HP [8].

The effect of HP on oxygen precipitation in Cz-Si:Ge is most pronounced just in the case of its processing at about 1270 K [2]. The deconvoluted absorption bands at IR for Cz-Si:Ge processed at 1270 K under 10^5 Pa and 1.1 GPa are presented in Fig. 3. IR absorption observed at about $1060\,cm^{-1}$, $1095\,cm^{-1}$ and $1119\,cm^{-1}$ results from light absorption by SiO_x precipitates [9,10] while that one at $1106\,cm^{-1}$ – by O_i's. Comparison of the deconvoluted IR

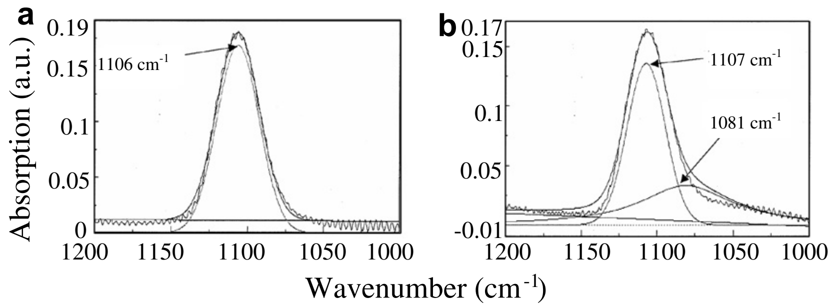

Fig. 2. Deconvolution of IR absorption of Cz-Si:Ge treated for 10 h under 1.1 GPa at 723 K (a) and 923 K (b).

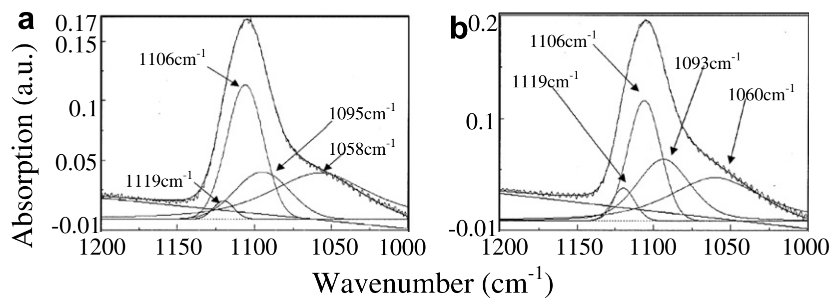

Fig. 3. Deconvolution of IR absorption of Cz-Si:Ge processed for 5 h at 1270 K under 10^5 Pa (a) and 1.1 GPa (b).

absorption bands for Cz-Si:Ge processed under 10^5Pa (Fig. 3(a)) with the these ones after processing the sample under 1.1 GPa (Fig. 3(b)), leads to conclusion that the kind of SiO_x clusters/precipitates is dependent on HP.

The relative intensities (in respect of IR absorption at 1106 cm^{-1}) of the IR absorption band at about 1060 cm^{-1} (corresponding to the presence of needle-like oxygen precipitates), observed after processing of Cz-Si:Ge at 1270 K under 10^5 Pa and under 1.1 GPa, are almost the same (equal to about 1.26 and 1.34, respectively). However, the relative intensities of the IR absorption bands at about 1095 cm^{-1}, caused by the presence of spheroidal precipitates [11,12], increase with HP, to reach 0.97 in the case of Cz-Si:Ge processed under 1.1 GPa, while only of about 0.52 after processing under atmospheric pressure. The same increase, with HP, concerns the relative intensities of the IR absorption band at about 1119 cm^{-1} (corresponding to platelet-like and/or polyhedral precipitates [13]), increasing from 0.08 after annealing under 10^5 Pa to 0.20 after the treatment of Cz-Si:Ge under 1.1 GPa, with other processing parameters maintained the same.

As follows from XRRSMs, processing of Cz-Si:Ge at 1270 K under 1.1 GPa results in the decreased intensity of diffusively scattered X-rays if compared to that for the sample annealed under 10^5 Pa (compare Fig. 4(a) and (b)). Processing under HP seems to affect the uniformity of the Si–Ge solid solution: the presence of single diffraction spot (as indicated by an arrow, Fig. 4(b)) evidences the presence of Si–Ge grain with the lattice parameter a little larger [2] than that of Si and so with the Ge content also exceeding its mean value for Cz-Si:Ge. Processing under HP resulted also in the increase of the RC full width at half maximum (FWHM): from 15 arc sec for the sample annealed for 5 h at 1270 K under 10^5 Pa to 27 arc sec for Cz-Si:Ge treated similarly but under 1.1 GPa.

It is interesting to note that processing at 1270 K-HP of Cz-Si:Ge with NC's introduced by the pre- treatment at 1070 K does not cause an increase in diffuse scattering of X-rays (compare Fig. 4(b) and (c)). This means that just the condition of final processing is a decisive factor in respect of the oxygen precipitation-related microstructure of processed Cz-Si:Ge. Processing of Cz-Si:Ge at 1400 K under 1.1 GPa results in a decreased intensity of the EHD line as well as of the other PL lines at the band-to-band transition region, near 1.1 eV (see also [2]). The IR absorption band near 1106 cm^{-1} is almost symmetric. Still its deconvolution allows for discrimination of at least of three sub-bands (Fig. 5). Absorption at about 1095 cm^{-1} increased with HP: its relative values were equal to about 0.9 and 1.24, respectively, after processing under 10^5 Pa and 1.1 GPa (Fig. 5(a) and (b)). The relative intensity of the IR band at about 1120 cm^{-1} remained practically unchanged (0.44 and 0.41, respectively). It means that more numerous spheroidal precipitates were created under HP, while the these ones of platelet shape were formed in about the same concentration both in effect of processing under 10^5 Pa and under 1.1 GPa. It means also that HP applied at 1400 K affects the shape/composition of SiO_xprecipitates to a lesser extent than in the case of processing at lower temperature, 1270 K.

As follows from XRRSMs, processing of Cz-Si:Ge at 1400 K under 1.1 GPa results in the increased intensity of diffusively scattered X-rays in comparison to that of the sample annealed under 10^5 Pa (Fig. 6). Processing of

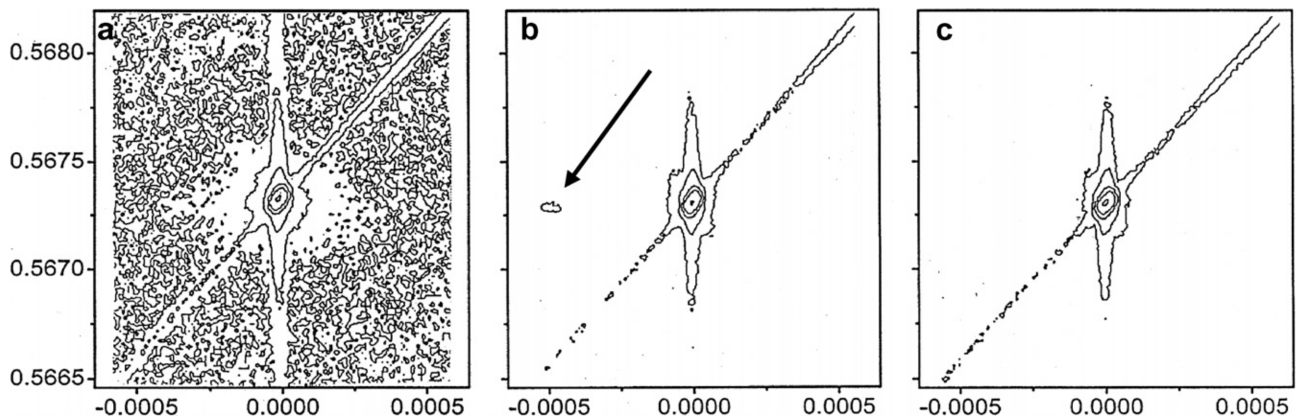

Fig. 4. 004 XRRSMs of Cz-Si:Ge processed for 5 h at 1270 K under 10^5 Pa (a), 1.1 GPa (b) and, sequentially, for 5 h under 1.1 GPa at 1070 K and for 5 h at 1270 K under 1.1 GPa (c).

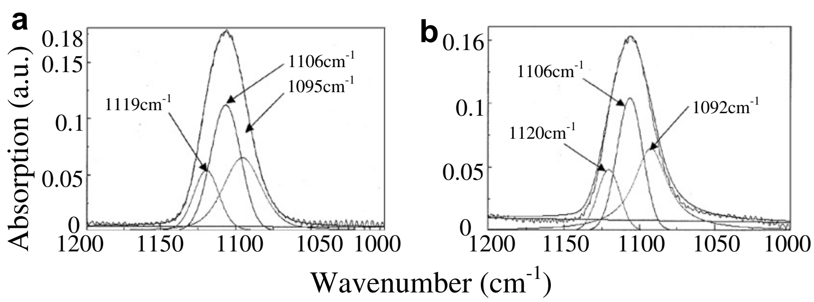

Fig. 5. Deconvolution of IR absorption of Cz-Si:Ge processed for 5 h at 1400 K under 10^5 Pa (a) and 1.1 GPa (b).

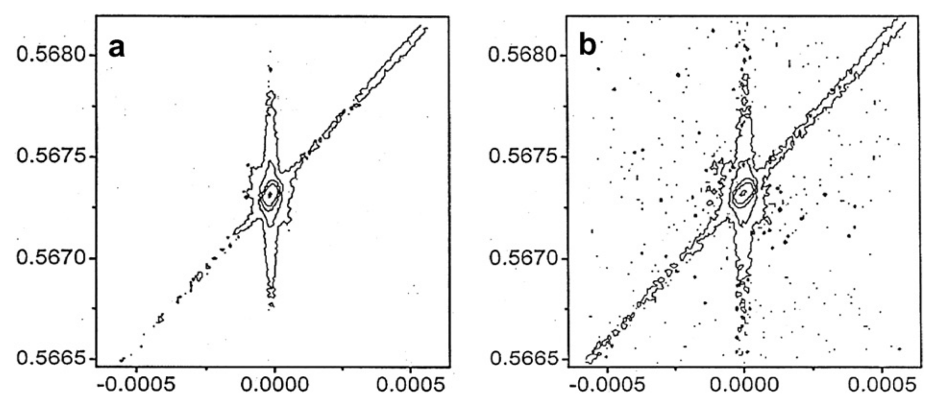

Fig. 6. 004 XRRSMs of Cz-Si:Ge processed for 5 h at 1400 K under 10^5 Pa (a) and 1.1 GPa (b).

Cz-Si:Ge under HP at 1400 K results in unchanged FWHM of RCs for the 004 reflection, equal to about 15 arc sec.

The decreased concentration of oxygen interstitials in the HT–HP treated Cz-Si:Ge samples indicates that precipitated oxygen interstitials agglomerate and create SiO_x clusters of different shapes, with their relative content critically dependent on applied hydrostatic pressure.

4. Conclusions

In the case of Cz-Si:Ge containing Ge at the 7×10^{17} cm^{-3} level, subjected to processing at up to 1400 K under hydrostatic pressure up to about 1.1 GPa, pressure-induced transformations of the interstitial oxygen are specific, to some extent similar to these observed for pressure treated Ge-lean Cz-Si. High hydrostatic pressure applied during processing of Cz-Si:Ge results in the distinct stress-induced effects, among them

- Marked increase of the carrier concentration with pressure applied during processing within the 698–748 K temperature range.
- Stress-dependent creation of oxygen-containing precipitates with different shapes.

In view of growing interest in the properties of Ge-doped silicon (expected to be useful for some applications in microelectronics [1]), further investigations on stress-induced effects in germanium-enriched Cz-Si can be recommended.

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