

Defects in Ge-doped Cz-Si annealed under high stress

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Abstract

The effect of stress induced by enhanced hydrostatic pressure (HP, up to 1.1 GPa) at annealing up to 1400 K of Ge-doped Czochralski silicon (Cz-Si:Ge) on a creation of thermal donors (TDs) and of oxygen-related defects is investigated by spectroscopic (FTIR) photoluminescence and electrical methods. While the presence of Ge results in reduced generation of TDs in Cz-Si:Ge annealed at 723 K under 10^5 Pa, HP applied at 698–748 K produces TDs in a much enhanced concentration. The treatments under 1.1 GPa at 1070–1270 K result in increasing, for up to 20%, precipitation of oxygen. An explanation of the HP effect on a creation of defects in Cz-Si:Ge is proposed.

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1. Introduction

Germanium doping of Czochralski silicon (Cz-Si) has attracted much attention. Substitutional Ge atoms result in lattice expansion; Cz-Si:Ge with a low level of Ge doping can be considered as a specific kind of Si with lattice parameter ($a_{\text{Si:Ge}}$) expanded by internal pressure. The presence of Ge improves some properties of Cz-Si:Ge at processing; Ge admixture suppresses a creation of thermal

donors (TDs) at about 720 K and oxygen precipitation at ≥ 1000 K [1]. External hydrostatic pressure (HP) at annealing results in the decreased a value of Cz-Si:Ge. Application of HP allows for discrimination of the effects related to increased a of Si:Ge and of the presence of substitutional Ge itself.

HP applied at enhanced temperatures (HT-HP treatment) affects a lot of Si-Ge properties, among them the Ge-Si interdiffusion [2] and creation of TDs [3]. However, no systematic research of the effect of stress on the temperature-induced creation of oxygen-related defects in Cz-Si:Ge (important e.g. for understanding the mechanisms of quantum dots formation in the Si-Ge system) has been

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reported as so far. This work presents the first systematic study of the HP effect on the formation of defects in Si:Ge processed at HT.

2. Experimental

Initially p-type boron-doped (001)-oriented Czochralski silicon, Cz-Si, with Ge concentration, $C_{Ge} \approx 7 \times 10^{17} \text{ cm}^{-3}$ and that of oxygen $C_{O_i} \approx 6.5 \times 10^{17} \text{ cm}^{-3}$, 2 mm thick Si:Ge wafers were used in present research. The samples were subjected to processing under Ar hydrostatic pressure up to 1.12 GPa at $HT \leq 1400 \text{ K}$ for up to 10 h; the details of experimental procedure have been reported elsewhere [4]. The effect of HP on Cz-Si:Ge was investigated by electrical (four points probe and C–V) and spectroscopic (absorption by FTIR, and photoluminescence (PL) measured at 6 K) methods.

3. Results and discussion

While much less TDs (in comparison to that in Ge-free Cz-Si) are generated in Cz-Si:Ge annealed at 723 K under 10^5 Pa , HP applied at 698–748 K results in markedly decreased resistivity of Cz-Si:Ge. In the case of Cz-Si:Ge treated at 723 K the concentration of electrons (their presence is directly related to the HP-induced creation of TDs [4]) in the conduction band increased for an order of magnitude; similar effects of HP on Cz-Si:Ge have been stated also at 698 K and 748 K (Fig. 1).

The increase of ΔN_e is approximately linear with HP; no traces of saturation (reported e.g. for oxygen-rich Cz-Si [5]) have been detected. Accounting for the low concentration of oxygen in Cz-Si:Ge, this effect of HP on the concentration of TDs (supplying electrons to the conduction band of silicon) is unusual. It is generally accepted that TDs are small clusters containing oxygen. 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 . Ge atoms with the radius exceeding that of Si tend to complex Ge and to form $Ge-V$, which suppresses the ejection of Si_i and so results in a retarded TDs formation [1].

Under HP, this mechanism seems not to work. For Ge-free Cz-Si, the HP effect on a TDs creation has been suggested to originate from enhanced oxygen diffusivity [3,5]. It should be noted, however, that an alternative suggestion has been also made to explain a promoted creation of TDs in Cz-Si under HP. It is based on assumption that, under HP, more nucleation centres for the TDs formation are activated [5]. Actually, as it follows from C–V measurements, the depth profile of TDs in Cz-Si:Ge processed at 723 K is highly non-uniform being related to enhanced concentration of structural non-homogeneities near the Cz-Si:Ge surface. Much more TDs are created at 723 K in Cz-Si:Ge processed under HP (Fig. 1) than under atmospheric pressure (10^5 Pa). An increase of electron concentration (ΔN_e) after processing of Cz-Si:Ge

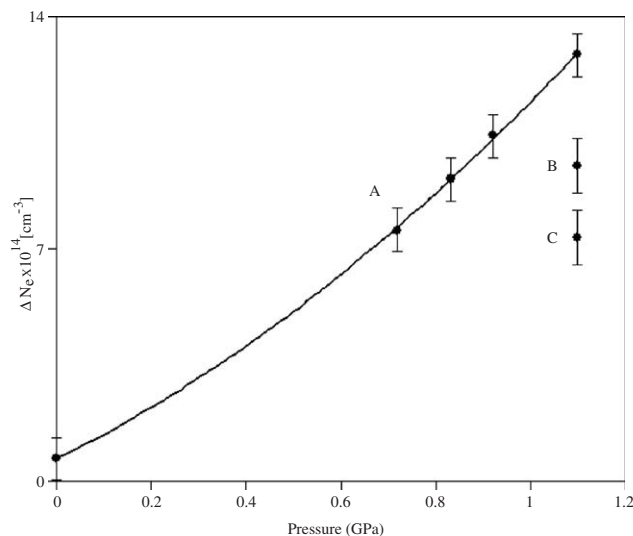


Fig. 1. An increase of electron concentration, ΔN_e ($\Delta N_e = N_e \text{ after HT-HP} - N_e \text{ initial}$), in Cz-Si:Ge samples treated for 10 h at 723 K (A), 698 K (B) and 748 K (C) under HP up to 1.1 GPa.

under 1.1 GPa at 748 K and at 698 K is relatively high, almost equal to that in Cz-Si:Ge treated at 723 K under the same pressure (Fig. 1). This also confirms specific mechanism of the HP induced creation of TDs in Cz-Si:Ge [3,5].

The PL spectra of Cz-Si:Ge processed at 723 K under 10^5 Pa and 1.1 GPa are presented in Fig. 2. No marked differences in PL are observed with an exception of the FE(TO) line much weaker in Cz-Si:Ge treated under 1.1 GPa.

The treatment of Cz-Si:Ge for 5 h under 1.1 GPa at 1070–1270 K results in distinctly increased (for up to 20%) precipitation of oxygen (Fig. 3). At 1400 K this effect is a little weaker. Even more enhanced HP-induced oxygen precipitation at 1270 K has been stated in the case of Cz-Si:Ge subjected to pre-annealing at 923 K under HP to create nucleation centres for precipitation and next treated at 1270 K under 1.1 GPa. The data in Fig. 3 are based on the assumption that absorption near 1107 cm^{-1} originates from the presence of oxygen interstitials only. Comparing to the effects of HP on oxygen precipitation in Cz-Si, one can state that in Cz-Si:Ge it is distinctly weaker. This is related to numerous nucleation centres present in Cz-Si:Ge from the very beginning because of some non-homogeneity of this material, caused by the non-uniform Ge distribution [6].

The treatment of Cz-Si:Ge at 1070 K under 1.1 GPa resulted in a decreased intensity of the PL lines around 1.1 eV related to the band-band

transitions while the intensity of emission at about 1.08 eV related to electron–hole droplets (EHD) increased with HP. Processing of Cz-Si:Ge at 1270 K results in the modified PL spectrum with the EHD line of the highest intensity, especially in the case of treatment under 1.1 GPa (Fig. 4).

Furthermore, the intensity of the EHD line, especially in relation to that of the FE(TO) line, seems to be much enhanced in the case of processing of Cz-Si:Ge under 1.1 GPa (compare Figs. 4 and 2). This can be considered as an evidence that some non-homogeneities (such as oxygen precipitates) and interfaces are created in Cz-Si:Ge if treated under HP (compare [7]). Some other PL lines at the near 1.1 eV range are of decreased intensity or even disappear (e.g. the NFL line) after the treatment of Cz-Si:Ge at 1270 K under HP (Fig. 4). The effect of HP on oxygen precipitation is most pronounced just at about 1270 K (Fig. 3).

Deconvolution of the asymmetric absorption band at infrared of Cz-Si:Ge treated at 1270 K under 1.1 GPa is presented in Fig. 5.

The **a** and **b** curves present an absorption by SiO_x precipitates while the **c** one, peaking at 1107 cm^{-1} —by oxygen interstitials. Accounting for highly asymmetric shape of the absorption band, one can state that, in fact, the concentration of oxygen interstitials remaining to be present in treated Cz-Si:Ge is for about 25% lower than that presented in Fig. 3. Moreover, if comparing the absorption deconvolution curves for Cz-Si:Ge treated under

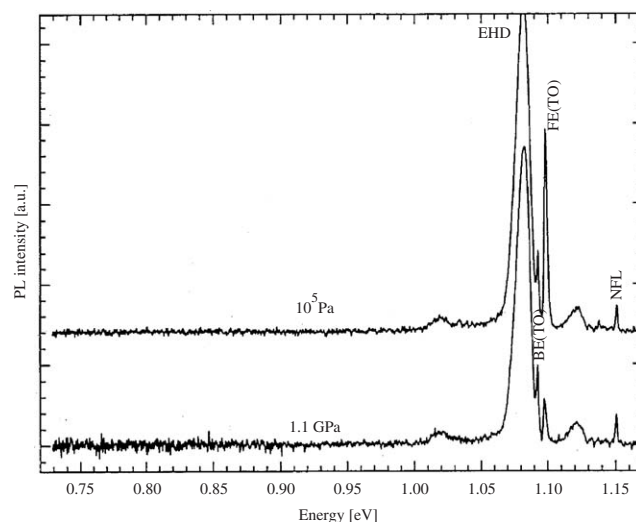


Fig. 2. PL spectra of Cz-Si:Ge processed for 10 h at 723 K under 10^5 Pa and 1.1 GPa. EHD—recombination related to electron–hole droplet; BE (TO) and FE(TO) are related to emissions involving transverse optical phonon replicas of boron bound exciton and of free exciton, respectively; NFL—non-phonon recombination of excitons.

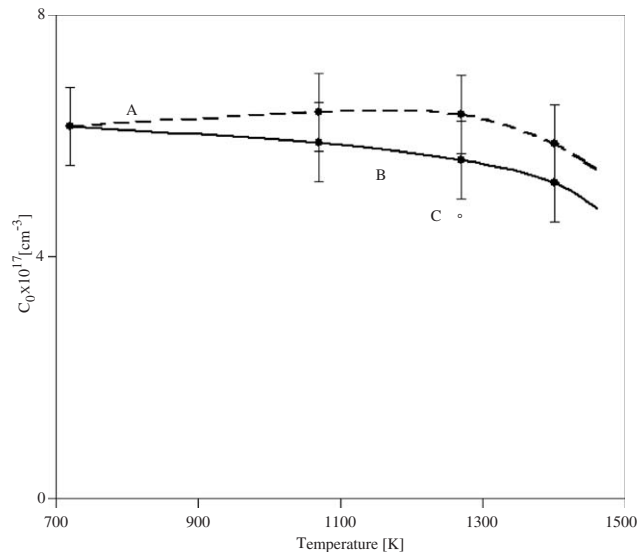


Fig. 3. C_0 versus HT for Cz-Si:Ge processed for 5 h under 10^5 Pa (A) and 1.1 GPa (B); C-Cz-Si:Ge annealed for 10 h at 923 K under 1.1 GPa and treated for 5 h at 1270 K under 1.1 GPa.

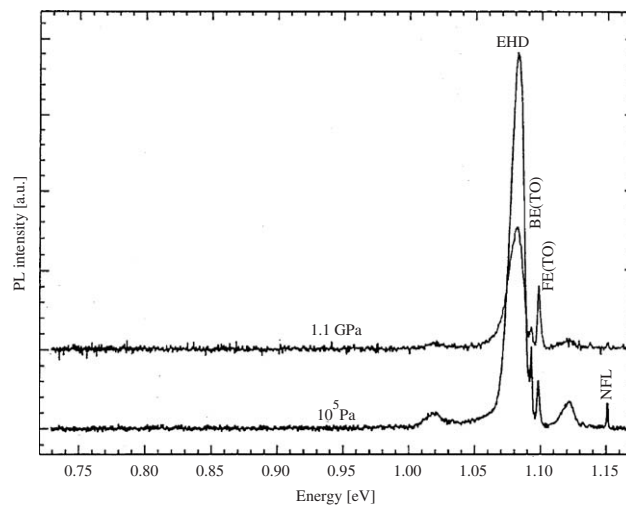


Fig. 4. PL spectra of Cz-Si:Ge processed for 5 h at 1270 K under 10^5 Pa and 1.1 GPa.

1.1 GPa (Fig. 5) with absorption of Cz-Si:Ge annealed under 10^5 Pa (not indicated in the Fig. 5), one can conclude that the composition of SiO_x precipitates is dependent on HP. Absorption peaks at about 1060 cm^{-1} after the treatment under 1.1 GPa while shifts to about 1020 cm^{-1} after annealing under 10^5 Pa, with other processing parameters maintained the same.

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 other PL lines at the 1.1 eV region (Fig. 6, compare Figs. 2 and 4). The absorption band near

1107 cm^{-1} is almost symmetric and its shape is almost nondependent on HP. This means that HP applied at 1400 K affects the composition of SiO_x precipitates to a lesser extent than in the case of processing at lower temperatures. On the other hand, decreased intensities of practically all PL lines near 1.1 eV in Cz-Si:Ge treated under 1.1 GPa confirm the presence of non-radiative recombination centres in a very high concentration. These centres are evidently related to SiO_x agglomerates produced in the highest concentration just in Cz-Si:Ge processed at 1400 K under HP (Fig. 3). The

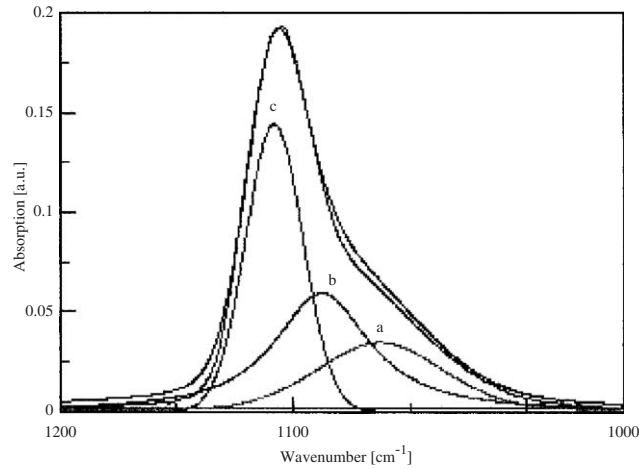


Fig. 5. Deconvolution of absorption for Cz-Si:Ge treated for 5 h at 1270 K under 1.1 GPa.

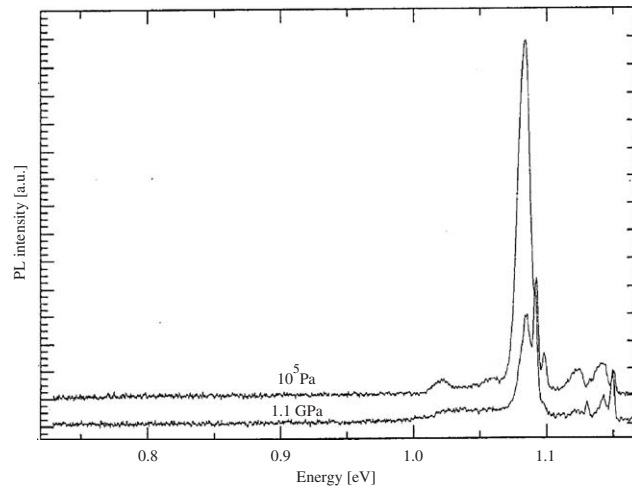


Fig. 6. PL spectra of Cz-Si:Ge processed for 5 h at 1400 K under 10^5 Pa and 1.1 GPa.

decreased concentration of oxygen interstitials in HT–HP treated Cz-Si:Ge indicates that precipitated oxygen interstitials agglomerate and create SiO_x clusters. This agglomeration results in decreased PL intensity.

In respect of interatomic distances in the Si lattice, the presence of Ge results in their dilatation ($a_{\text{Ge}} = 0.566$ nm, $a_{\text{Si}} = 0.543$ nm, so $a_{\text{Si:Ge}} > a_{\text{Si}}$). Contrary to effect of the presence of Ge admixture, the Si lattice is contracted under HP. The Ge concentration in the investigated Cz-Si:Ge samples, equal to about $7 \times 10^{17} \text{ cm}^{-3}$, corresponds to rather low atomic Ge content in Cz-Si:Ge, of about $1.2 \times 10^{-3}\%$. Assuming the Vegard law valid for Si:Ge, relative expansion of the lattice parameter of

Si:Ge caused by the presence of Ge can be estimated as equal to about 5×10^{-7} . It means that the Ge-related expansion of the Si lattice in Cz-Si:Ge can be considered as negligible. On the other hand, HP at the GPa range results in much larger contraction of the Si lattice, of about 0.4% under 1 GPa (other estimation found this contraction about 1% [8]). This quantity is not easy to be determined precisely because of uncertainty of the Si-Ge material parameters at HT–HP.

Still it is clear that the contraction of the Cz-Si:Ge lattice under applied HP (for the case of Cz-Si:Ge investigated) is almost the same as that of Ge-free Cz-Si. It means further that one can expect for Cz-Si:Ge rather the same HP induced changes at

HT as reported for the HT–HP treated Cz-Si (see e.g. [3–5]). In most respects it is just the case, at least as concerns the HP–stimulated creation of TDs, of oxygen precipitation etc.

However, Ge atoms, present in Cz-Si:Ge even at so low concentration ($\approx 10^{-3}$ at%), modify the HP-induced transformations of oxygen considerably. Notice that no dislocations (evidenced e.g. by the strong PL line at about 0.81 eV) were detected in processed Cz-Si:Ge, contrary to these observed usually in HT–HP treated Ge-free Cz-Si [4].

4. Conclusions

In the case of Cz-Si:Ge containing Ge at the $7 \times 10^{17} \text{ cm}^{-3}$ level, being subjected to processing at up to 1400 K under hydrostatic pressure up to above 1.1 GPa, most pressure-induced transformations of the interstitial oxygen are similar as these in similarly treated Ge-free Cz-Si. The presence of Ge in Cz-Si:Ge results, however, in the specific effects observed after the HT–HP treatments, among them:

- non-typical increase of TDs concentration with HP in Cz-Si:Ge treated at 698–748 K (lack of saturation),
- lowered stress-induced oxygen precipitation, and
- restrained creation of extended defects, such as dislocations.

Our findings confirm benefits from Ge doping of Cz-Si, also at conditions of processing under high stress (what is quite usual e.g. in the quantum dots Si–Ge-based structures).

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