Effect of high temperature–pressure on nitrogen-doped Czochralski silicon

2004 J. Phys.: Condens. Matter 16 473

(http://iopscience.iop.org/0953-8984/16/3/023)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 473–481 PII: S0953-8984(04)65811-5

Effect of high temperature–pressure on nitrogen-doped Czochralski silicon

Andrzej Misiuk[1], Barbara Surma[1,2], Deren Yang[3] and Artem Shalimov[4]

[1] Institute of Electron Technology, Aleja Lotnikow 32/46, 02-668 Warsaw, Poland
[2] Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland
[3] State Key Lab of Silicon Materials Science, Zhejiang University, Hangzhou 310027, People's Republic of China
[4] Institute of Physics, PAS, Aleja Lotnikow 32/46, 02-668 Warsaw, Poland

E-mail: misiuk@ite.waw.pl

Received 4 July 2003, in final form 6 November 2003
Published 9 January 2004
Online at stacks.iop.org/JPhysCM/16/473 (DOI: 10.1088/0953-8984/16/3/023)

Abstract
The effects of enhanced hydrostatic pressure (HP, up to 1.2 GPa) on the properties of nitrogen-containing Cz-Si:N (N content $\leqslant 5 \times 10^{14}$ cm^{-3}, interstitial oxygen concentration 9×10^{17} cm^{-3}) and of Czochralski-grown silicon (Cz-Si, reference samples) treated for 5 h at 1070–1570 K–HP have been investigated by photoluminescence, x-ray and infrared absorption methods. HP acts on Cz-Si:N and on Cz-Si in a similar way: oxygen precipitation and creation of numerous cluster-like and extended defects are stimulated, especially at 1230–1400 K. The small cluster-like oxygen-related defects are, however, more numerous in HP treated Cz-Si:N while the extended ones (dislocations) are created at 1230 K in a lowered concentration. A qualitative explanation of the observed effects has been proposed.

1. Introduction

The favourable impact of nitrogen doping on the microstructure and other properties of single crystalline Czochralski-grown silicon (Cz-Si, containing an oxygen admixture mostly in the form of oxygen interstitials, O_i) has motivated interest in applying such nitrogen-containing material (Cz-Si:N) to microelectronics [1]. The presence of nitrogen is known to affect some properties of Cz-Si:N annealed under atmospheric pressure (10^5 Pa). Nitrogen suppresses the creation of microdefects while enhanced oxygen precipitation, especially at $\leqslant$1000 K, as well as the increased activation energy for the creation of dislocations have already been discussed [2, 3]. The creation of thermal donors (TDs) has been reported as being markedly suppressed at 720/920 K [4].

Precipitation and other transformations of an oxygen admixture in Cz-Si annealed at some particular temperature are strongly influenced by the hydrostatic pressure (HP) of the ambient atmosphere, especially at HT (high temperature) above 670 K. This phenomenon is related to the creation under HP of more numerous nucleation sites for oxygen precipitation (NCs); the diffusion rates of oxygen and silicon as well as the misfit at the oxygen-related and other defects/Si matrix boundary are also affected significantly and usually decrease at HP [5].

It is expected that the properties of annealed Cz-Si:N also depend on the HP exerted by the ambient gas, similarly to the case of Cz-Si doped with helium, hydrogen or oxygen [6]. This presumption has been confirmed recently [7]. For example, the treatment of Cz-Si:N with low nitrogen content ($C_N \leqslant 5\times10^{14}$ cm^{-3}) at 720 K–1.2 GPa results in a strongly enhanced electron concentration in the conduction band (while almost no TDs are produced in the same material if annealed under 10^5 Pa). This pressure-stimulated TD creation in Cz-Si:N is practically the same as that detected for nitrogen-free Cz-Si treated under the same conditions. For example, for the mentioned Cz-Si:N samples (with the electron concentration in the conduction band, $N_e = 5.4 \times 10^{15}$ cm^{-3}, and the O_i concentration, $C_O = 9.2 \times 10^{17}$ cm^{-3}) and for nitrogen-free Cz-Si (with $N_e = 7.8 \times 10^{15}$ cm^{-3} and $C_O = 9 \times 10^{17}$ cm^{-3}), the N_e values after the treatment at 720 K–1.2 GPa for 10 h were almost the same, 9×10^{16} and 1.1×10^{17} cm^{-3}, respectively [7].

The effect of HT–HP treatment on the microstructure of low-dose nitrogen-doped Cz-Si is investigated in the present work in more detail.

2. Experimental details

Cz-Si:N samples of about $15 \times 8 \times 0.5$ mm^3 were cut from $\langle 111 \rangle$ oriented wafers prepared from a single crystalline Si rod grown by the Czochralski method in a nitrogen ambient. The nitrogen and oxygen concentrations in Cz-Si:N were $\leqslant 5 \times 10^{14}$ cm^{-3} and $\approx 9 \times 10^{17}$ cm^{-3}, respectively (compare [8]). The Cz-Si:N as well as the reference nitrogen-free Cz-Si samples with the same oxygen content ($C_O \approx 9 \times 10^{17}$ cm^{-3}) were subjected to annealing under 10^5 Pa (mostly for reference reasons) and to the HT–HP treatments [9] at up to 1570 K, under argon HP up to 1.23 GPa, typically for 5 h. To create NCs, some Cz-Si:N and Cz-Si samples were pre-annealed for 10 h at 1000 K under 10^5 Pa.

The properties of annealed/HT–HP treated Cz-Si:N and of reference Cz-Si were investigated by measurements of photoluminescence (PL, at 6 and 14 K, excitation by Ar laser, $\lambda = 488$ nm), Fourier transform infrared absorption (FTIR) and x-ray reciprocal space mapping (XRRSM).

3. Results and discussion

The PL spectra of Cz-Si:N and Cz-Si annealed/HT–HP at 1070, 1230, 1270 and 1400 K are presented in figures 1–3.

Excitonic emission in the near-band-gap region was observed in the most studied samples measured at 6 K (figures 1, 2). This emission is related to the recombination of the boron bound exciton (BE_{TO}) at about 1.088 eV (figure 2) and of the transverse longitudinal optical phonon replica of the free exciton (FE_{TO}) at about 1.095 eV; the PL line at about 1.081 eV is related to the multiexciton complex recombination of the electron–hole droplet (EHD_{TO}). Other PL lines in these spectra are of similar origin [10].

The PL spectra (taken at 6 K) of the Cz-Si:N and reference Cz-Si samples subjected to annealing/treatment at 1070 K are presented in figure 1. The EHD_{TO} line of the highest intensity (especially if compared with that for the reference Cz-Si sample subjected to the same treatment) for the Cz-Si:N sample treated under 1.2 GPa can be considered as evidence of its

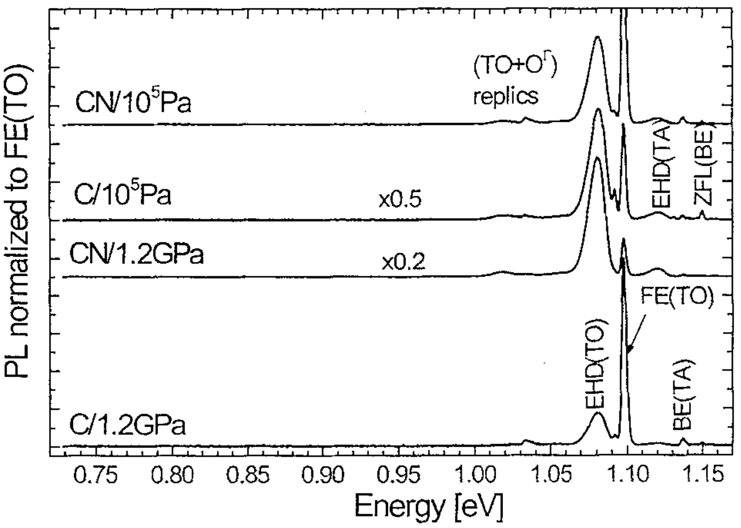

Figure 1. PL spectra of Cz-Si (marked as C) and Cz-Si:N (marked as CN) annealed/treated for 5 h at 1070 K under 10^5 Pa and 1.2 GPa. PL intensity (at 6 K) is normalized to the intensity of the FE(TO) line. Scaling factors (×0.2, ×0.5) are indicated for some spectra.

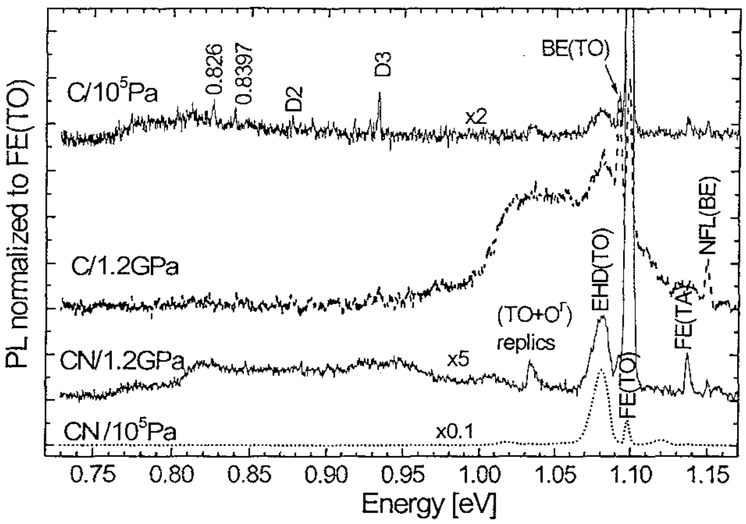

Figure 2. Effect of annealing/HT–HP treatment for 5 h at 1270 K on the PL spectra of Cz-Si (C) and Cz-Si:N (CN) samples. The PL intensity (at 6 K) is normalized to the intensity of the FE(TO) line. Scaling factors (×0.1, ×2, ×5) are indicated for some spectra.

relatively good structural perfection; most probably only small oxygen-containing clusters were created in this HT–HP treated sample (compare [10]).

Annealing of Cz-Si:N at 1270 K–10^5 Pa for 5 h also results in a very high intensity of the EHD_{TO} line, while the similar HT–HP treatment at 1270 K but under 1.2 GPa leads to its lowered intensity (figure 2, observe the magnification factors indicated). While some very weak PL peaks related to the presence of dislocations (such as D2 at 0.87 eV and D3 at 0.94 eV)

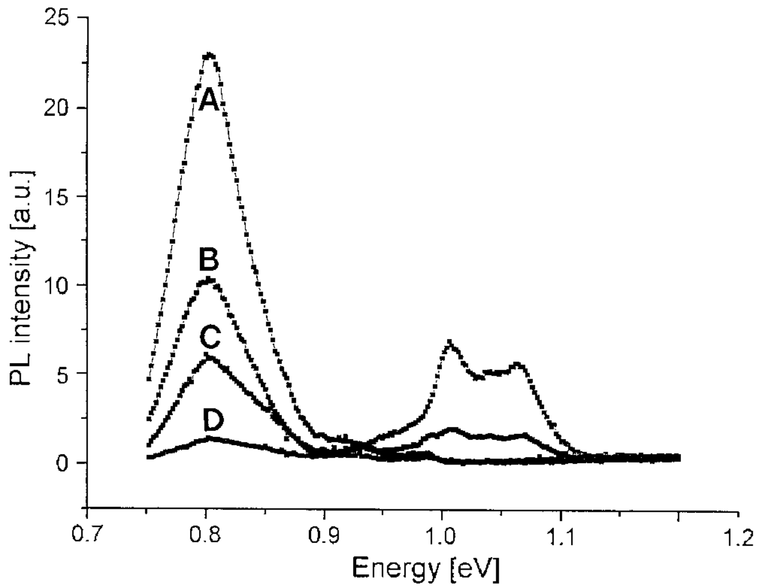

Figure 3. PL spectra (at 14 K, intensity in arbitrary units) of Cz-Si (A and D) and Cz-Si:N (B and C) treated for 5 h at 1230 K (A and B) and at 1400 K (C and D) under 1 GPa.

were observed in the case of Cz-Si annealed at 1270 K–10^5 Pa, they were practically absent in the Cz-Si:N samples annealed/HT–HP treated under these conditions (figure 2).

PL measurements performed at 14 K indicate the presence of extended defects (dislocations, as evidenced by the presence of the D1 PL line at about 0.81 eV) in the Cz-Si:N and reference Cz-Si samples treated at 1230 K–1 GPa (figures 3(A) and (B)). The D1 line was of lowered intensity for Cz-Si:N (figure 3(B)) if compared with that for Cz-Si (figure 3(A)).

The treatment at 1230 K/1270 K–HP resulted in markedly HP-stimulated oxygen precipitation in Cz-Si:N, similarly for the Cz-Si samples (compare full and empty symbols in figure 4). As follows from the XRRSMs, the x-ray diffuse scattering intensity was practically the same for the Cz-Si:N and Cz-Si samples annealed/treated at 1230 K (figures 5(a), (b), (d)). Also the mean defect dimensions (for the defects producing diffusively scattered x-rays), determined from the scattering data in the Huang range [11], were practically the same, equal to about 0.28 μm.

The treatment at 1400 K–HP for 5 h also resulted in the creation of extended defects (dislocations) as evidenced by the D1 PL line detected for the Cz-Si:N and Cz-Si samples (figures 3(C), (D)). The D1 line of Cz-Si was of the lower intensity; this sample also revealed the presence of the D4 dislocation-related line at about 1.0 eV superimposed with some unresolved PL lines at about 1.02–1.08 eV. That last lines (of lower intensity) were also detectable in Cz-Si:N treated at 1400 K–1 GPa (figure 3(C)).

The treatment of Cz-Si:N at 1400 K–HP also resulted in HP-stimulated oxygen precipitation, as in the case of Cz-Si (figure 4).

Pre-annealing of Cz-Si and Cz-Si:N at 1000 K–10^5 Pa for 10 h is known to produce numerous NCs. After the subsequent treatment of such pre-annealed samples at 1230 K–1.1 GPa for 5 h, the oxygen interstitial concentration decreased: $C_O = 7.0 \times 10^{17}$ cm^{-3} for Cz-Si:N and $C_O = 4.2 \times 10^{17}$ cm^{-3} for Cz-Si.

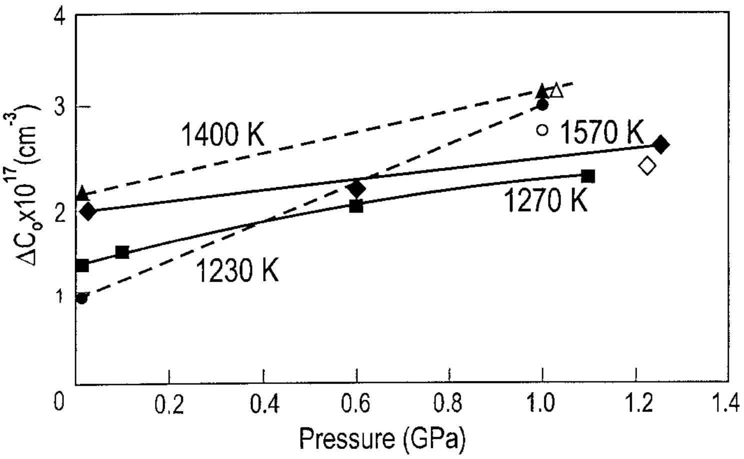

Figure 4. Dependence of interstitial oxygen concentration change, ΔC_O ($\Delta C_O = C_{Oi} - C_{OHT-HP}$, where C_{Oi} and C_{OHT-HP} mean C_O for as-prepared and treated samples, respectively), on HP for Cz-Si:N (full symbols) and reference Cz-Si (empty symbols), HT–HP treated for 5 h. Treatment temperatures are indicated.

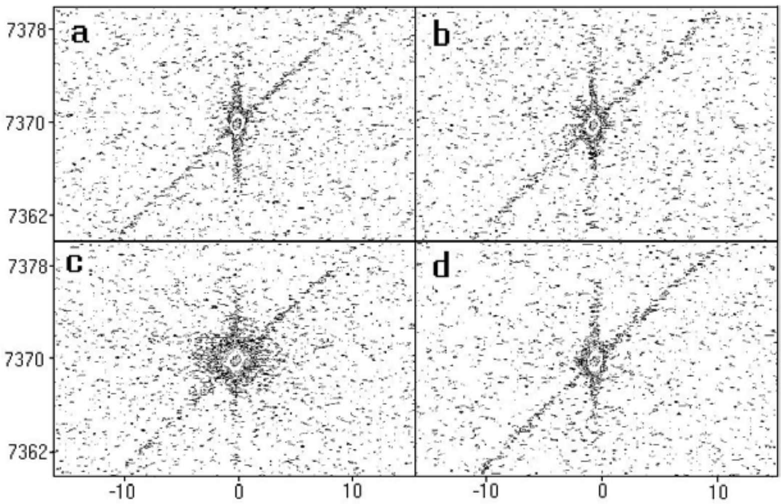

Figure 5. 333 XRRSMs of Cz-Si:N (a)–(c) and of Cz-Si (d) annealed/treated for 5 h at 1230 K under 10^5 Pa (a) and 1 GPa (b)–(d). The XRRSM of Cz-Si:N pre-annealed for 10 h at 1000 K–10^5 Pa is presented in (c). Coordinates are given in $\lambda/2d$ units; λ—wavelength, d—inter-planar distance.

The effect of the treatment at 1230 K–1.1 GPa for 5 h on the PL spectra of these pre-annealed samples is presented in figure 6.

While the D1 line was detected for the Cz-Si sample after the mentioned treatment, practically no PL lines were seen in Cz-Si:N. The most probable explanation of this effect would be to assume that numerous non-radiative recombination centres were created in Cz-Si:N under HT–HP, completely quenching PL in the investigated spectral region. This supposition was confirmed by the XRRSM results (figure 5(c)); the Cz-Si:N sample under consideration indicated the enhanced intensity of diffusively scattered x-rays which demonstrated the

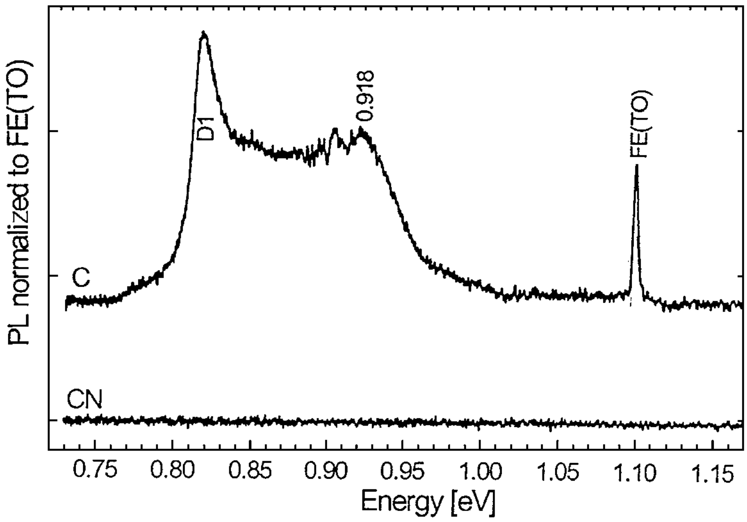

Figure 6. PL spectra of Cz-Si (C) and Cz-Si:N (CN) samples pre-annealed at 1000 K–10^5 Pa for 10 h and subsequently treated for 5 h at 1230 K under 1.1 GPa. PL intensity (at 6 K) is normalized to the intensity of the FE(TO) line.

presence of numerous defects. The mean defect dimension (of the strained areas related to the presence of defects) determined from the scattering data in the Huang range [11], was about 0.46 μm.

The HT–HP treatment at 1570 K, the temperature close to the melting point of Si (of about 1680 K under 10^5 Pa, but decreasing to about 1630 K under HP = 1 GPa) leads to the less marked, but still observable, dependence of the O_i precipitation (as evidenced by HP-dependent ΔC_O) on hydrostatic pressure (figure 4).

It is not clear, however, what the reason is for this effect. All oxygen-containing defects are expected to dissolve in the Si matrix at temperatures close to the Si melting point. So, possibly, the higher ΔC_O value detected for the Cz-Si:N sample treated at 1570 K–1.23 GPa for 5 h, in comparison to that for the sample treated at 1570 K–0.01 GPa, evidences enhanced oxygen precipitation during sample cooling (the cooling time was equal to about 20 min). Similar, but less pronounced, oxygen precipitation was found for the reference Cz-Si sample treated at 1570 K–1.23 GPa (empty symbols in figure 4).

The PL spectra (taken at 14 K) of the Cz-Si:N and Cz-Si samples treated for 5 h at 1570 K–HP are presented in figure 7. No substantial differences between the Cz-Si:N and reference Cz-Si samples were detected. However, the lowered PL intensity (in comparison to those coming from Cz-Si) at about 1.1 eV (unresolved but evidently related to the inter-band transitions) confirms the presence of non-radiative recombination centres in the Cz-Si:N samples subjected to the mentioned treatments.

The HT–HP treatment of Cz-Si:N and Cz-Si at $\leqslant$1400 K results in a strongly HP-dependent oxygen precipitation (most pronounced at about 1400 K, figure 4). This phenomenon is probably related to the HP-stimulated creation of nucleation sites for oxygen precipitation [12]. To some extent the O_i precipitation is also dependent on the presence of nitrogen; the empty symbols in figure 4, corresponding to the oxygen concentration change in Cz-Si treated under the same conditions, are below those observed for the Cz-Si:N samples.

Nitrogen atoms form nitrogen pairs in the silicon lattice. Nitrogen pairs might exist either in interstitial positions forming a N_2 complex or in substitutional sites by capturing

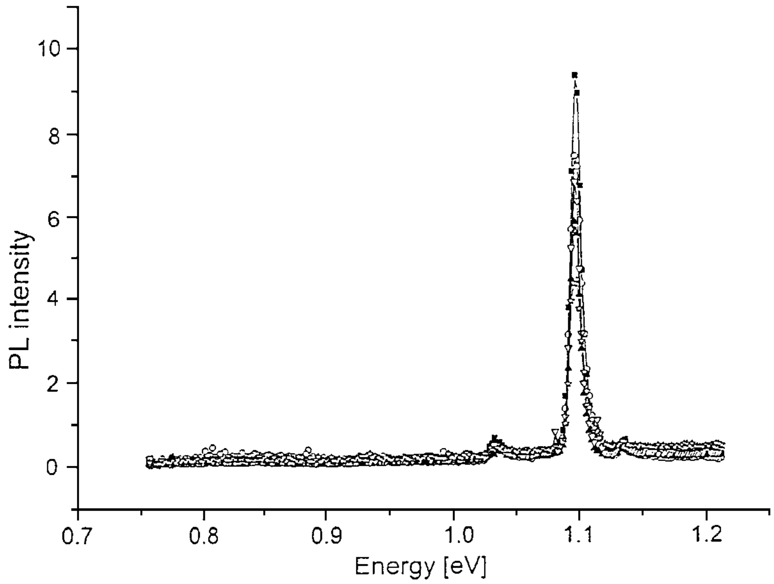

Figure 7. PL spectra (at 14 K, intensity in arbitrary units) of Cz-Si:N (▲, ▽, ✧) and of Cz-Si (■, ○) treated for 5 h at 1570 K: ■, ▲—under 0.01 GPa; ▽—under 0.6 GPa; ○, ✧—under 1.23 GPa.

vacancies (V) to create nitrogen-vacancy complexes (e.g. VN_2 or V_2N_2). The V_2N_2 complex has a strong capability for attracting oxygen thus it can act as a nucleation centre for oxygen precipitation [13].

As it has been derived, the concentration of vacancies in Czochralski-grown silicon increases with external pressure [14]. This means that more nucleation-active V_2N_2 complexes would be formed in Cz-Si:N at HP and so the oxygen precipitation at HT–HP would be enhanced (in comparison to the case of nitrogen-free Cz-Si with the same interstitial oxygen content), owing to the presence of such complexes acting as NCs.

On the other hand, the pressure-induced changes of the concentration of silicon self-interstitials and of vacancies favour the reduction of the critical radius of oxygen-containing clusters in Cz-Si [14]. It is reasonable to assume that enhanced hydrostatic pressure at annealing would also promote the creation of smaller oxygen precipitates in nitrogen-containing Cz-Si:N.

Nitrogen has been reported to react with oxygen at >820 K, creating a nitrogen–oxygen complex [8]. Generation of the grown-in oxide precipitate nuclei, stable above 1070 K in silicon, is enhanced by nitrogen doping [15]. Just as with V_2N_2 and similar complexes (more numerous in Cz-Si:N treated under enhanced pressure), the N–O pairs and as-grown nuclei act at HT–HP as the nucleation sites for oxygen precipitation.

Extended defects (dislocations) are observed in some Cz-Si:N and Cz-Si, HT–HP treated at 1230–1400 K (figures 2, 3, 6). While the effects of the treatment of Cz-Si:N and of Cz-Si at 1230 K–1 GPa are similar (the presence of a strong D1 dislocation-related PL peak at about 0.81 eV), they differ considerably for the samples treated at 1400 K–HP. In that case the D1 line as well as the other, also dislocation-related, D4 line were detected in the Cz-Si:N sample. The D1 line in similarly treated Cz-Si was weaker. This means that the Cz-Si:N samples treated at 1400 K contained dislocations in a higher concentration and/or they contained defects acting as non-radiative recombination centres, but in a lower concentration (as compared to Cz-Si treated at the same conditions).

The PL peaks at the 1.1 eV region (e.g. the BE_{TO} and FE_{TO} lines) correspond to inter-band transitions. Their higher intensities (for the samples annealed at 1230/1400 K–10^5 Pa) can be interpreted as an indication of relatively good overall structural perfection of the samples. As a result of the HT–HP treatment these peaks disappear, evidencing the poorer, treatment-dependent sample perfection.

4. Conclusions

The effects of enhanced hydrostatic pressure (up to 1.2 GPa) at annealing (at up to 1570 K) on some characteristics of nitrogen-containing Czochralski silicon were investigated. The HT–HP effect on Cz-Si:N (with $C_N \leqslant 5 \times 10^{14}$ cm^{-3} and $C_O = 9.2 \times 10^{17}$ cm^{-3}) is similar to that detected for similarly treated nitrogen-free Cz-Si, containing oxygen interstitials in a similar concentration. Still, some marked differences in the properties of HT–HP treated Cz-Si:N and Cz-Si have been found, among them:

- smaller oxygen-related defects (acting as non-radiative recombination centres) are created in Cz-Si:N, especially if pre-annealed to produce NCs;
- contrary to the effects observed at 1230/1270 K–HP, more dislocations are created in the Cz-Si:N samples at 1400 K–HP;
- more oxygen interstitials are removed from the Cz-Si:N lattice than from that of nitrogen-free Cz-Si.

It is worth remembering that, contrary to the case of Cz-Si:N annealed at 10^5 Pa, the rate of creation of TDs (at least of those produced at 720 K) is not suppressed [7] at high pressure (at HP $\geqslant$ 0.6 GPa).

No specific HP related effects were detected for the Cz-Si:N samples HT–HP treated at the highest temperatures–pressures (1570 K–1.23 GPa).

The HT–HP induced effects in Cz-Si:N are most probably related to the HP-stimulated creation of complexes/clusters (also of those ones containing nitrogen, such as N_2V_2), acting as the nucleation centres for oxygen precipitation. Further research is needed to obtain a better understanding of the HT–HP induced effects in nitrogen-doped silicon.

Acknowledgment

The authors are grateful to Dr J Jun from HPRC, PAS, Warsaw, Poland, Dr I V Antonova from the Institute of Semiconductor Physics, RAS, Novosibirsk, Russia, Dr L Bryja from the University of Technology, Wroclaw, Poland as well as Mr T Koska and Mr M Prujszczyk from the Institute of Electron Technology, Warsaw, Poland for performing sample preparation and some measurements and for participating in valuable discussions.

This work was supported in part by the Polish Committee for Scientific Research under grant no 4T08A 034 23 and by the National Natural Science Foundation of the People's Republic of China.

References

[1] Nakai K, Inoue Y, Yokota H, Ikari A, Takshashi J, Tachikawa A, Kitahara K, Ohta Y and Ohashi W 2001 *J. Appl. Phys.* **89** 4301

[2] Yang D, Ma X, Fan R, Zhang J, Li L and Que D 1999 *Physica* B **273/274** 308

[3] Li D, Yang D and Que D 1999 *Physica* B **273/274** 553

[4] Yang D, Fan R, Li L, Que D and Sumino K 1996 *J. Appl. Phys.* **80** 1493

[5] Misiuk A, Surma H B, Jun J, Bak-Misiuk J, Domagala J, Antonova I V, Popov V P, Romano-Rodriguez A and Lopez M 1999 *J. Alloys Compounds* **286** 258

[6] Misiuk A, Bak-Misiuk J, Antonova I V, Raineri V, Romano-Rodriguez A, Bachrouri A, Surma H B, Ratajczak J, Katcki J, Adamczewska J and Neustroev E P 2001 *Comput. Mater. Sci.* **21** 515

[7] Misiuk A, Surma B, Yang D, Que D, Antonova I V, Prujszczyk M, Bryja L and Lukaszewicz M 2001 *Proc. 25th Int. Conf. Exh. IMAPS (Rzeszow University of Technology, Poland, 2001)* p 91

[8] Yu X, Yang D, Ma X, Yang J, Li L and Que D 2002 *J. Appl. Phys.* **92** 188

[9] Misiuk A 2000 *Mater. Phys. Mech.* **1** 119

[10] Nakashima H and Shiraki Y 1981 *Solid State Commun.* **40** 195

[11] Lomov A, Zaumseil P and Winter U 1985 *Acta Crystallogr.* A **41** 223

[12] Misiuk A, Surma B and Hartwig J 1996 *Mater. Sci. Eng.* B **36** 30

[13] Karoui F S, Karoui A, Rozgonyi G A, Hourai M and Sueoka K 2004 *Solid State Phenom.* **95/96** 99

[14] Xu J, Yang D, Li C, Ma X, Que D and Misiuk A 2003 *Mater. Sci. Eng.* B **102** 84

[15] Aihara K, Takeno H, Hayamizu Y, Tamatsuka M and Masui T 2000 *J. Appl. Phys.* **88** 3705