

Optical studies of defects generated in neutron-irradiated Cz-Si during HP-HT treatment

B. Surma^{*1}, A. Misiuk², A. Wnuk¹, C. A. Londos³, and A. Bukowski^{1,4}

¹ Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland

² Institute of Electron Technology, Al. Lotników 32/46, 02-668 Warsaw, Poland

³ Department of Physics, Panepistimiopolis, GR-15784 Zografos, Athens, Greece

⁴ Silicon CEMAT, Wólczyńska 133, 01-919 Warsaw, Poland

Received 16 May 2004, accepted 30 July 2004

Published online 1 March 2005

Key words silicon, irradiation, absorption, photoluminescence, hydrostatic pressure.

PACS 81.10.-h

Neutron-irradiated Czochralski grown silicon subjected to heat treatment (HT) at 350°C and 1000°C under enhanced hydrostatic pressure (HP) was studied in this work. It has been shown that external hydrostatic pressure enhances the creation of VO₂ defects in neutron irradiated silicon subjected to the HP - HT treatment at 350°C. Enhanced formation of platelet-like oxygen precipitates was found in the samples treated at 1000°C under 1.1 GPa. This effect was more pronounced in the samples with VO₂ defects. Presented results seem to suggest that probably HP helps to transform VO₂ to some kind of defects or change alone VO₂ defects in the form that can act as an additional nucleus for an additional oxygen precipitation at 1000°C. No correlation between the plate-like oxygen precipitates related absorption at 1225 cm⁻¹ and dislocation-related emission has been confirmed.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Oxygen is a common residual impurity in silicon grown by Czochralski method (Cz-Si). It occupies an interstitial position (O_i) in silicon lattice and its concentration, [O_i], determined from the intensity of the absorption band at 1107 cm⁻¹ related to stretching vibration mode of Si-O bond can reach >2*10¹⁸ atom / cm³. During heat treatment (HT) oxygen atoms agglomerate in form of different in size, kind and shape precipitates [for review see 1]. Recent publication [2] suggests that precipitation of oxygen can follow different paths depending on the kind of grown-in nuclei created during pre-annealing or introduced by any other method e.g. after irradiation [3] or quenching [4] and still the phenomenon is not fully cleared up. A small globular precipitates was observed at temperature T ≥ 500°C after long time annealing [5]. In the temperature range 650°C - 1050°C the plate-like or spherical [2, 5-9] and from 950°C to 1200°C polyhedrons-like (mainly octahedral in shape) [2, 5, 7, 8] oxygen precipitates are created. It has been stated that they are a form of amorphous silica SiO_{2-x} with x ~ 1.1-1.2 [10].

The presence of precipitates can be monitored by IR absorption spectra in 1250 - 1000 cm⁻¹ spectral range where the new absorption bands appear. At present it is commonly accepted that observed IR absorption band at 1220 - 1225 cm⁻¹ is related to the disc-shaped precipitates [3 - 10] and moves to 1100 - 1120 cm⁻¹ when their shapes became more and more spherical [10]. The presence of spherical precipitates created after annealing at 950°C preceded with two-step pre-annealing giving rise to the absorption band at 1070 cm⁻¹ was reported [2]. According to the calculations based on effective medium theory [6], considering the sample as homogenous dispersion of disk-shaped SiO_x particles in silicon, it has been shown that the shift in the absorption band position from ~ 1230 cm⁻¹ to ~ 1120 cm⁻¹ can be related to the existence of platelet-like precipitates composed of such substoichiometric oxides. For the spherical precipitates the maximum of absorption band moves below

* Corresponding author: e-mail: surma_b@sp.itme.edu.pl

1100 cm^{-1} . Although this problem still leaves open questions to be solved the absorption bands appearing on the high energetic side of 1107 cm^{-1} band (HEA) are generally observed when platelet-like oxygen precipitates are present while an additional absorption on the low-energetic side (LEA) is observed when the spherical - or polyhedron-like precipitates are created.

In silicon irradiated with high-energy neutrons or electrons a huge number of lattice defects such as vacancies and interstitials. Vacancies easily interact with oxygen atoms creating VO, VO₂ and other V_nO_m defects [11,12,13]. Thus additional processes for the capturing of oxygen atoms are possible. It has been shown [14] that the formation kinetics of the thermal donors (TDDs), being the smallest oxygen aggregates, in electron-irradiated materials is the same as that in standard Cz-Si and, hence, the [V-O] defects should be ruled out as the “core” of TDDs, while enhanced oxygen precipitation in neutron-irradiated silicon was observed [15]. The aim of this work was to study deeper this problem. Applying hydrostatic pressure (HP) during annealing one can additionally influence the interaction between the defects, which can be useful in the interpretation of the experimental results [15,16].

2 Experimental details

(100)-oriented p-type (in what follows denoted as T1) and (111) oriented n-type (denoted as S) 2 mm thick Czochralski grown silicon (Cz-Si) samples of 10x6x2mm³ dimensions were used in this study. The interstitial oxygen [O_i] and substitutional carbon [C_s] concentrations were determined from the intensity of IR absorption bands at 1107 cm^{-1} and 605 cm^{-1} , respectively. Concentration of carbon was below the detection limit ($< 2 \cdot 10^{16}$ at / cm^3 at 300 K) for the both studied sample types. Concentration of oxygen was determined by making use of the $3.14 \cdot 10^{17}$ at / cm^2 calibration factor; it was equal to $1.19 \cdot 10^{18}$ at / cm^3 and $1.24 \cdot 10^{18}$ at / cm^3 for the T1 and S samples, respectively. Some T1 and wafer S samples were irradiated with 5 MeV neutrons at room temperature to a dose of $1 \cdot 10^{17}$ n/ cm^2 (in what follows such samples are denoted as NT1) or to a dose of $5 \cdot 10^{16}$ n/ cm^2 (samples S4 and S8). The S samples were subjected to pre-treatment at 350°C for 1.5 h under atmospheric pressure (sample S8) or external argon hydrostatic pressure (HP) of 1GPa (sample S4). Then all T1, NT1 and S samples were subjected to the annealing at 1000°C under atmospheric pressure (10^5 Pa) or to the treatment also at 1000°C but under external argon hydrostatic pressure of 0.01 GPa and 1.1 GPa. Next the surface oxide was removed in HF acid.

Following the HP – HT treatment, infrared (IR) absorption and photoluminescence measurements were performed. IR measurements were carried out at 300 K with a resolution 4 cm^{-1} over a spectral range of 1500 cm^{-1} – 400 cm^{-1} with an aid of Bruker IFS 113v Fourier Transform Infrared Spectrometer (FTIR). The amount of precipitated oxygen $\Delta[\text{O}_i]$ was calculated as a difference between the [O_i] concentrations in the initial material (reference sample) and the treated one (Table 1).

The PL measurements were performed at 6 K by pumping with the 488 nm line of Ar⁺ laser. In order to compare the PL intensities from various samples, all PL spectra were normalized to the intensity of transverse optical phonon-assisted free exciton emission, FE(TO). In all below presented figures, the PL and IR spectra were vertically shifted for clarity. A magnification indicator (e.g. x 0.1) means that the presented spectrum is ten times decreased compared to the measured one.

Table 1 Parameters of studied samples.

Sample	Irradiation dose n / cm^2	Pre-annealing	Temperature /pressure / time during HP – HT treatment	[O] $\times 10^{17}$ at / cm^3	$\Delta\text{O}\times 10^{17}$ at / cm^3
T1 initial	-	-	-	11.9-11.0	-
T1	-	-	1000°C/0.1MPa/5h	11.8	-
T1	-	-	1000°C/1.1GPa/5h	9.5	1.5-2.4
NT1	1×10^{17}	-	1000°C/0.1MPa/5h	9.7	1.3-2.2
NT1	1×10^{17}	-	1000°C/1.1GPa/5h	4.5	6.5-7.4
S initial	-	-	-	12.4	-
S as irradiated	5×10^{16}	-	-	11.9	0.5
S4	5×10^{16}	350°C/1GPa/1.5h	1000°C/1.1GPa/5h	3.1	9.3
S8	5×10^{16}	350/10MPa/1.5h	1000°C/1.1GPa/5h	3.1	9.3

3 Results and discussion

The IR spectra in the range between 900 cm^{-1} and 1350 cm^{-1} are shown in Fig. 1 for the initial samples and for these ones HP-HT treated at 1000°C . The band with a maximum at 1107 cm^{-1} dominates in the spectra. It is related to the asymmetric stretching vibrational mode of oxygen atom occupying interstitial positions in the silicon lattice [17].

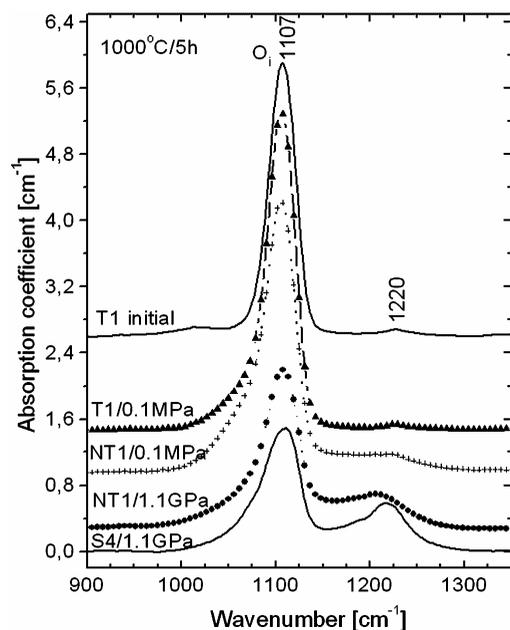


Fig. 1 Oxygen-related IR absorption spectra at 300K for neutron-irradiated and unirradiated samples subjected to different HP-HT treatment at 1000°C for 5 h. For comparison the absorption for an initial material is also shown.

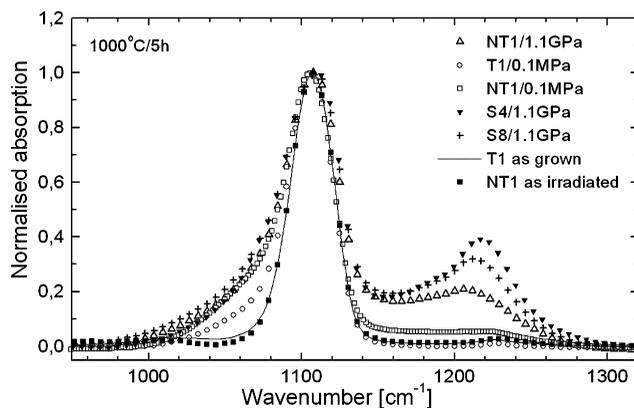


Fig. 2 Precipitation-related IR absorption spectra normalised to the intensity of 1107 cm^{-1} band for neutron-irradiated and unirradiated silicon samples subjected to different HP-HT treatments.

Its intensity was used to evaluate the oxygen concentration $[\text{O}_i]$. During HP-HT treatment, due to the agglomeration process of oxygen atoms, a band with well marked maximum between 1218 cm^{-1} and 1225 cm^{-1} appeared. Simultaneously a decrease of oxygen occupying an interstitial position as well as significant widening of the 1107 cm^{-1} band were observed.

The absorption spectra normalised to their maximum at around 1107 cm^{-1} are presented in Fig.2. Such a kind of presentation allows for the comparing of 1107 cm^{-1} band shapes for all studied samples. One can see that, except the absorption band at $\sim 1220\text{ cm}^{-1}$, an additional absorption on the low energy side of the 1107 cm^{-1} band appears. Its intensity depends on the HP-HT treatment parameters.

To estimate the amount of oxygen atoms precipitated during the HP - HT treatment it was necessary to deconvolute the obtained absorption spectra. It is known that the full width at half maximum (FWHM) of the 1107 cm^{-1} band at room temperature equals to 32 cm^{-1} [18]. After the HP - HT treatment, its value increased up to $40 - 50\text{ cm}^{-1}$. It can originate from the imperfections introduced into the silicon lattice by neutron irradiation or due to overlapping with the appearance of the new absorption related to the oxygen precipitation process. To solve this problem we have measured the absorption in the as irradiated silicon where the disturbance of the silicon lattice is relatively high; no increase of FWHM has been stated (see Fig. 2). For this reason we have assumed that the widening of the 1107 cm^{-1} band is due to the overlapping with an appearance of an additional absorption and so the deconvolution was done with an assumption that FWHM of the band related to the presence of O_i has not changed during the HP-HT treatment. A Gaussian shape of the absorption bands has been also assumed, what is commonly accepted when the randomly spread deviations are taken into consideration [2].

Deconvolution of absorption originating from the S4 sample is shown in Fig. 3. In all HP-HT treated samples the best fit to the experimentally measured absorption in the 900 cm^{-1} and 1350 cm^{-1} spectral range

was obtained by deconvolution into six absorption bands with the maxima at 1220 – 1225 cm^{-1} , 1156 – 1160 cm^{-1} , 1120 cm^{-1} , 1107 cm^{-1} , 1070 – 1080 cm^{-1} , and at 1050 - 1060 cm^{-1} , respectively. As it has been mentioned in the introduction, the features of absorption are related to oxygen precipitates; the bands at 1120 cm^{-1} , 1160 cm^{-1} and 1225 cm^{-1} mean the presence of platelet-like precipitates that can differ in their shape from more spherical to disk, respectively. This absorption is denominated by us as the high-energy absorption (HEA). The bands on the low energy side of the 1107 cm^{-1} absorption indicate on creation of the spherical and polyhedron-like precipitates of amorphous silica. This absorption is denominated as low energy absorption (LEA).

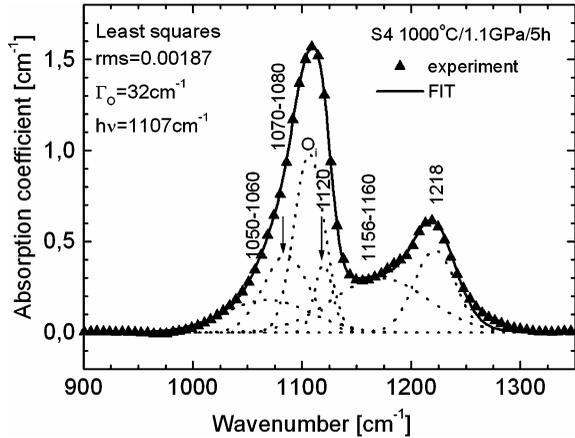


Fig. 3 Hypothetical deconvolution of IR absorption spectra related to O_i and oxygen precipitates for sample S4.

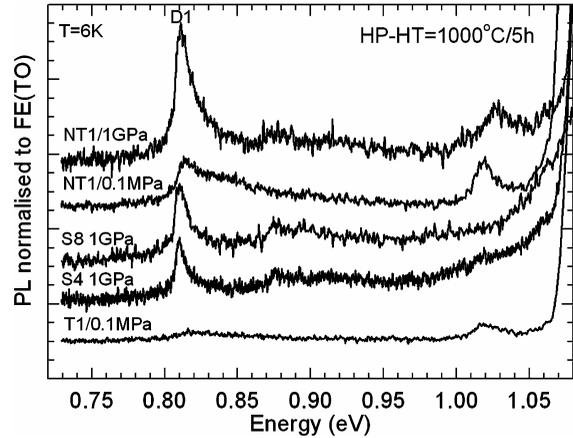


Fig. 4 Dislocation-related photoluminescence spectra at 6 K for neutron-irradiated and unirradiated samples subjected to different HP-HT treatment at 1000°C for 5 h.

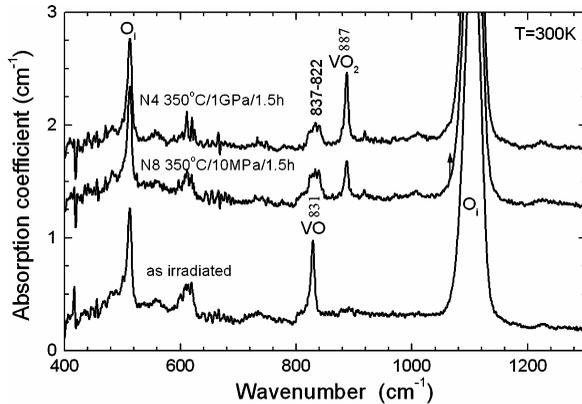


Fig. 5 IR absorption spectra at 300 K for S4 and S8 samples subjected to pre-annealing at 350°C for 1.5 h and for as-irradiated sample.

It has been shown [19] that compressive and tensile stress fields up to 240 MPa exist around the platelet-like oxygen precipitates. During further growing of the precipitates when the strain exceeds its critical value they are relaxed and Si atoms are pushed into silicon lattice. They agglomerate in form of intrinsic defects among which dislocations play significant role [20 21].

Defect-related emission for HP - HT treated samples is shown in Fig. 4. The so-called D1 line at 0.81 eV is related to the presence of dislocations as observed for heat treated Cz-Si [21]; it dominates in the PL spectra in all studied samples, while its intensity depends on the HP-HT treatment conditions. Only very weak photoluminescence related to the presence of dislocations was observed for the T1 sample treated under 0.1 MPa (Fig. 4). This coincides with significantly lower LEA absorption in this sample (Fig. 2). More intensive LEA absorption observed for the NT1 sample, HP - HT treated under 1.1 GPa or 0.1MPa (Fig. 2) results in the much stronger D1 emission (Fig. 4). However, in the second case D1 band was much wider, meaning the higher spread of energetic levels, but the integrated emission of D1 PL band in both NT1 samples was almost the same. On the other hand one can also easily notice that the D1 emission does not correspond to the total amount of precipitated oxygen atoms in these samples. In the NT1 sample annealed under atmospheric

pressure ΔO_i was three times lower than that one in the NT1 HP treated under 1.1 GPa. Simultaneously in the NT1 sample treated under 1.1 GPa much stronger HEA absorption confirming the existence of the unrelaxed platelet-like defects was observed (Fig. 2).

To clear more up this behaviour, the irradiated S4 and S8 samples was pre-annealed at 350°C for 1.5 h. During such an annealing the VO defects that are already created in as irradiated material easy join, movable at this temperature, an additional oxygen atoms creating VO₂. In general version V_nO_m defects are created. The presence of these defects can be easily recognised due to their characteristic local vibration modes giving rise to the absorption bands: VO at 831 cm⁻¹, VO₂ at 887 cm⁻¹ and V_nO_m at 827–834 cm⁻¹ [11,12,13]. Absorption between 400 cm⁻¹ and 1350 cm⁻¹ for the as-irradiated sample (the defect-related spectra were the same for the samples from NT1 and S wafers) and of the S4 and S8 samples after pre-treatment is shown in Fig. 5. Only VO defect was detected in the absorption spectrum for as-irradiated samples. After the pre-treatment at 350°C for 1.5 h, absorption originating from VO₂ defects as well as the broad band between 822 cm⁻¹ and 837 cm⁻¹ have been observed.

The latter one originates probably from superposition of the absorption bands from V_nO_m defects and, partly, from residual VO defects. One can easily notice that hydrostatic pressure stimulates creation of the VO₂ defects. For both S4 and S8 samples after HP-HT treatment at 1000°C for 5h under 1.1 GPa (Fig. 2), a distinct absorption band with maximum at ~ 1220 cm⁻¹ was observed (Fig. 2). The most intensive absorption band at ~ 1220 cm⁻¹ was observed for S4 sample for which the VO₂-related absorption was the strongest and the largest amount of oxygen atoms have precipitated (Table 1). For the NT1 sample, HP-HT treated at 1000°C for 5 h under 1.1 GPa, where only the VO defects were present before the HP-HT treatment (Fig. 5), the intensity of 1225 cm⁻¹ band is markedly lower but anyway significantly higher than that one in the NT1 sample treated under atmospheric pressure. Enhanced HEA is also observed for the NT1 sample if compared with that one for the T1 sample treated under atmospheric pressure (Fig. 1). This effect is, however, much less pronounced.

Presented results have shown that oxygen precipitation process at 1000°C is significantly enhanced when VO₂ defects are present in the starting material and this effect is strongly simulated by hydrostatic pressure. Up to now there is no any evidence for the stability of VO₂ defects at so high temperature during annealing at atmospheric pressure. There are also missing any results regarding the role of the hydrostatic pressure on their stability at high temperature. But presented results seem to suggest that may be HP helps to transform VO₂ to some kind of defects or change alone VO₂ defects in the form that can act as an additional nucleus for an additional oxygen precipitation at 1000°C. The results presented for NT1 sample HP treated under 1.1 GPa have shown that HP helps to create similar kind of defects also in as-irradiated sample (where only VO defects were present). Anyway the stability of VO₂ defects during treatment under hydrostatic pressure is under study.

Presented results have also shown that treatment under an external hydrostatic pressure favour the creation of the platelet-like oxygen precipitates. This is in the agreement with the theoretical analysing done in [22]. When the ratio of surface energy to strain energy exceeds critical value that is proportional to P²/R where P is pressure inside the strained precipitate, and R is precipitate radius, the sum of the two energies is reduced only when flattening of spherical particle into platelet occurs. The chemical potential of host atoms changes along precipitate/matrix interface depends on the curvature, the strain energy field and strained volume of the matrix around precipitate. When the critical value of the ratio is exceeded the transport of silicon atoms through the oxide toward more curvature part of the precipitate becomes essential. This part of the interface moves outwardly and the precipitates become more platelet-like in shape. Thus under an additional external compressive pressure transformation of the precipitate shape into platelet-like should start for smaller precipitates radius and platelet-like precipitates should be created in higher number.

4 Conclusions

From above presented results it follows that:

- enhanced hydrostatic pressure stimulates the creation of VO₂ defects in neutron irradiated silicon subjected to the HP-HT treatment at 350°C;
- Treatment under external hydrostatic pressure helps to transform VO₂ to some kind of defects or change alone VO₂ defects in the form that can act as an additional nucleus for an additional oxygen precipitation at 1000°C.
- Creation of the platelet-like in shape oxygen precipitates is favourable during HP-HT treatment at 1000°C under 1.1 GPa. This is in an agreement with the theoretical analysing of the evolution of the oxygen precipitates shape extracted by the compressive strain field [22].

References

- [1] F. Shimura (Ed.), Oxygen in Silicon, Semiconductors & Semimetals **Vol. 42**, Academic Press. Inc., 1994.
- [2] C. Maddalon-Vinante, J. P. Vallard, and D. Barbier, *J. Electrochem. Soc.* **142**, 2071 (1995).
- [3] T. Hallberg, J. Lemmart, and J. L. Lindström, *J. Appl. Phys.* **72**, 5130 (1992).
- [4] A. Hara, T. Fukuda, T. Miyabo, and I. Hirai, *J. Appl. Phys.* **66**, 3958 (1989).
- [5] P. Goworzewski, E. Hild, F. G. Kirscht, and L. Vecsernyes, *Phys. Stat. Sol. (a)* **133**, 133 (1984).
- [6] S. M. Hu, *J. Appl. Phys.* **5**, 5945 (1980).
- [7] K. Sueoka, N. Ikeda, T. Yamamoto, and S. Kobayashi, *J. Appl. Phys.* **74**, 5437 (1993).
- [8] Ch. Y. Kung, *J. Appl. Phys.* **65**, 4654 (1989).
- [9] C. Veve, M. Stemmer, and S. Martinuzzi, *Mat. & Sci. Eng.* **B36**, 200 (1996).
- [10] O. de Gryse, P. Clauws, O. Lebedev, J. Van Landuyt, J. Vanhellefont, C. Claeys, and E. Simoen, *Physica B*, **308–310** 294 (2001).
- [11] B. Svenson, J. L. Lindström, *Phys. Rev.* **B34**, 8709 (1986).
- [12] L. A. Buyanova, B. Monemar, J. L. Lindström, T. Halberg, L. I. Murin, and V. P. Markevich, *Mater. Sci. Eng.* **B72**, 146 (2000).
- [13] L. G. Frytos, G. J. Georgiu, C. A. Londos, and V. V. Emtsev, *Physica B*, **273–274**, 312 (1999).
- [14] J. Svensson, B. G. Svensson, and J. L. Lindström, *Appl. Phys. Lett.* **21**, 1435 (1986).
- [15] B. Surma, C. A. Londos, V. V. Emtsev, A. Misiuk, A. Bukowski, and M. S. Potsidi, *Mat. Sci. Eng.* **B102**, 339 (2003).
- [16] B. Surma, L. Bryja, A. Misiuk, G. Gawlik, J. Jun, I. V. Antonova, and M. Pruszczyk, *Cryst. Res. Technol.* **8–10**, 943 (2001).
- [17] T. J. Shaffner and D. K. Schroder, in Ref. [1]; Chapter 3, p.55.
- [18] W. M. Bullis, in Ref. [1], Chapter 4, p. 133.
- [19] T. Okuyama, M. Nakayama, S. Saidamitsu, J. Nakashima, and Y. Tomokiyo, *Jpn. J. Appl. Phys.* **36**, 3359 (1997).
- [20] W. Bergholz, in Ref. [1], Chapter 12, p.513.
- [21] S. Binetti, S. Pizzini, E. Leoni, R. Somascini, A. Castaldini, and A. Cavallini, *Solid State Phenom.* **82–84**, 75 (2002).
- [22] V. V. Voronkov, R. Flaster, *Solid State Phenom.* **82–84**, 121 (2002).