Solid State Phenomena Vols. 108-109 (2005) pp. 267-272
online at http://www.scientific.net
© (2005) Trans Tech Publications, Switzerland

VO_n (n≥3) Defects in Irradiated and Heat-Treated Silicon

L.I. Murin[1,a], J.L. Lindström[2,b], B.G. Svensson[3,c]
V.P. Markevich[1,4,d], A.R. Peaker[4,d] and C.A. Londos[5,e]

[1]Institute of Solid State and Semiconductor Physics, Minsk, Belarus
[2]Lund University, Division of Solid State Physics, Lund, Sweden
[3]Oslo University, Physics Department/Centre for Materials Science and Nanotechnology, Norway
[4]Centre for Electronic Materials, University of Manchester, Manchester M60 1QD, UK
[5]Physics Department, Athens University, Athens, Greece
[a]murin@ifttp.bas-net.by, [b]Lennart.Lindstrom@ftf.lth.se, [c]b.g.svensson@fys.uio.no
[d]v.markevich@manchester.ac.uk, [d]peaker@manchester.ac.uk, [e]hlontos@phys.uoa.gr

Key Words: Silicon, oxygen, vacancy, vibrational modes.

Abstract. Local vibrational mode (LVM) spectroscopy has been used to study the evolution of vacancy-oxygen-related defects (VO_n) in the temperature range 300-700°C in carbon-lean Cz-Si samples irradiated with MeV electrons or neutrons. New experimental data confirming an attribution of the absorption bands at 910, 976 and 1105 cm^{-1} to the VO_3 complex are obtained. In particular, a correlated generation of VO_3 and the oxygen trimer is observed upon irradiation of Cz-Si crystals in the temperature range 300-400°C. Strong evidence for the assignment of the bands at 991 and 1014 cm^{-1} to a VO_4 defect is presented. The lines are found to develop very efficiently in the VO_2 containing materials enriched with the oxygen dimer. In such materials the formation of VO_4 is enhanced due to occurrence of the reaction $O_{2i}+VO_2 \Rightarrow VO_4$. Annealing of the VO_3 and VO_4 defects at T ≥ 550C °C is found to result in the appearance of new defects giving rise to a number of O-related LVM bands in the range 990-1110 cm^{-1}. These bands are suggested to arise from VO_5 and/or VO_6 defects. Similar bands also appear upon the annihilation of oxygen-related thermal double donors at 650°C in Cz-Si crystals pre-annealed at 450°C.

Introduction

Pre-irradiation of Cz-Si is known to result in enhanced oxygen precipitation at temperatures above 600°C [1, 2]. It has been suggested that some vacancy-oxygen-related defects induced by irradiation and subsequent annealing can be responsible for the enhancement effect. In recent models of oxygen precipitate nucleation at elevated temperatures, a key role of the VO_n complexes in the early stages of oxygen precipitation has been proposed [3,4] However, very little information on the origin of such defects stable at about 600°C or higher temperatures is available.

Among these VO_n complexes only the simplest ones, the VO (A-centre) and VO_2 defects have been investigated in detail [5-12]. The A-center is the dominant defect in CZ silicon after MeV-electron irradiation. It can be observed using local vibrational mode (LVM) spectroscopy in two charge states, a neutral one and a negative one. The LVM for the neutral state, which occurs usually in Cz-Si sample irradiated for IR absorption studies, is at 836 cm^{-1} in spectra measured at low temperatures (LT, ≤ 20 K) and is at about 830 cm^{-1} at room temperature (RT). During annealing around 300°C the VO center starts to disappear and a new complex, VO_2, is formed. In the ground state this complex gives rise to only one LVM at 889 cm^{-1} (RT) or 895.5 cm^{-1} (LT). Recently [13,14], the bistability of VO_2 has been revealed and a pair of LVMs at 928 and 1004 cm^{-1} (LT) has been assigned to a metastable state, called as VO_2*.

After annealing at 450-500°C the band at 889 cm^{-1} disappears and four new LVM bands positioned at 910, 976, 1105 and 991 cm^{-1} (LT) or 905, 969, 1000 and 985 cm^{-1} (RT) appear [7,9]. It has been suggested [7] that the first three bands arise from a VO_3 complex, and some additional

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of the publisher: Trans Tech Publications Ltd, Switzerland, www.ttp.net. (ID: 195.134.94.101-17/09/07,11:41:57)

experimental [9] and theoretical [10] confirmations of such an assignment have been found later. It is suggested the VO_3 are formed when diffusing single oxygen atoms are trapped by VO_2 [7,9] or alternatively, VO_2 is mobile and interacts with interstitial oxygen atoms [7,13]. There were, however, some doubts in the assignment of all three bands to the VO_3 defect since the formation and annealing behaviour of the third band (at 1000 cm^{-1}) were found to be slightly different from those of the first two bands. In addition, the intensity of the latter band was always substantially lower as compared with that of the first two bands.

The identification of the band located at 985 cm^{-1} is even less certain. This band appears in the spectra with some delay relative to the three bands of VO_3 and has been suggested to arise from the VO_4 defect which is formed when diffusing O_i atoms are captured by VO_3 defects. Evidently, the VO_4 defect even being in the symmetrical configuration [15,16] should give rise at least to two oxygen-related vibrational bands. However, the second band possibly related to VO_4 and located at 1014 cm^{-1} has been detected only in oxygen implanted silicon [17] and has not been observed in electron or neutron irradiated samples. In this paper we present new experimental data confirming a previous identification of the VO_3 and VO_4 related LVMs and report about a new set of absorption bands appearing upon the VO_3 and VO_4 annihilation.

Experimental details

The samples used in this investigation were prepared from n-type commercial Cz-Si crystals (ρ = 10-50 Ω-cm, $[O_i] = (0.8\text{-}1.3)\text{x}10^{18}$ cm^{-3}) with low ($[C_s] \leq 1\text{x}10^{15}$ cm^{-3}) and intermediate ($[C_s] = (5.0\text{-}50)\text{x}10^{15}$ cm^{-3}) content of carbon. The concentrations of O_i and C_s were determined from measurements of intensities of absorption bands at 1107 and 605 cm^{-1} using the calibration coefficients 3.14×10^{17} and 0.94×10^{17} cm^{-2}, respectively [18]. The samples were polished to an optical surface on two sides and the dimensions were 10×5×3 mm^3. Some of the samples were enriched with oxygen-dimers and trimers by "hot-irradiation" at about 350 °C [18]. Another set of the samples was enriched with thermal double donors (TDDs) by heat-treatment at 450°C. The samples were irradiated with fast electrons (E = 2 and 10 MeV) or neutrons (E = 5 MeV) at room temperature. Isochronal as well as isothermal annealing studies have been carried out in the temperature range 100-700°C. IR absorption analysis was carried out using a Bruker IFS 113v spectrometer. A spectral resolution of 0.5-1.0 cm^{-1} was used and the samples were measured at 20 and 300 K.

Experimental results and discussion

VO_3 defects. One of the possible mechanisms of the VO_3 formation is an interaction of free vacancies with the oxygen trimers. Normally the content of oxygen trimers in Cz-Si crystals is rather low, much less than 0.1% of that of interstitial oxygen. However, in samples subjected to electron irradiation at elevated temperatures concentration of oxygen trimers can be increased substantially along with the oxygen dimer content. When analyzing the spectra for samples irradiated at 300-400°C we have noted that intensities of the bands assigned to VO_3 always correlate with those of the oxygen trimer related bands. As an example, Fig. 1 shows absorption spectra of Cz-Si samples irradiated with 2 MeV electrons at 320°C and at 350°C. In the first case only weak traces of the bands related to VO_3 and O_{3i} defects can be seen. In the case of irradiation at 350°C when more oxygen trimers are generated due to interaction of mobile oxygen dimers with O_i atoms the bands assigned to VO_3 are much more stronger.

Another striking example of a close connection between the VO_3 and O_{3i} defects is a recent observation of the VO_3 transformation into O_{3i} defects upon room temperature irradiation of samples previously enriched with VO_3 defects [19]. Apparently, in this case an interaction of Si self-interstitials with VO_3 occurs, resulting in the appearance of O_{3i}.

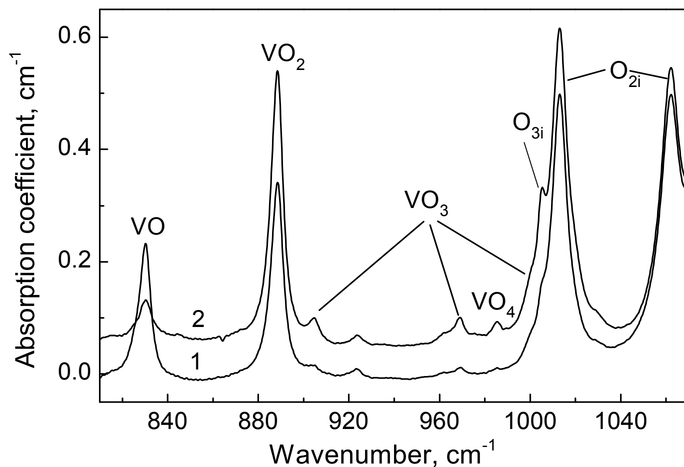


Fig. 1. Fragments of absorption spectra measured at RT for Cz-Si samples ([O_i] = 1.3×10^{18}, [C_s] $\leq 1\times10^{15}$, [P] = 7×10^{13} cm^{-3}) irradiated with 2.5 MeV electrons for a dose $4\cdot10^{18}$ cm^{-2} at 320°C (spectrum 1) and at 350°C (spectrum 2).

The recent discovery of the bistability of VO_2 allows us to explain some deviations observed earlier in the formation and annealing behavior of the VO_3 band at 1000 cm^{-1} from that of the bands at 905 and 969 cm^{-1}. The position of this band practically coincides with the position of one of the bands arising from a metastable VO_2* state [13,14] and the total absorption by these two defects is measured at about 1000 cm^{-1}. It should be also noted that in the VO_2* defect the oscillator strength of the oxygen atom located outside the vacancy is noticeably lower than that of the oxygen atom which occupies the vacancy. Apparently, due to the same reason the intensity of the 1000 cm^{-1} band of the VO_3 defect is significantly lower than intensities of the 905 and 969 cm^{-1} bands. The similar situation appears to occur for a VO_4 defect as well.

VO_4 defects. It has been already noted in previous studies [7,9], that the band at 985 cm^{-1} displays slightly higher thermal stability as compared with that of the VO_3 related bands, in agreement with the suggested mechanism of the VO_4 formation via capture of diffusing O_i atoms by VO_3 defects. This is also clearly demonstrated in Fig. 2, where a difference between the spectra measured after anneals of an irradiated Cz-Si sample at 550 and 600°C is shown. One can see that the disappearance of the VO_3 related bands is accompanied by a growth up of new bands, the most intense of which are positioned at 985 and 1009 cm^{-1}. Obviously, these bands should be the same as detected by Stein [17] in oxygen implanted silicon. The weakness of the 1009 cm^{-1} band prevented its detection in the previous studies of electron [7,9] and neutron [15,16] irradiated silicon. A big difference in the intensities of the 985 and 1009 cm^{-1} bands is related likely to a difference in the oscillator strength of the oxygen atom located inside and outside the vacancy.

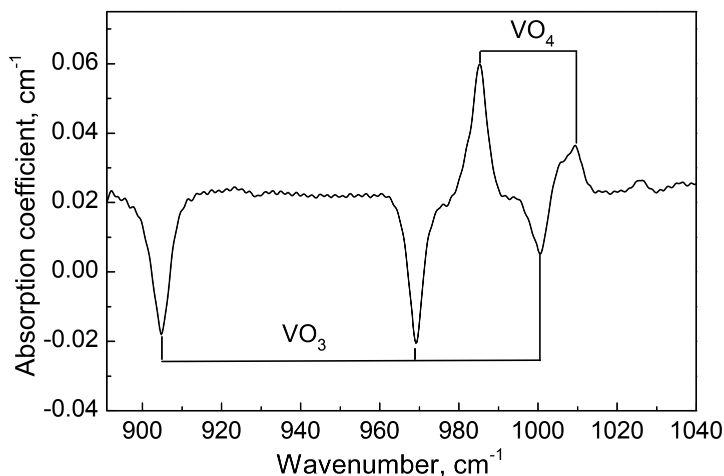


Fig. 2. Fragment of a difference absorption spectrum obtained by a subtraction of the spectrum of Cz-Si sample ([O_i] = 8×10^{17}, [C_s] = 5×10^{16}, [P] = 1×10^{14} cm^{-3}) irradiated with 10 MeV electrons for a dose 3×10^{17} cm^{-2} at RT and then isochronally (30 min) annealed up to 550°C from the spectrum measured after subsequent annealing at 600°C. The spectra were measured at RT.

Another mechanism of the VO_4 formation can be an interaction of the mobile oxygen dimers with the VO_2 defects [15,20]. To check this possibility we have studied the transformations of VO_n defects in Cz-Si crystals with different initial concentrations of the oxygen dimers. Fig. 3 shows a development of the absorption spectra upon isothermal annealing at 450°C of the sample enriched with the oxygen dimers. A very rapid generation of the VO_4 defects (bands at 985 and 1009 cm^{-1}) is observed in such material and intensity of the 985 cm^{-1} band exceeds even the intensities of the 905 and 969 cm^{-1} bands. Evidently, these features are related to the high content of the oxygen dimer and generation of VO_4 defects in this material occurs most likely via the reaction $O_{2i}+VO_2 \rightarrow VO_4$.

This is evidenced also in Fig. 4, where the spectra of two VO_2 containing samples with different contents of oxygen dimers are shown after annealing at 450°C for 1 h. The spectrum 2 in this figure is the same as shown in Fig. 3, i.e. it corresponds to a sample enriched with the oxygen dimers. The spectrum 1 corresponds to a sample with "as-grown" content of the dimers. It can be seen that in the latter case a noticeable generation of only VO_3 related bands is observed and there are practically no indications on the bands at 985 and 1009 cm^{-1}.

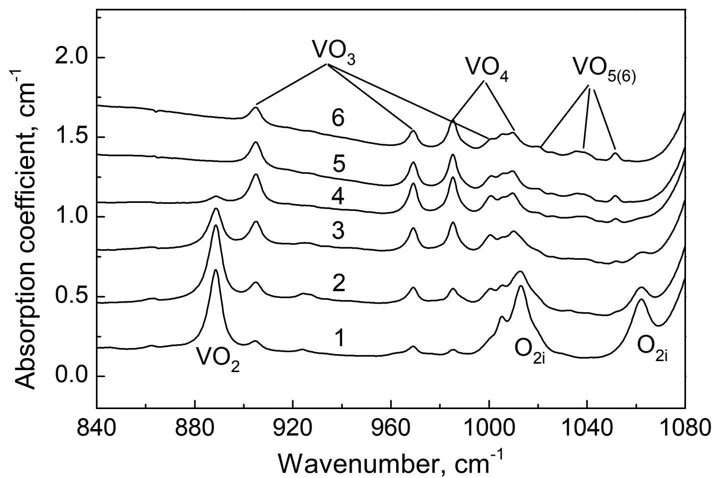


Fig. 3. Fragments of absorption spectra measured at RT for Cz-Si sample ([O_i] = 1.1×10^{18}, [C_s] = 5×10^{15}, [P] = 7×10^{13} cm^{-3}) after irradiation with 2.5 MeV electrons for a dose 4×10^{18} cm^{-2} at 350°C (spectrum 1) and after annealing at 450°C for 1, 4, 16, 60 and 120 hrs (spectra 2, 3, 4, 5 and 6, respectively.

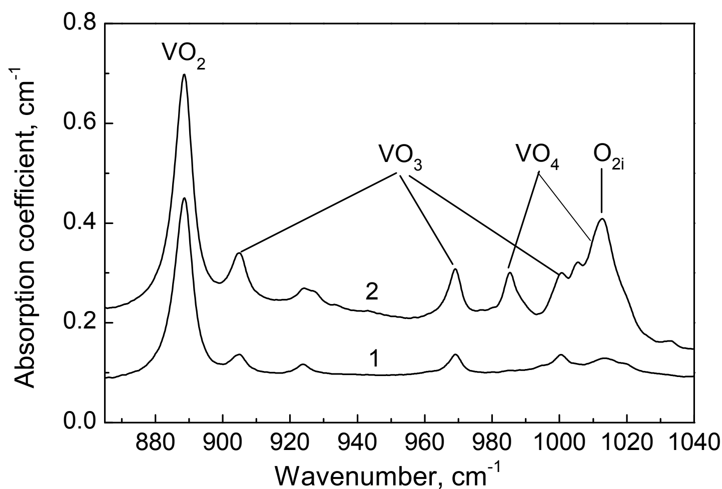
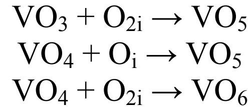


Fig. 4. Fragments of absorption spectra measured at RT for Cz-Si samples ([O_i] = 1.1×10^{18}, [C_s] = 5×10^{15}, [P] = 7×10^{13} cm^{-3}) irradiated with 2.5 MeV electrons for a dose 1×10^{18} cm^{-2} at RT (spectrum 1) and for a dose 4×10^{18} cm^{-2} at 350°C (spectrum 2). Both samples were annealed at 450°C for 1 h.

VO_n (n≥5) defects. Annealing of irradiated Cz-Si samples at temperatures above 600°C results in disappearance of all the bands related to VO_3 and VO_4 defects and formation of a number of new LVM bands located in the range 990-1110 cm^{-1} [7,15,21]. These bands are relatively weak and their behaviour has not been studied in detail previously [7,15]. Only in our recent work [21] has special attention been paid to these bands and it has been suggested that they are related to the VO_5 and

VO_6 defects. Formation of VO_5 and VO_6 may occur via capture of mobile interstitial oxygen atoms and oxygen dimers by VO_3 and VO_4 defects, i.e. via reactions



$$VO_3 + O_{2i} \rightarrow VO_5$$
$$VO_4 + O_i \rightarrow VO_5$$
$$VO_4 + O_{2i} \rightarrow VO_6$$

The results, presented in Figs. 3 and 5, give an additional support for an occurrence of such mechanisms of the VO_3 and VO_4 annihilation. Upon prolonged heating at 450°C of the dimer enriched material, one can observe transformation of VO_2 into VO_3 and VO_4, and then transformation of the latter defects into new complexes, which apparently should be the next species in this chain, i.e. the VO_5 and VO_6 defects.

The corresponding bands appearing upon VO_3 and VO_4 annihilation can be always observed in both electron and neutron irradiated samples that is consistent with their identification as arising from the VO_5 and VO_6 defects. Such an assignment is also in agreement with the observed appearance of the bands upon the annihilation of oxygen-related thermal double donor at 650°C [21].

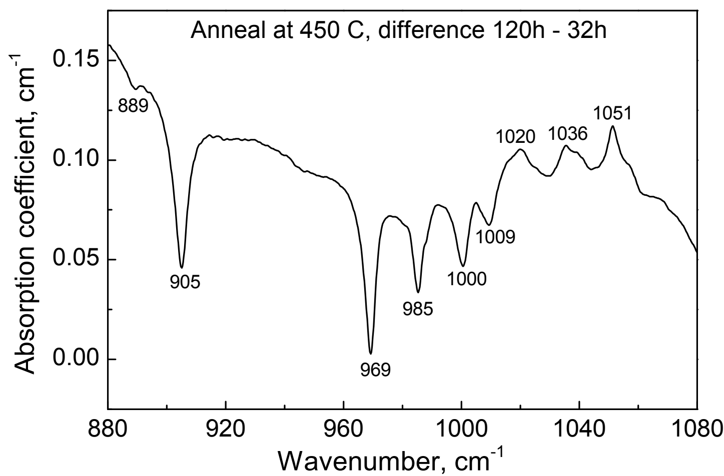


Fig. 5. Fragment of a difference absorption spectrum obtained by a subtraction of the spectrum of Cz-Si sample ($[O_i] = 1.1\times10^{18}$, $[C_s] = 5\times10^{15}$, $[P] = 7\times10^{13}$ cm^{-3}, irradiated with 2.5 MeV electrons for a dose $4\cdot10^{18}$ cm^{-2} at 350°C) annealed at 450°C for 32 h from the spectrum measured after annealing for 120 h. The spectra were measured at RT.

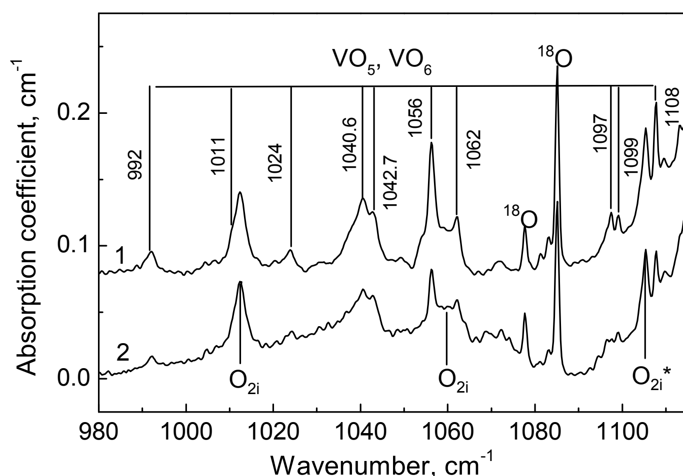


Fig. 6. Fragments of absorption spectra measured at 20 K for Cz-Si samples ($[O_i] = 1.3\times10^{18}$, $[C_s] \le 1\times10^{15}$, $[P] = 7\times10^{13}$ cm^{-3}) annealed at 650°C for 1 h after: 1 – irradiation with 5 MeV neutrons at RT for a dose 1×10^{17} cm^{-2}; 2 - annealing at 450°C for 240 h.

Similarity of the bands generated upon TDD annihilation and radiation-induced defect transformation is clearly manifested in Fig. 6 where the low-temperature spectra for the neutron irradiated Cz-Si sample and the sample pre-annealed at 450°C (TDD containing) after anneal at 650°C for one hour are shown. According to the present models of TDDs, they are oxygen clusters

(chains) involving different numbers of interstitial oxygen atoms. Formation of the VO_5 and VO_6 defects in the TDD containing crystals at high temperatures can occur most likely via the injection of a Si self-interstitial by O_{in} (n > 4) cluster, i.e. via the reaction $O_{in} \rightarrow VO_n + I_{Si}$. Apparently, one of the TDD annihilation mechanisms is their transformation into VO_5 and VO_6 defects.

Conclusions

We have presented new experimental data confirming the previous attributions of LVM bands at 910, 976, and 1105 cm^{-1} and at 991 and 1014 cm^{-1} (LT positions) to the VO_3 and VO_4 defects, respectively. A set of LVM bands appearing upon VO_3 and VO_4 annihilation is assigned to the VO_5 and VO_6 defects. Further studies of the latter defects should provide a new insight into the problem of oxygen precipitate nucleation in Si at temperatures above 600°C.

Acknowledgments

INTAS, the State Committee for Science and Technology and Fund for Fundamental Research of the Republic of Belarus (grants 03-50-4529 and F04MC-029) are thanked for financial supports.

References

[1] T. Hallberg and J.L. Lindström, J. Appl. Phys. Vol. 72 (1992), p. 5130.
[2] V.B. Neimash, Yu.V. Pomozov, V.I. Shakhovtsov, A.N. Kabaldin and V.M. Tsmots: Fiz. Tekh. Poluprovodn. Vol. 27 (1993), p. 1651 [Semiconductors Vol. 27 (1993), p. 912].
[3] V.V. Voronkov and R. Falster: J. Electrochem. Soc: Vol. 149 (2002), p. G167.
[4] V.V. Voronkov and R. J. Falster: J. Appl. Phys. Vol. 91 (2002), p. 5802.
[5] G.D. Watkins and J.W. Corbett: Phys. Rev.Vol. 121 (1961), p. 1001.
[6] J.W. Corbett, G.D. Watkins, R.M. Chrenko and R.S. McDonald: Phys. Rev. Vol. 121 (1961), p. 1051.
[7] J.W. Corbett, G.D. Watkins and R.S. McDonald: Phys. Rev. Vol. 135 (1964), p. A1381.
[8] B.G. Svensson and J.L. Lindström: Phys. Rev. B Vol. 34 (1986), p. 8709.
[9] J.L. Lindström and B.G. Svensson: Mat. Res. Soc. Symp. Proc. Vol. 59 (1986), p. 45.
[10] C.P. Ewels, R. Jones and S. Oberg: Mater. Sci. Forum. Vol. 196-201 (1995), p. 1297.
[11] J.L. Lindström, L.I. Murin, V.P. Markevich, T. Hallberg and B.G. Svensson: Physica B: Condensed Matter. Vol. 273-274 (1999), p. 291.
[12] L.I. Murin, V.P. Markevich, T. Hallberg and J.L Lindström: Solid State Phenomena Vol. 69-70 (1999) p. 309.
[13] J.L. Lindström, L.I. Murin, B.G. Svensson, V.P. Markevich and T. Hallberg: Physica B: Condensed Matter Vol. 340-342 (2003), p. 509.
[14] L.I. Murin, J.L. Lindström, V.P. Markevich, I.F. Medvedeva, V.J.B. Torres, J. Coutinho, R. Jones and P.R. Briddon: this conference.
[15] C.A. Londos, L.G. Fytros and G.J. Georgiou: Defect and Diffusion Forum Vol. 273-274 (1999), p. 1.
[16] C.A. Londos and L.G. Fytros: J. Appl.Phys. Vol. 89 (2001), p. 928.
[17] H.J. Stein: Mater. Sci. Forum Vol. 10-12 (1986), p. 935.
[18] J.L. Lindström, L.I. Murin, T. Hallberg, V.P. Markevich, B.G. Svensson, M. Kleverman and J. Hermansson: Nuclear Inst. and Methods in Physics Research B Vol. 186 (2002), p. 121.
[19] L.I. Murin, V.P. Markevich and J.L. Lindström: to be published elsewhere.
[20] L.I. Murin, J.L. Lindström and A. Misiuk: Physica B: Condensed Matter Vol. 340-342 (2003), p. 565.
[21] L.I. Murin, J.L. Lindström, V.P. Markevich, A. Misiuk and C.A. Londos: J. Phys.: Condensed Matter Vol. 17 (2005), p. S2237.