

## ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

# Bistability and Electrical Activity of the Vacancy–Dioxygen Complex in Silicon

L. I. Murin<sup>a</sup>, V. P. Markevich<sup>a</sup>, I. F. Medvedeva<sup>a</sup>, and L. Dobaczewski<sup>b</sup>

<sup>a</sup>Joint Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus, Minsk, 220072 Belarus

<sup>e-mail</sup>: murin@ifttp.bas-net.by

<sup>b</sup>Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

Submitted March 14, 2006; accepted for publication March 24, 2006

**Abstract**—The methods of infrared absorption, Hall effect, and deep-level transient spectroscopy are used to study the complexes that consist of a vacancy and two oxygen atoms (the vacancy–dioxygen complexes, VO<sub>2</sub>) in irradiated *n*-Si crystals with various levels of doping. The previously observed bistability of VO<sub>2</sub> is confirmed and evidence is provided for electrical activity of this defect in the metastable configuration VO<sub>2</sub><sup>\*</sup>. It is established that the defect with this configuration features an acceptor level located at  $E_C - 0.06$  eV. It is shown that the absorption bands at 967 and 1023 cm<sup>-1</sup> are caused by the negatively charged VO<sub>2</sub><sup>\*</sup> state, while the bands peaking at 928 and 1004 cm<sup>-1</sup> correspond to the neutral charge state of the defect.

PACS numbers: 61.80.Fe, 61.82.Fk, 71.55.Cc, 78.30.Am

DOI: 10.1134/S1063782606110066

## 1. INTRODUCTION

It is well known [1–4] that oxygen in silicon represents one of the most efficient traps for vacancies. The vacancy–oxygen (V–O) complex also referred to as the *A* center was the first radiation defect identified in irradiated Si crystals [5, 6]. At present, the properties of the *A* center are adequately studied. This defect introduces the acceptor level with  $E_C - 0.17$  eV [1, 7] into the band gap and can be observed in the spectra of electron spin resonance (ESR) and infrared (IR) absorption both in the neutral state (the Si-S1 spectrum [8], the absorption band peaking at 836 cm<sup>-1</sup> [2, 9]) and in the negatively charged state (the Si-B1 spectrum [1], the absorption band peaking at 885 cm<sup>-1</sup> [9, 10]). The *A* center is annealed out in the temperature range of 300–400°C. In this case, two processes can occur simultaneously, i.e., dissociation of the complex and its migration as a whole to sinks [11]. These sinks are mainly represented by interstitial oxygen atoms O<sub>i</sub> in the Si crystals with a high oxygen concentration; a complex consisting of a vacancy and two oxygen atoms is formed as a result of interaction of VO with O<sub>i</sub>. As an *A* center dissociates, the predominant repeat (multiple) capture of vacancies by O<sub>i</sub> atoms and/or their interaction with other defects [12, 13] (including the oxygen dimers, O<sub>2i</sub>) occurs. In the latter case, the complex consisting of a vacancy and two oxygen atoms can be formed according to the reaction  $V + O_{2i} \Rightarrow VO_2$ .

It has been established in numerous studies that, indeed, the complex consisting of a vacancy and two

oxygen atoms is the main radiation defect that is formed as a result of annealing of the VO complex in the silicon crystals grown by the Czochralski method (Cz-Si) and irradiated with fast electrons [11, 12, 14–16]. The VO<sub>2</sub> complex is also quite efficiently formed in the course of the so-called hot irradiation [12, 15]. This defect is stable at temperatures as high as 450–500°C. As temperature is increased further, the defect is transformed into the VO<sub>3</sub> and VO<sub>4</sub> complexes as a result of interaction of VO<sub>2</sub> with O<sub>i</sub> and O<sub>2i</sub> [12, 14, 16, 17]; the VO<sub>5</sub> and VO<sub>6</sub> complexes can then be formed [17, 18]. It is assumed [17, 18] that it is these complexes that are responsible for enhanced precipitation of oxygen in the irradiated Cz-Si crystals. On the other hand, theoretical calculations show [19, 20] that the VO<sub>2</sub> complex can play an important role in the formation of centers for precipitation of oxygen even in unirradiated Cz-Si crystals. According to a model developed by Voronkov and Falster [19, 20], practically all equilibrium (thermal) vacancies in silicon with a high oxygen content should exist in the form of the VO and VO<sub>2</sub> complexes at temperatures as high as 1000–1100°C, since the lifetime of vacancies as constituents of these complexes is much longer than that of vacancies in the free state. In addition, it is assumed that the VO<sub>2</sub> complex should be prevalent. In this context, there is considerable interest in the structure and electronic properties of this defect.

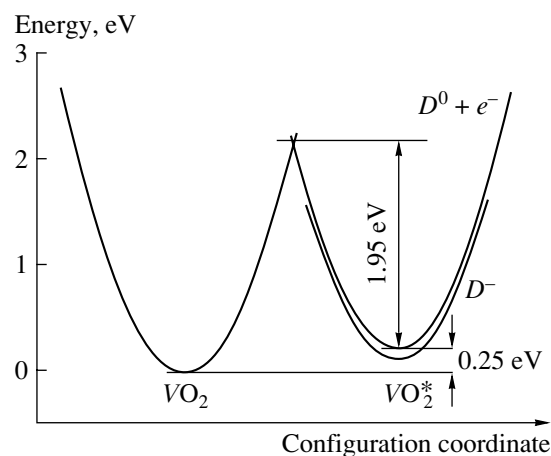
According to a structural model of the VO<sub>2</sub> complex suggested for the first time by Corbett et al. [14] as far back as in 1964 and confirmed by recent theoretical calculations [3, 4], the two oxygen atoms in this complex

saturate all four dangling bonds of the vacancy. It is noteworthy that oxygen atoms occupy the equivalent sites and each of them is connected to two silicon atoms. It has been believed for a long time that the defect under consideration does not exhibit electrical activity. Its presence in irradiated samples was detected using the IR absorption band peaking at  $895\text{ cm}^{-1}$  and caused by stretching vibrations of oxygen atoms [14].

It was found only quite recently [21] that the  $\text{VO}_2$  complex is in fact bistable and there exists another, metastable, configuration of this complex denoted as  $\text{VO}_2^*$ ; in this configuration, one oxygen atom occupies the vacancy, while the second atom resides at the interstitial site in the center of the nearest Si-Si bond. The total energy of the defect in this configuration exceeds only by 0.25 eV the ground-state energy of the  $\text{VO}_2$  complex (Fig. 1); as a result, a significant fraction of the complexes can be found in the  $\text{VO}_2^*$  state at high temperatures. In particular, as temperature is increased from 250 to  $480^\circ\text{C}$ , the equilibrium occupancy of the metastable state increases from  $\sim 5$  to  $\sim 20\%$  [21]. The presence of a fairly high barrier ( $\sim 2\text{ eV}$ ) between the  $\text{VO}_2^*$  and  $\text{VO}_2$  states makes it possible to retain the non-equilibrium occupation of the  $\text{VO}_2^*$  state in the course of rapid cooling from high temperatures to room temperature; as a result, the properties of the defect in this configuration can be studied. It was established in [21] that the metastable  $\text{VO}_2^*$  complex is responsible for the vibrational bands peaked at  $928.4$  and  $1003.7\text{ cm}^{-1}$ ; certain evidence for electrical activity of this complex was also obtained. In this paper, we report the results of more detailed studies of the  $\text{VO}_2$  complex in Si crystals with various levels of doping using the optical (the spectroscopy of local vibrational modes) and electrical (the Hall effect and the deep-level transient spectroscopy) measurements. These results were presented in part at the 11th International Conference on the Gettering and Defect Engineering in Semiconductors (GADEST-2005) [22].

## 2. EXPERIMENTAL

We studied  $n$ -type Cz-Si crystals with the resistivity in the range from 1 to  $60\ \Omega\text{ cm}$ . The samples for optical measurements were irradiated with fast electrons ( $E = 10\text{ MeV}$ ,  $F = 5 \times 10^{16} - 4 \times 10^{18}\text{ cm}^{-2}$ ) at room temperature with subsequent heat treatment for 20–30 h at  $300 - 320^\circ\text{C}$ . As a result of this treatment, a significant fraction of the  $A$  centers were transformed into complexes that consisted of a vacancy and two oxygen atoms. In order to increase the occupancy of the  $\text{VO}_2^*$  state, we subjected the samples to a short-term (3–5 min) heat treatment at  $480^\circ\text{C}$ , which did not affect to any appreciable extent the total concentration of the defects under consideration. In order to execute the reverse



**Fig. 1.** The coordinate-configuration diagram of a complex consisting of a vacancy and two oxygen atoms in silicon.

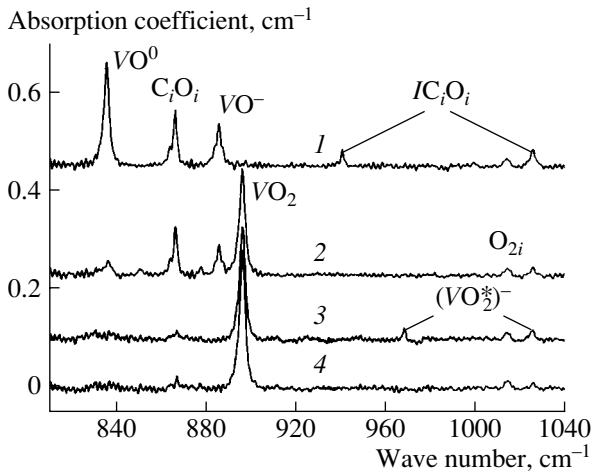
transition of the defects from the metastable  $\text{VO}_2^*$  state to the ground state, we annealed the samples for a long time (as long as 50 h) at  $250^\circ\text{C}$ . According to [21], the characteristic time for establishing the equilibrium between two states of the complex that consists of a vacancy and two oxygen atoms is equal to  $\sim 8$  h and  $\sim 0.1$  s at  $250$  and  $480^\circ\text{C}$ , respectively.

We measured the IR absorption spectra using a Bruker IFS 113v Fourier spectrometer. The spectral resolution was  $0.5 - 1.0\text{ cm}^{-1}$ ; the measurements were carried out either at room temperature or at 20 K.

The  $n$ -type Cz-Si crystals intended for electrical measurements were irradiated with 4-MeV electrons or the  $^{60}\text{Co}$   $\gamma$ -ray photons at room temperature and were then subjected successively to heat treatments at  $320^\circ\text{C}$  (30 h),  $480^\circ\text{C}$  (3–5 min), and  $250^\circ\text{C}$  (for as long as 50 h). The Schottky barriers were formed using thermal deposition of Au. The electron traps were studied using the deep-level transient spectroscopy (DLTS). The Hall effect measurements were performed in the temperature range of 77–400 K using the standard method; the results were used to determine the energy level of the defect under study.

## 3. RESULTS AND DISCUSSION

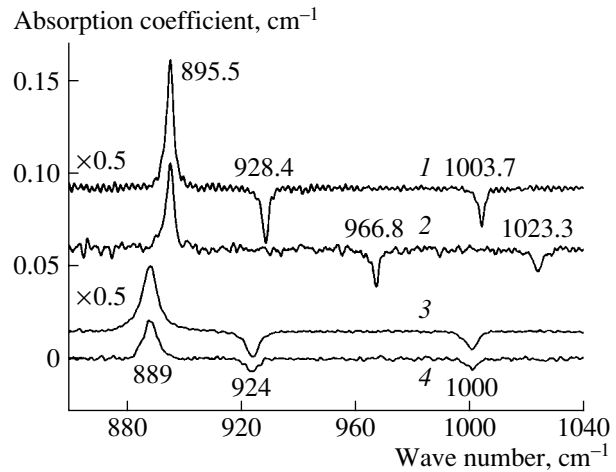
The  $\text{VO}_2^*$  complex can be considered as the  $A$  center (the VO complex) that is located in the vicinity of an interstitial oxygen atom. We can expect that the  $\text{VO}_2^*$  complex would exhibit the electrical activity, similarly to the  $A$  center. The latter, as mentioned above, can be observed in the IR absorption spectra in two charge states: neutral and negatively charged. At low temperatures, the band corresponding to the neutral state is located at  $836\text{ cm}^{-1}$ ; this band shifts to  $885\text{ cm}^{-1}$  for the negatively charged state [9, 10]. Studies of the  $n$ -Si samples irradiated with relatively low doses of fast electrons showed that a shift of vibrational bands



**Fig. 2.** Fragments of the absorption spectra for an *n*-type Cz-Si sample ( $[O_i] = 1 \times 10^{18} \text{ cm}^{-3}$ ,  $[C_s] = 1 \times 10^{16} \text{ cm}^{-3}$ , and  $[P] = 5 \times 10^{15} \text{ cm}^{-3}$ ); the spectra were measured at 20 K. Spectrum 1: after irradiation with electrons ( $E = 10 \text{ MeV}$ ,  $F = 9 \times 10^{16} \text{ cm}^{-2}$ ) at room temperature; spectrum 2: after subsequent annealing for 24 h at  $300^\circ\text{C}$ ; spectrum 3: after an additional annealing for 5 min at  $480^\circ\text{C}$ ; and spectrum 4: after final annealing for 30 h at  $250^\circ\text{C}$ .

caused by the  $\text{VO}_2^*$  complex is also observed for these crystals.

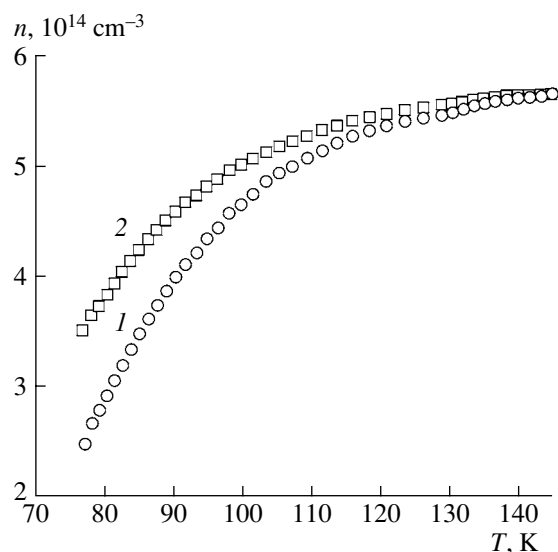
In Fig. 2, we show the low-temperature absorption spectra for an *n*-type Cz-Si sample ( $\rho \approx 1 \text{ } \Omega \text{ cm}$ ) irradiated with electrons (spectrum 1) and then annealed successively at 300, 480, and  $250^\circ\text{C}$  (spectra 2, 3, and 4, respectively). Immediately after irradiation, the main defects are the A centers, the complexes consisting of interstitial carbon and interstitial oxygen ( $\text{C}_i\text{O}_i$ ), and the complexes consisting of self-interstitials and oxygen atoms ( $\text{IC}_i\text{O}_i$ ). The simultaneous presence of bands peaking at 836 and  $885 \text{ cm}^{-1}$  (see spectrum 1) indicates that the A centers in this material can exist in both the neutral and negatively charged states at a low temperature. An annealing for 24 h at  $300^\circ\text{C}$  brings about both an appreciable decrease in the intensity of the VO bands and the formation of a band peaked at  $895 \text{ cm}^{-1}$  and caused by the  $\text{VO}_2$  complex. It is worth noting that practically all A centers after the above heat treatment are found in the negatively charged state at low temperatures (the intensity of the band peaking at  $885 \text{ cm}^{-1}$  greatly exceeds that of the band peaking at  $836 \text{ cm}^{-1}$ , see spectrum 2), which indicates that the concentration of the deep-level compensating centers is relatively low. The bands related to the A centers disappear completely, a further increase in the intensity of the band peaked at  $895 \text{ cm}^{-1}$  is observed, and new bands peaking at 967 and  $1023 \text{ cm}^{-1}$  appear after a short-term annealing at  $480^\circ\text{C}$  (spectrum 3). The subsequent annealing for 30 h at  $250^\circ\text{C}$  leads to an appreciable decrease in the intensity of these bands and to an increase in the intensity of the band peaking at  $895 \text{ cm}^{-1}$  (spectrum 4). This



**Fig. 3.** Fragments of the difference absorption spectra obtained by subtracting the spectra measured after annealing of irradiated Cz-Si samples for 5 min at  $480^\circ\text{C}$  from the spectra measured after annealing for 30 h at  $250^\circ\text{C}$ . The samples were irradiated with 10-MeV electrons (for spectra 1 and 3:  $F = 4 \times 10^{18} \text{ cm}^{-2}$ ,  $[O_i] = 1 \times 10^{18} \text{ cm}^{-3}$ ,  $[C_s] = 5 \times 10^{16} \text{ cm}^{-3}$ , and  $[P] = 2 \times 10^{14} \text{ cm}^{-3}$ ; for spectra 2 and 4:  $F = 9 \times 10^{16} \text{ cm}^{-2}$ ,  $[O_i] = 1 \times 10^{18} \text{ cm}^{-3}$ ,  $[C_s] = 1 \times 10^{16} \text{ cm}^{-3}$ , and  $[P] = 5 \times 10^{15} \text{ cm}^{-3}$ ). Spectra 1 and 2 were measured at 20 K, while spectra 3 and 4 were measured at  $300 \text{ K}$ .

behavior is characteristic of the absorption bands related to the bistable  $\text{VO}_2$  complex [21].

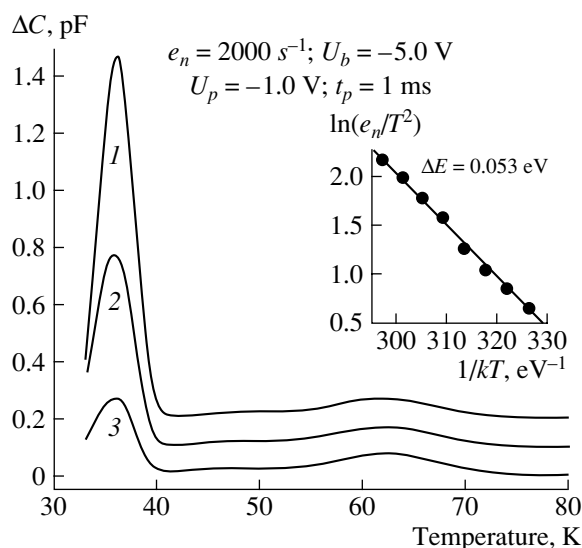
The above-mentioned transformations of the bands manifest themselves more clearly in the differential (difference) absorption spectra. In Fig. 3, we show the fragments of these absorption spectra obtained by subtracting the spectra measured after the short-term annealing of *n*-type Cz-Si at  $480^\circ\text{C}$  from the spectra measured after the long-term annealing at  $250^\circ\text{C}$ . These spectra represent a variation in the equilibrium distribution of the complexes consisting of a vacancy and two oxygen atoms over the  $\text{VO}_2^*$  and  $\text{VO}_2$  states as the annealing temperature is varied from 480 to  $250^\circ\text{C}$ . In addition to the sample whose spectra are shown in Fig. 2, we also studied the heavily compensated material (irradiated with the  $4 \times 10^{18} \text{ cm}^{-2}$  dose of electrons) whose conductivity after all heat treatments remained close to the intrinsic conductivity; i.e., the Fermi level was located near the midgap. The spectra were measured either at 20 K or at room temperature. It can be clearly seen from the shown low-temperature spectra (see Fig. 3, spectra 1, 2) that the  $\text{VO}_2^*$  vibrational bands peaking at 928.4 and  $1003.7 \text{ cm}^{-1}$  are absent in the case of the *n*-type Si sample, in contrast to heavily irradiated crystal. At the same time, new bands are observed in this spectrum; these bands peak at 966.8 and  $1023.3 \text{ cm}^{-1}$ . By analogy with the A-center bands, we may assume that these new bands are related to the negatively charged state of the  $\text{VO}_2^*$  complex.



**Fig. 4.** Temperature dependences of the charge-carrier concentration in an *n*-type Cz-Si sample ( $[O_i] = 1.1 \times 10^{18} \text{ cm}^{-3}$ ,  $[C_s] = 5 \times 10^{15} \text{ cm}^{-3}$ , and  $[P] = 6 \times 10^{14} \text{ cm}^{-3}$ ) irradiated with 4-MeV electrons ( $F = 4 \times 10^{16} \text{ cm}^{-2}$ ) and subjected then to a sequence of heat treatments: (1) at 320°C (30 h) + 480°C (5 min) and (2) at 320°C (30 h) + 480°C (5 min) + 250°C (50 h).

In the spectra measured at room temperature (spectra 3, 4), the positions of the bands related to the  $VO_2^*$  complex for the *n*-Si samples coincide with those for the samples compensated profoundly by irradiation. Evidently, all defects in the  $VO_2^*$  configuration are in the neutral charge state in both materials at room temperature. This inference implies that the acceptor level of the  $VO_2^*$  complex is located higher than the Fermi level in the studied *n*-type Cz-Si semiconductor at room temperature ( $E_C - 0.2 \text{ eV}$ ), and is relatively shallow with respect to the conduction-band bottom.

Studies of the electrical properties of irradiated *n*-type Cz-Si crystals with different doping levels subjected to similar heat treatments (at 320°C for 30 h + 480°C for 5 min + 250°C for 50 h) showed that the  $VO_2^*$  complex is indeed an electrically active defect with a shallow acceptor level in the upper half of the band gap. In Fig. 4, we show the temperature dependences of the free-electron concentration; these dependences were obtained from the Hall effect measurements for one of the samples after the heat treatments at 480 and 250°C. It can be seen that, in the region of low temperatures, these dependences differ appreciably from one another owing to a decrease in the concentration of the defect with a shallow (with respect to the conduction-band bottom) acceptor level after the heat treatment at 250°C. An analysis of temperature dependences of the free-electron concentration for the crystals with various doping levels using a two-level model



**Fig. 5.** Fragments of the DLTS spectra for an *n*-type Cz-Si sample ( $[O_i] = 1.1 \times 10^{18} \text{ cm}^{-3}$ ,  $[C_s] = 5 \times 10^{15} \text{ cm}^{-3}$ , and  $[P] = 6 \times 10^{14} \text{ cm}^{-3}$ ) irradiated with 4-MeV electrons ( $F = 1 \times 10^{16} \text{ cm}^{-2}$ ) and then annealed for 30 h at 320°C. Spectrum 1 was measured after subsequent annealing for 5 min at 480°C and spectra 2 and 3 were measured after additional heat treatments at 250°C for 6 and 50 h, respectively.

(taking into account the ionization of the main doping impurity, phosphorus) showed that the acceptor level of the defect whose behavior corresponds to that for  $VO_2^*$  is located at  $E_C - (0.06 \pm 0.01) \text{ eV}$ .

In Fig. 5, we show the DLTS spectra obtained in the temperature range of 30–80 K for irradiated *n*-type Cz-Si samples after their annealing at 480 and 250°C. The peak with the maximum at  $T = 36 \text{ K}$  ( $E_{36}$ ) is dominant in the spectrum. The maximum value of the  $E_{36}$  peak amplitude is observed after short-term storage of the samples at  $T = 480^\circ\text{C}$ . The subsequent heat treatments at a temperature of 250°C bring about an appreciable decrease in the amplitude of the  $E_{36}$  peak. The rate of this process corresponds to the rate of transformation of the complex consisting of a vacancy and two oxygen atoms from the metastable state ( $VO_2^*$ ) into the ground state ( $VO_2$ ) at a temperature of 250°C [21]. This fact makes it possible to identify unambiguously the  $E_{36}$  trap with the  $VO_2^*$  complex. It was found from the activation dependences (see the inset in Fig. 5) that the activation energy for the emission of electrons from this trap is equal to  $\Delta E = 0.053 \text{ eV}$ . However, we cannot rule out the possibility that this value is somewhat underestimated owing to the electric-field effect. As is known [23], this effect in doped Si crystals brings about an appreciable decrease in the activation energy for the electron emission from the *A* center.

## 4. CONCLUSIONS

The results of the performed studies of the complexes that consist of a vacancy and two oxygen atoms in *n*-Si crystals with various levels of doping and/or with various degrees of compensation indicate unambiguously that the complex under consideration is electrically active if it is found in ("frozen") metastable  $VO_2^*$  configuration. In the highly compensated crystals where the Fermi level is located near the midgap, the absorption bands peaking at 928 and 1004  $\text{cm}^{-1}$  correspond to the  $VO_2^*$  defect at low temperatures. At room temperature, these bands are found to be shifted to lower energies (to 924 and 1000  $\text{cm}^{-1}$ , respectively). Such a temperature-related shift of the bands is typical of the  $VO_m$  complexes ( $m \geq 1$ ) in silicon [16, 17]. The same bands peaking at 924 and 1000  $\text{cm}^{-1}$  are also observed for lightly compensated *n*-type CZ-Si crystals in the spectra measured at room temperature. At the same time, in the spectra measured at a low temperature in the situation where the Fermi level was located near the conduction-band bottom, the bands peaked at 967 and 1023  $\text{cm}^{-1}$  corresponded to the  $VO_2^*$  defect. By analogy with the *A* center, whose absorption band shifts to higher energies as the charge state changes from neutral to negatively charged, the bands peaking at 967 and 1023  $\text{cm}^{-1}$  were attributed to the  $VO_2^*$  complex in the negatively charged state.

The presence of the bistable complex consisting of a vacancy and two oxygen atoms in Si crystals also manifests itself in electrical measurements. The data obtained by the Hall effect and DLTS methods made it possible to determine with adequate reliability the position of the  $VO_2^*$  acceptor level as  $E_C - (0.06 \pm 0.01) \text{ eV}$ .

## ACKNOWLEDGMENTS

We thank Lennart Lindström for his assistance with optical measurements and helpful discussions.

This study was supported in part by the Belarussian Republican Foundation for Basic Research, project no. F04MS-029.

## REFERENCES

1. *Semiconductors and Semimetals*, Vol. 42: *Oxygen in Silicon*, Ed. by F. Shimura (Academic, London, 1994).
2. R. C. Newman, *J. Phys.: Condens. Matter* **12**, R335 (2000).
3. M. Pesola, J. Von Boehm, T. Mattila, and R. M. Nieminen, *Phys. Rev. B* **60**, 11449 (1999).
4. J. Coutinho, R. Jones, P. R. Briddon, and S. Oberg, *Phys. Rev. B* **62**, 10824 (2000).
5. G. D. Watkins and J. W. Corbett, *Phys. Rev.* **121**, 1001 (1961).
6. J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, *Phys. Rev.* **121**, 1015 (1961).
7. V. P. Markevich, A. R. Peaker, L. I. Murin, and N. V. Abrosimov, *Appl. Phys. Lett.* **82**, 2652 (2003).
8. K. L. Brower, *Phys. Rev. B* **4**, 1968 (1971).
9. L. I. Murin, V. P. Markevich, T. Hallberg, and J. L. Lindström, *Solid State Phenom.* **69–70**, 309 (1999).
10. A. R. Bean and R. C. Newman, *Solid State Commun.* **9**, 271 (1971).
11. B. G. Svensson and J. L. Lindström, *Phys. Rev. [Sect. B]* **34**, 8709 (1986).
12. J. L. Lindström, L. I. Murin, T. Hallberg, et al., *Nucl. Instrum. Methods Phys. Res. B* **186**, 121 (2002).
13. L. I. Murin, V. P. Markevich, J. L. Lindström, et al., *Solid State Phenom.* **82–84**, 57 (2002).
14. J. W. Corbett, G. D. Watkins, and R. S. McDonald, *Phys. Rev. [Sect. A]* **135**, 1381 (1964).
15. J. L. Lindström, L. I. Murin, V. P. Markevich, et al., *Physica B (Amsterdam)* **273–274**, 291 (1999).
16. J. L. Lindström and B. G. Svensson, *Mater. Res. Soc. Symp. Proc.* **59**, 45 (1986).
17. L. I. Murin, J. L. Lindström, B. G. Svensson, et al., *Solid State Phenom.* **108–109**, 267 (2005).
18. L. I. Murin, J. L. Lindström, V. P. Markevich, et al., *J. Phys.: Condens. Matter* **17**, S2237 (2005).
19. V. V. Voronkov and R. Falster, *J. Electrochem. Soc.* **149**, G167 (2002).
20. V. V. Voronkov and R. Falster, *J. Appl. Phys.* **91**, 5802 (2002).
21. J. L. Lindström, L. I. Murin, B. G. Svensson, et al., *Physica B (Amsterdam)* **340–342**, 509 (2003).
22. L. I. Murin, J. L. Lindström, V. P. Markevich, et al., *Solid State Phenom.* **108–109**, 223 (2005).
23. B. A. Komarov and V. I. Sopryakov, *Phys. Status Solidi A* **66**, 783 (1981).

*Translated by A. Spitsyn*