
DEFECTS, DISLOCATIONS, AND PHYSICS OF STRENGTH

Interaction with Charge Carriers and the Optical Absorption Spectrum of an Associate Formed by Elementary Defects (an Oxygen Vacancy and a Silylene Center) in SiO_2

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Received December 9, 2003

Abstract—The ability of intrinsic defects in SiO_2 to capture electrons and holes is investigated by quantum-chemical methods. It is established that a twofold-coordinated silicon atom with two unpaired electrons, namely, the silylene center $=\text{Si}^\cdot$, and a silicon–silicon bond, namely, the oxygen vacancy $\equiv\text{Si}-\text{Si}\equiv$, are electron–hole traps in SiO_2 . The properties of a defect in the form of an associate of the two above centers are studied. It is shown that this defect can capture electrons and holes; i.e., it is an amphoteric defect in SiO_2 . The optical absorption spectrum of the studied associate virtually coincides with that of the oxy radical ($\equiv\text{Si}-\text{O}^\cdot$) in silicon dioxide. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Amorphous SiO_2 and Si_3N_4 have been widely used as materials for modern semiconductor electronic devices. In this respect, it is important to elucidate the influence of external factors on the physical characteristics of dielectrics. In particular, dielectric materials subjected to strong electric fields (up to 10^8 V/m) or exposed to ionizing radiation and high temperatures undergo structural transformations with the formation of defect centers, such as electron and hole traps. Electric charges induced in a dielectric material or at an $\text{Si}-\text{SiO}_2$ interface can bring about a shift in the threshold voltage of metal–insulator–semiconductor transistors, parasitic leakage in $p-n$ junctions, and a decrease in the gain of bipolar transistors. For silicon devices at a standard supply voltage $U = 3$ V, the field strength in the dielectric is approximately equal to 10^8 V/m and the mean field strength in the channel amounts to $1-5 \times 10^6$ V/m. In such strong fields, the following phenomena can be observed in a dielectric material: (i) electrons and holes can be injected from contacts, (ii) surface states can be generated, and (iii) injected charge carriers can be trapped by deep-level centers.

A large number of theoretical and experimental works have been devoted to the identification and investigation of defects in SiO_2 . In the present work, we studied two intrinsic defects in SiO_2 , namely, the silylene center $=\text{Si}^\cdot$ and the oxygen vacancy $\equiv\text{Si}-\text{Si}\equiv$. Hereafter, the symbols $(-)$, $(:)$, and (\cdot) denote a chemical bond, a lone electron pair, and an unpaired electron, respec-

tively. For convenience, we introduce the following designations: S is a silylene center, V is an oxygen vacancy, and VS is an associate formed by a silylene center and an oxygen vacancy. Earlier [1–3], it was shown that the $\text{Si}-\text{Si}$ bond can capture a hole. A similar inference regarding the S center was made in [4, 5]. The purpose of this work was, first, to refine the results obtained in our previous studies of the V and S centers and, second, to elucidate how direct contact between these defects affects their parameters, i.e., to investigate the electronic structure and optical properties of the VS center. This center is an oxygen vacancy in which one of the two silicon atoms is coordinated by the other silicon atom and by one oxygen atom. The structural formula of this defect has the form $-\text{Si}^\cdot-\text{Si}\equiv$.

2. COMPUTATIONAL TECHNIQUE

We carried out *ab initio* calculations in the framework of the density-functional theory according to the Gaussian98 program package. All the calculations were performed in the cluster approximation with the use of two variants of the cluster model. This made it possible to investigate the properties of defects located both in the bulk of the dielectric material and near the surface. In order to simulate the bulk of SiO_2 and bulk defects, we used fragments of crystalline α -quartz. Dangling bonds at the cluster boundary were saturated with hydrogen atoms whose positions were fixed in the course of the geometric optimization (search for the minimum in the hypersurface of the total electronic energy of the system). The bulk oxygen vacancy was

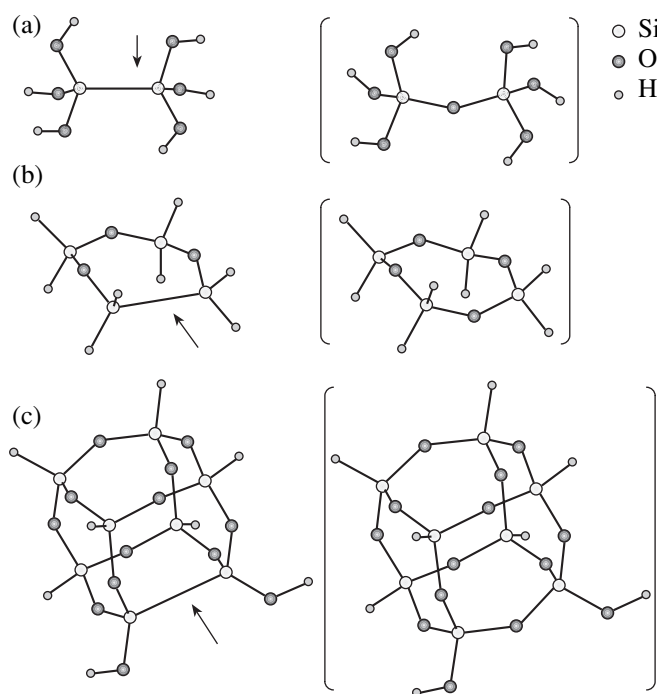


Fig. 1. Cluster models of an oxygen vacancy in SiO_2 : (a) $\text{Si}_2\text{O}_6\text{H}_6$ [$\text{Si}_2\text{O}_7\text{H}_6$], (b) $\text{Si}_4\text{O}_3\text{H}_8$ [$\text{Si}_4\text{O}_4\text{H}_8$], and (c) $\text{Si}_8\text{O}_{13}\text{H}_8$ [$\text{Si}_8\text{O}_{14}\text{H}_8$]. The corresponding model of the regular structure is given in brackets to the right of the structure containing the defect (indicated by an arrow).

simulated by the $\text{Si}_2\text{O}_6\text{H}_6$ [$\text{Si}_2\text{O}_7\text{H}_6$] clusters (Fig. 1a) (hereafter, the corresponding models of the regular structures are given in square brackets). The silylene center was simulated using the $\text{Si}(\text{OH})_2$ [$\text{Si}(\text{OH})_4$] and $\text{Si}_3\text{O}_8\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$] clusters (Figs. 2a, 2b). When simulating the surface defects, we used the $\text{Si}_4\text{O}_3\text{H}_8$ [$\text{Si}_4\text{O}_4\text{H}_8$] and $\text{Si}_8\text{O}_{13}\text{H}_8$ [$\text{Si}_8\text{O}_{14}\text{H}_8$] clusters for the oxygen vacancy (Figs. 1b, 1c) and the $\text{Si}_4\text{O}_4\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$] clusters for the silylene center (Fig. 2b). These clusters consisted of one or several closed rings. Such structures enabled us to arrange the defect centers on the “surface” of the cluster model. The sole exception is the bulk silylene center, whose geometry makes it impossible to construct a cluster in which a defect can be positioned at the center of a regular coordination sphere (in accordance with the geometry of crystalline α -quartz). However, it should be remembered that the method used for determining the energy gain due to capture of charge carriers by a defect involves calculation of the total energy of two structures, namely, a regular structure (which either has the geometry of α -quartz in the case of bulk defects or contains closed rings formed by $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ fragments in the case of surface defects) and the corresponding defect-containing structure in different charge states. For this reason, as was noted above, we used fragments of crystalline α -quartz, namely, the $\text{Si}(\text{OH})_4$ and $\text{Si}_5\text{O}_{16}\text{H}_{12}$ clusters, as models

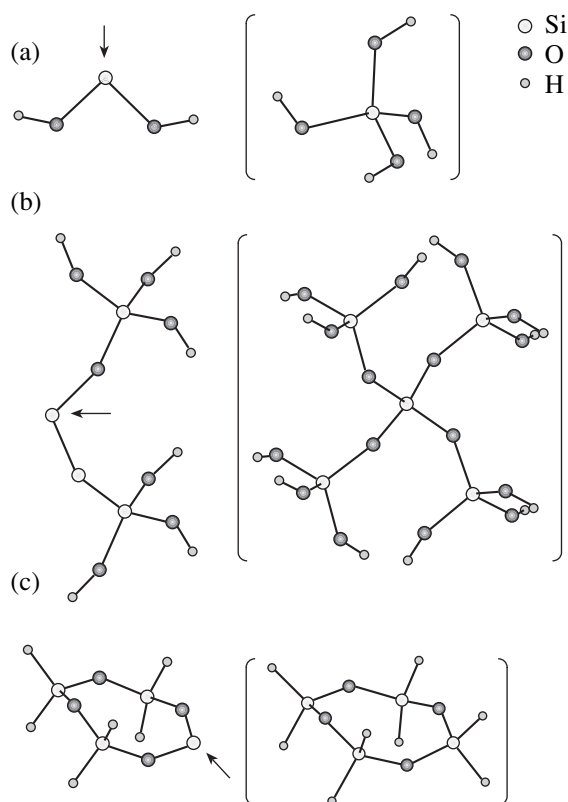


Fig. 2. Cluster models of a silylene center in SiO_2 : (a) $\text{Si}(\text{OH})_2$ [$\text{Si}(\text{OH})_4$], (b) $\text{Si}_3\text{O}_8\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$], and (c) $\text{Si}_4\text{O}_4\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$]. The corresponding model of the regular structure is given in brackets to the right of the structure containing the defect (indicated by an arrow).

of regular structures for studying the bulk silylene center. In the clusters simulating surface defects, the positions of the hydrogen atoms were not fixed.

The Kohn–Sham molecular orbitals were constructed using the split-valence (double-zeta) basis set augmented with $3d$ polarization functions (the standard 6–31G* basis set) for all the silicon atoms. The positions of all the Si and O atoms were optimized with the B3LYP gradient-corrected exchange–correlation functional [6, 7].

The energy gain due to capture of charge carriers (an electron and a hole) by a defect was determined from the following relationships:

$$\Delta E^e = (E_{\text{bulk}}^0 + E_{\text{def}}^-) - (E_{\text{bulk}}^- + E_{\text{def}}^0), \quad (1)$$

$$\Delta E^h = (E_{\text{bulk}}^0 + E_{\text{def}}^+) - (E_{\text{bulk}}^+ + E_{\text{def}}^0). \quad (2)$$

Here, E_{bulk}^0 , E_{bulk}^- , and E_{bulk}^+ are the energies of the neutral, negatively charged, and positively charged clusters simulating the bulk of the dielectric, respectively; and E_{def}^0 , E_{def}^- , and E_{def}^+ are the energies of the neutral, negatively charged, and positively charged

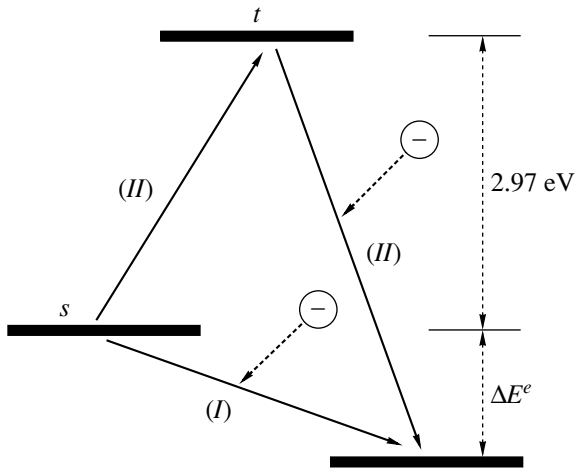


Fig. 3. Schematic diagram of the electronic structure of a $=\text{Si}:$ defect in SiO_2 . Designations: s is the ground (singlet) state of the silylene center, and t is the excited (triplet) state. Solid arrows indicate the possible paths of the reaction $=\text{Si}: + e \longrightarrow =\text{Si}:$ (I) capture of an electron in the ground state of the defect with a decrease in the energy of the system by 1.16 eV and (II) excitation of the defect ($E_{\text{ex}} = 2.97$ eV) with subsequent capture of an electron and a decrease in the energy of the system by 4.05 eV.

clusters simulating the defect, respectively. An electron (hole) is captured when the quantity ΔE^e (ΔE^h) is negative in sign.

3. RESULTS AND DISCUSSION

The results of our calculations are presented in Table 1. It was assumed that the silylene center can exist in two states in which the total spin of the electronic system is equal to zero (singlet state) and unity (triplet state). The triplet state is an excited state, and the excitation energy is equal to 2.97 eV. The two possible paths of the reaction $=\text{Si}: + e \longrightarrow =\text{Si}^*$ are shown in Fig. 3. A similar situation occurs with the capture of a hole.

From analyzing the results presented in Table 1, we can make the inference that the quantities ΔE^e and ΔE^h characterizing the energy location of the electron and hole traps do not depend on the location of defects with respect to the cluster boundaries (for bulk and surface defects, the values of ΔE^e and ΔE^h are nearly identical).

In order to investigate the properties of the VS defect, which is an associate formed by an oxygen vacancy V and a silylene center S , we used the $\text{Si}_4\text{O}_3\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$] and $\text{Si}_3\text{O}_7\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$] cluster models for the surface and bulk defects, respectively (Figs. 4a, 4b). As in the case of the S center, the calculations were performed for the triplet and singlet states. It was found that the energy of the singlet state of the defect is 1 eV less than the energy of the triplet state. The calculated

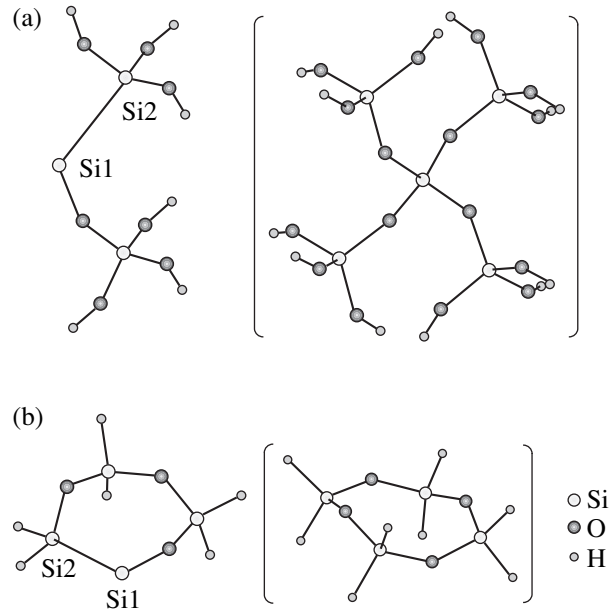


Fig. 4. Cluster models of a VS defect (an associate formed by an oxygen vacancy and a silylene center) in SiO_2 : (a) $\text{Si}_3\text{O}_7\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$] and (b) $\text{Si}_4\text{O}_4\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$]. The corresponding model of the regular structure is given in brackets to the right of the structure containing the defect.

energy gains due to the capture of an electron and a hole are listed in Table 2.

The Si–Si bond length in the neutral $\text{Si}_4\text{O}_3\text{H}_8$ cluster is equal to 2.37 Å. The capture of an electron does not lead to considerable structural distortions, whereas the capture of a hole results in an increase in the length of the Si–Si bond to 2.61 Å. A somewhat different situation arises with the $\text{Si}_8\text{O}_{13}\text{H}_8$ and $\text{Si}_2\text{O}_6\text{H}_6$ clusters. The capture of an electron leads to an increase in the Si–Si bond length from 2.33 to 2.48 Å in the $\text{Si}_8\text{O}_{13}\text{H}_8$ cluster

Table 1. Energy gains due to capture of an electron (ΔE^e) and a hole (ΔE^h) by an oxygen vacancy and a silylene center in SiO_2 according to calculations from formulas (1) and (2)

Defect	Cluster	ΔE^e (eV)	ΔE^h (eV)
V	$\text{Si}_4\text{O}_3\text{H}_8$ [$\text{Si}_4\text{O}_4\text{H}_8$]	–0.63	–0.98
	$\text{Si}_8\text{O}_{13}\text{H}_8$ [$\text{Si}_8\text{O}_{14}\text{H}_8$]	–0.61	–0.95
	$\text{Si}_2\text{O}_6\text{H}_6$ [$\text{Si}_2\text{O}_7\text{H}_6$]	–0.59	–0.97
S	$\text{Si}_4\text{O}_4\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$]	–1.16(s)	–1.12(s)
		–4.05(t)	–4.1(t)
	$\text{Si}(\text{OH})_2$ [$\text{Si}(\text{OH})_4$]	–1.45(s)	–1.62(s)
		–4.2(t)	–4.3(t)
	$\text{Si}_3\text{O}_8\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$]	–1.19(s)	–1.35(s)

Note: (s) and (t) stand for the singlet and triplet states of the silylene center, respectively. The models of bulk defects are marked with bold type.

Table 2. Energy gains due to capture of an electron (ΔE^e) and a hole (ΔE^h) by a VS defect (an associate formed by an oxygen vacancy and a silylene center) in SiO_2 according to calculations from formulas (1) and (2)

Defect	Cluster	ΔE^e (eV)	ΔE^h (eV)
VS	$\text{Si}_4\text{O}_3\text{H}_6$ [$\text{Si}_4\text{O}_4\text{H}_8$]	-2.16(s)	-2.39(s)
		-3.24(t)	-3.3(t)
	$\text{Si}_3\text{O}_7\text{H}_6$ [$\text{Si}_5\text{O}_{16}\text{H}_{12}$]	-2.15(s)	-2.37(s)

Table 3. Energies T_{ex} of optical transitions for an oxygen vacancy V , a silylene center S , and an associate VS according to the TD-DFT (B3LYP/6-31G*) calculations

Defect	Cluster	Transition	T_{ex} (eV)	f
V	$\text{Si}_2\text{O}_6\text{H}_6$	$S_0 \rightarrow S_1$	7.04	0.1
		$S_0 \rightarrow S_2$	7.11	0.13
		$S_0 \rightarrow T_1$	5.1	0.0
	$\text{Si}_8\text{O}_{13}\text{H}_8$	$S_0 \rightarrow S_1$	7.17	0.06
		$S_0 \rightarrow S_2$	7.6	0.0006
		$S_0 \rightarrow T_1$	5.3	0.0
S	$\text{Si}_3\text{O}_8\text{H}_6$	$S_0 \rightarrow S_1$	4.86	0.1
		$S_0 \rightarrow S_2$	5.66	0.003
		$S_0 \rightarrow T_1$	3.0	0.0
	$\text{Si}_4\text{O}_4\text{H}_6$	$S_0 \rightarrow S_1$	5.19	0.1
		$S_0 \rightarrow S_2$	6.04	0.005
		$S_0 \rightarrow T_1$	2.9	0.0
VS	$\text{Si}_3\text{O}_7\text{H}_6$	$S_0 \rightarrow S_1$	1.7	0.002
		$S_0 \rightarrow S_2$	4.2	0.01
	$\text{Si}_4\text{O}_4\text{H}_6$	$S_0 \rightarrow S_1$	2.02	0.003
		$S_0 \rightarrow S_2$	4.16	0.02
		$S_0 \rightarrow T_1$	1.0	0.0

and from 2.48 to 3.00 Å in the $\text{Si}_2\text{O}_6\text{H}_6$ cluster. The capture of a hole also results in an increase in the Si–Si bond length from 2.33 to 2.58 Å in the $\text{Si}_8\text{O}_{13}\text{H}_8$ cluster and from 2.48 to 2.90 Å in the $\text{Si}_2\text{O}_6\text{H}_6$ cluster. The attractive forces between the silicon atom of the defect and the oxygen atoms of the nearest environment and an increase in the repulsive force (in the case of the hole capture) between the silicon atoms can lead to an increase in the length or even to the breaking of the Si–Si bond with the formation of a positively charged E' center [2, 3]. However, in the framework of our model, we can only be sure that the Si–Si bond length increases by ~12% of the initial length in the case of the hole capture and by ~5% of the initial length for the electron capture. For both defects, the spin density distribution is symmetric with respect to the plane perpendicular to the Si–Si bond and, hence, there are no grounds to believe that the Si–Si bond is broken.

In the neutral $\text{Si}_4\text{O}_3\text{H}_6$ cluster simulating the VS surface defect, the Si–Si bond length is equal to 2.46 Å. Structural relaxation due to the capture of an electron or a hole is insignificant. The Si–Si bond lengths in the $\text{Si}_4\text{O}_3\text{H}_6$ cluster upon capture of an electron and a hole are equal to 2.41 and 2.56 Å, respectively. The behavior of the bulk defect does not differ radically from that of the surface defect. However, it should be noted that the spin density distribution is nonsymmetric for the bulk defect. In particular, the spin density in the $\text{Si}_4\text{O}_3\text{H}_6$ cluster is approximately equal to 0.86 at the Si1 atom and 0.1 at the Si2 atom for the electron capture and 0.52 at the Si1 atom and 0.3 at the Si2 atom for the hole capture. Therefore, the captured charge carrier is predominantly localized at the silylene center of the associate.

The optical properties of the defects, namely, the energies and intensities of the electron transitions, were calculated in the framework of the time-dependent density functional response theory (TD-DFT). This approach offers new possibilities for investigating the properties of excited states of defects in dielectric materials. Although the TD-DFT method was devised rather recently, it has managed to show good performance in the study of the optical properties of point defects in SiO_2 [8]. The energies of optical transitions were calculated in the adiabatic approximation; i.e., upon excitation of the electronic system, the geometric parameters of the cluster models remained unchanged. For each of the three defects (S , V , or VS), we calculated the excitation energies T_{ex} and the oscillator strengths f for the two lowest singlet \rightarrow singlet transitions ($S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$) and one singlet \rightarrow triplet transition ($S_0 \rightarrow T_1$). The results of the calculations are given in Table 3. It can be seen from the data presented in Table 3 that the calculated energy of the $S_0 \rightarrow S_1$ transition for the oxygen vacancy almost coincides with the experimental value (7.6 eV) [9]. It should be noted that the augmentation of the basis set with s and p polarization functions, i.e., the use of the standard 6-31G* basis set in the quantum-chemical calculations (which we performed only for the oxygen vacancy), leads to slightly underestimated energies of the optical transitions as compared to the experimental values. For example, we obtained the excitation energy $T_{\text{ex}} = 6.57$ eV ($f = 0.2$) for the $S_0 \rightarrow S_1$ transition. This discrepancy suggests that the inclusion of the polarization functions in the basis set used in calculating the optical absorption spectrum of oxygen-deficient defects is not necessary and, in some cases, is even deleterious. The data calculated for the silylene center are in reasonable agreement with the results obtained in [8, 10, 11]. The optical absorption spectrum of the VS defect is of particular interest because the energy of the $S_0 \rightarrow S_1$ transition coincides with the energy of the $D_0 \rightarrow D_2$ (doublet \rightarrow doublet) transition for another intrinsic defect in SiO_2 , namely, the $\equiv\text{Si}-\text{O}^\bullet$ oxy radical ($f \sim 0$ for the $D_0 \rightarrow D_1$ transition), whose optical spectrum has been repeatedly

investigated theoretically [8, 12] and experimentally [13, 14]. Therefore, although this coincidence, in our opinion, is accidental, it indicates that the identification of defects only on the basis of the optical absorption spectra can be problematic.

In an earlier work [4], we noted that the method for calculating the energy gain upon interaction of defects with charge carriers on the basis of formulas (1) and (2) disregards the long-range Coulomb polarization induced in the lattice by a charged defect. However, the correction to the energy gain for lattice polarization can be estimated in the framework of the classical Born model [15]. For the cluster models used, this correction falls in the range from ~ -0.4 to ~ -0.5 eV. Therefore, the error of the method almost coincides in magnitude with the energy gain ΔE^e for the oxygen vacancy. Hence, we cannot draw correct inference concerning the role played by the V defect in the accumulation of negative charges in SiO_2 . On the other hand, as follows from our data, the S defect is an electron-hole trap in SiO_2 . By analogy with the capture of a hole [4], the capture of an electron by a neutral diamagnetic center brings about the formation of a negatively charged S center, i.e., a twofold-coordinated silicon atom with an unpaired electron. The direct contact of the oxygen vacancy and the silylene center also results in the formation of an electron-hole trap whose depth (i.e., the energy gains ΔE^e and ΔE^h) is considerably greater than the depths (energy gains) of the constituent elementary defects.

ACKNOWLEDGMENTS

This work was supported by the Siberian Division of the Russian Academy of Sciences, project no. 116.

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Translated by O. Borovik-Romanova

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