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A NEW INTRINSIC DEFECT IN AMORPHOUS SiO_2: TWOFOLD COORDINATED SILICON

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The well known optical absorption band at 5.03 eV (the "B_2 band") and luminescence band at 4.3 eV in amorphous SiO_2 are due to singlet-to-singlet transitions, while the luminescence band at 2.65 eV – due to triplet-to-singlet transitions in a silicon-related intrinsic defect. This defect occurs both in the bulk and on the surface. Luminescence polarization data indicate C_{2v} symmetry. The most probable model for this center is a silicon atom with only two neighboring oxygens. Such defects form a separate class of valence alternation defects, characteristic for amorphous materials having atoms in tetrahedral coordination.

THE CENTER, which gives rise to the absorption band at 5.03 eV (the "B_2 band") is one of the longest known defects in amorphous SiO_2 (a-SiO_2). Starting from the work of Mitchell and Page [1] more than 40 papers concerning this defect and related phenomena have been published (see, e.g. [2–6] and refs. therein). The main experimental findings established there are that: (i) the center is intrinsic and directly related to oxygen deficiency, (ii) the center is diamagnetic (although it has been tentatively correlated with an ESR signal recently [7]), (iii) intrinsic photoluminescence at 4.3 eV is excited into "B_2" absorption band [5, 6].

In the absence of any "structural" spectroscopic information on this defect, it is commonly ascribed to a neutral, diamagnetic oxygen vacancy in SiO_2 network [2, 4, 5, 8]. However, more exotic defects such as valence alternation pairs [9] or Si–Si bonds [7] have also been proposed.

The purpose of this work is to show that: (i) this defect has *two* luminescence bands, corresponding to singlet and triplet excited states, (ii) it occurs both as a bulk and a surface center, (ii) the spectroscopic data do not fit any of the previously proposed models and are consistent with a twofold coordinate silicon model for this center.

1. EXPERIMENTAL

The samples of a-SiO_2 were prepared by melting of natural quartz crystals in reducing environment (type "I") and by vapor phase oxidation of $SiCl_4$ (types "III" and "IV"). Type I is non-stoichiometric (oxygen deficient) and has 5 ppm O–H groups and 100 ppm metallic impurities. Samples of types III and IV are considered stoichiometric and contain 1000 and 5 ppm O–H correspondingly and less than 1 ppm metallic impurities. Some samples were irradiated by γ-rays (10^9 rad Si) or neutrons (10^{20} n cm^{-2}). The surface centers were produced by crushing of type I a-SiO_2 in a vibration mill in He atmosphere. Details of this procedure are given in [10]. The mean diameter of SiO_2 particles was 100 nm. The photoluminescence (PL) spectra were measured using two crossed monochromators with deuterium or mercury lamps or a pulsed N_2 laser ($h\nu = 3.68$ eV) as excitation light sources. In order to separate the "slow" component of PL, the excitation light was chopped at 60 Hz and the photon counter was gated to collect the light emitted during the dark periods. A multichannel counter was used for luminescence decay measurements. The excitation spectra were corrected for variations in the intensity of exciting light using a sodium salicylate screen. Luminescence spectra were corrected for the spectral band pass and for the dispersion of the monochromator. The PL polarization degree P was measured in the conventional rectangular geometry. It was determined as $P = (I_{\parallel} - I_{\perp})(I_{\parallel} + I_{\perp})^{-1}$, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of PL with the directions of E-vector parallel and perpendicular to the direction of vertically oriented E-vector of the exciting light.

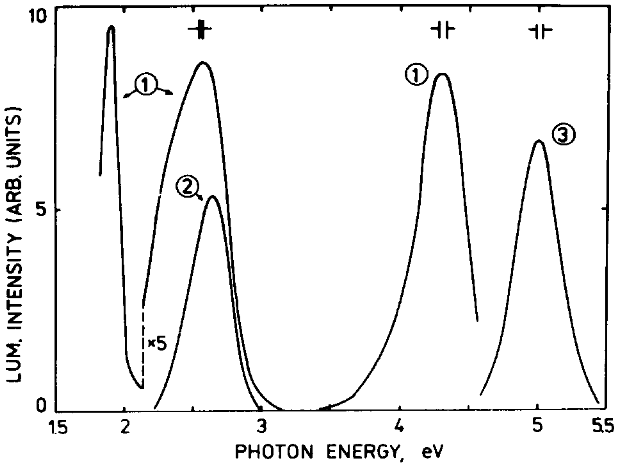

Fig. 1. Photoluminescence spectrum (1) and the spectrum of the "slow" component of luminescence (2) under 4.89 eV excitation; the excitation spectrum of 2.65 and 4.3 eV bands (3). Band 3 coincides with the well-known "B_2" absorption band. Sample: type III a-SiO_2 irradiated 10^{20} neutrons cm^{-2}. $T = 300$ K. Resolution is shown by vertical bars.

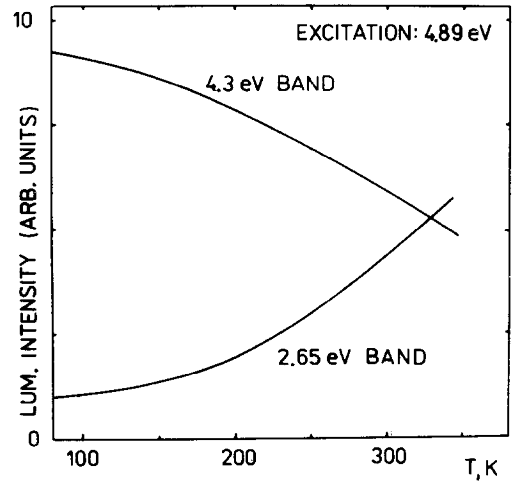

Fig. 2. Temperature dependence of luminescence bands. The scale is the same for both bands.

2. RESULTS

The PL spectrum of neutron-irradiated type III a-SiO_2 shows a band at 4.3 eV and a number of bands in the visible (Fig. 1). However, the "slow" component of the PL consists of only one band at 2.65 eV. The excitation spectrum of this band coincides with the excitation spectrum of the 4.3 eV PL band (maximum at 5.03 eV). The temperature dependences of intensities of these PL bands are given in Fig. 2.

In *unirradiated* samples the 2.65 and 4.3 eV PL bands are very intense in type I a-SiO_2, 100 to 1000 times weaker in type IV and absent in type III a-SiO_2. These bands cannot be enhanced by γ-irradiation.

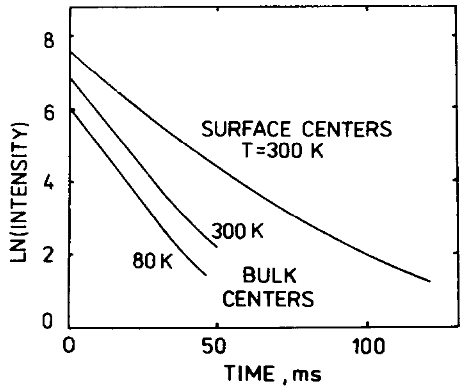

Fig. 3. Luminescence decay kinetics in 2.65 eV band. Excitation at 4.89 eV. Bulk sample: type III a-SiO_2, 10^{20} neutrons cm^{-2}.

The same two PL peaks with the same excitation band are present also in the spectrum of the surface centers. The surface luminescence centers are immediately and irreversibly destroyed upon contact with atmospheric air.

The decay of the 2.65 eV bulk PL is exponential and temperature independent with $\tau = 10.2 \pm 0.2$ msec (Fig. 3). In the case of surface centers a distribution of decay rates from 13.5 to 19 msec is observed in the first 70 msec after the exciting light pulse. Decay in the 4.3 eV band is faster than 10 nsec [11, 12].

The PL polarization degree is $+21 \pm 2\%$ in the 4.3 eV band and $-24 \pm 4\%$ in the 2.65 eV band when excited in the 5.03 eV band.

The light of N_2 laser excites extremely weak PL band at 2.65 eV with decay time $\tau = 9 \pm 2$ msec. The polarization degree in this case is $22 \pm 5\%$.

3. DISCUSSION

The coincidence of the excitation spectra of 2.65 and 4.3 eV PL bands, the non-zero polarization degree as well as the constant ratio between intensities of both PL bands under irradiation or annealing of the samples show that these bands belong to the same center. The key experimental finding here is the slow decay rate ($\tau = 10.2$ msec) of the 2.65 eV band. This indicates that the associated electronic transition is spin-forbidden, as the symmetry forbidden transitions commonly yield τ shorter than 100 μsec [13]. The "solid state" type phosphorescence associated with charge trapping is excluded by the independence of τ on temperature (Fig. 3).

The ground state of this center is a singlet, as no ESR signal is detected in unirradiated type I samples, containing at least 10^{16} centers per cm^3 (an estimate, based upon magnitude of the 5.03 eV absorption band). Then the 2.65 eV PL band corresponds to the triplet-to-singlet ($T_1 \rightarrow S_0$) transition. The 4.3 eV PL band has an appropriate spectral position and decay rate for a singlet-to-singlet ($S_1 \rightarrow S_0$) transition. The reverse temperature dependences of the 2.65 and 4.3 eV band intensities then show that the spin conversion here is thermally activated (Fig. 2). The 2.65 eV PL band, excited by the N_2 laser then is due to direct $S_0 \rightarrow T_1$ excitation.

It is well established (e.g. [14]) that the "B_2" band is due to a silicon related defect, because it is enhanced in reduced samples and is decreased by oxidation. In SiO_2 glass network Si atoms occupy sites with the highest local symmetry: T_d. It is likely that the symmetry will lower, when a defect involving this site is formed. Then D_{3h}, C_{3v}, C_{2v}, C_s, $D_{\infty h}$ or $C_{\infty v}$ symmetry groups should be considered as candidates for the local symmetry group of this defect.

The PL polarization data may be used to decide between these groups. The following analysis was performed for each group: (i) from the condition $\langle \Gamma_1 | \mathbf{T} | \Gamma_2 \rangle \neq 0$ (Γ_i – orbital states, **T** – translation vector) the allowed dipole transitions $S_0 \rightarrow S_1$ and the expected polarization degree P for the singlet $S_1 \rightarrow S_0$ PL were determined, (ii) the condition $\langle \Gamma_2 | \mathbf{R} | \Gamma_3 \rangle \neq 0$ (**R** – axial vector) yields orbital singlet states Γ_3 which may admix to excited Γ_2 triplet state via the spin–orbit coupling in the central atom approximation [13], (iii) from the condition $\langle \Gamma_3 | \mathbf{T} | \Gamma_1 \rangle \neq 0$ the expected P values for $T_1 \rightarrow S_0$ PL were obtained for both cases of $S_0 \rightarrow S_1$ and direct singlet-to-triplet $S_0 \rightarrow T_1$ excitation. The theory of PL polarization for the case of randomly oriented centers and the limiting values of P for various cases is given in [15].

The negative value of P (-24%) for $T_1 \rightarrow S_0$ luminescence (with $S_0 \rightarrow S_1$ excitation) allows one to exclude the C_1 and C_s groups. If non-degenerate ground state is assumed, the finding that $P > 1/7$ for both $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ (with $S_0 \rightarrow T_1$ excitation) luminescence bands allows to exclude C_{3v}, D_{3h}, $C_{\infty v}$, $D_{\infty h}$ groups. Thus only C_{2v} group is consistent with the PL polarization data. The upper limits for P in this case are $+50\%$ ($S_0 \rightarrow S_1 \rightarrow S_0$), -33.3% ($S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0$) and $+50\%$ ($S_0 \rightarrow T_1 \rightarrow S_0$), but they are almost never approached in practice [13, 15]. Therefore the agreement between the theory and the experimental values ($+21\%$, -24%, $+22\%$) should be considered as good.

Thus we are dealing with Si-related defect having C_{2v} symmetry. The simplest model, obviously, is a *twofold coordinated silicon* with only two neighboring oxygen atoms. In the notation, developed for valence-alternation defects in a-SiO_2 (e.g. [9]) this defect may be denoted as Si_2^0, where 2 stands for coordination and 0 is the net charge.

Besides the polarization data, such a model is consistent also with the almost complete similarity between the surface and bulk centers, as well with the weakness of inhomogeneous broadening effects for the bulk centers (good exponentiality of PL decay, Fig. 3). Those effects should be small in this model, because the geometry of SiO_4 tetrahedron is preserved in the SiO_2 glass [16] and hence – also the distance between the two oxygens, interacting with Si_2^0.

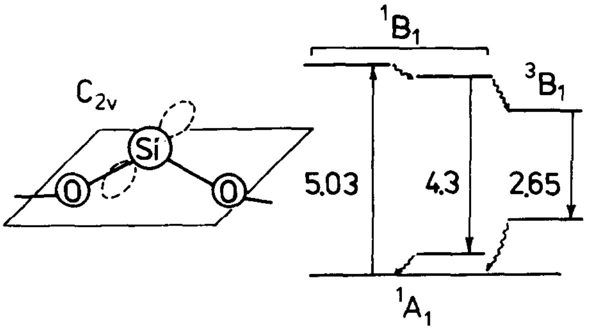

Fig. 4. A steric picture and energy levels of the Si_2^0 center. The empty b_1 (Si $3p$) orbital which is populated in the excited states is schematically shown by dashed line. The energies of the observed optical transitions are given in eV. Singlet-to-triplet absorption is not shown because the band maximum position is not precisely known.

On the other hand, the alternative models – oxygen vacancies [2, 5, 8], valence alternation defects [9] – include interactions between atoms, belonging to two *different* SiO_4 units. The randomness of their mutual orientations (angle Si–O–Si changes from 120° to 180° [16]) should lead to strong inhomogeneous broadening effects, not observed in the experiment. Furthermore, the PL polarization data and the lack of correlation [3] between "B_2" absorption band and E' centers (an oxygen vacancy with a trapped hole) also contradict these models.

The Si_2^0 center may be represented as a bent quasi-molecule SiO_2^{2-}. The ground state of such molecule is $^1A_1$ (Fig. 4). The first excited singlet $^1B_1$ is due to the transition from a_1 orbital to b_1 orbital, consisting mainly of the "non-bonding" Si $3p$ atomic orbital. In a free Si atom the distance between $3s$ and $3p$ states is 5.4 eV [17]. The first allowed transition $^1A_1 \rightarrow {}^1B_1$ in the isoelectronic SiF_2 molecule is at 5.45 eV, the angle F–Si–F is 101° [18].

Our data (in press) on the PL of Ge-related impurity centers in a-SiO_2 indicate the existence of a similar isoelectronic Ge_2^0 center. The faster kinetics ($\tau = 109$ μsec) in the triplet PL band (max. at 3.1 eV), the larger triplet vs singlet luminescence intensities ratio, the identical PL polarization properties – all these features are in accord with what should be expected when silicon in Si_2^0 center is substituted by a heavier isoelectronic atom. An analysis of the experimental data of [19] shows that similar Ge_2^0 center occurs also in pure amorphous GeO_2.

In the valence alternation defect approach the discussed Si_2^0 and Ge_2^0 defects are the first directly observed examples of a separate class of VA defects, where the coordination is changed by *two*. Such T_2^0 defects may be characteristic for amorphous materials with tetrahedrally coordinated atoms. The energy, required for the formation of T_2^0 defects is lowered not by a formation of "wrong" bonds (as is commonly assumed in VA theories [9]), but because the sp^3 hybridization energy is saved when T_2^0 forms.

In the case of SiO_2 or GeO_2 this energy (≈ 5 eV) is comparable to the energies of Si–O or Ge–O bonds. Therefore the net energy, required for the formation of Si_2^0 center should be close to that of a single broken Si–O bond. Consequently, Si_2^0 centers may be present in significant concentrations in oxygen deficient SiO_2, particularly in the non-stoichiometric Si–SiO_2 interface region of MOS structures. They may play an important, though so far neglected role in radiation processes in SiO_2.

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