# Flame Emission Spectra in the Region 400–600 nm during Low-Pressure Silane and Dichlorosilane Oxidation

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**Abstract**—The flame emission in the region 400–600 nm during monosilane and dichlorosilane oxidation (initial pressures of 3–20 torr; T = 300 K) is caused by radical luminescence processes on the surface of aerosol microparticles of the SiO<sub>2</sub> formed. The generation of energy by the interaction of gas-phase species with the SiO<sub>2</sub> surface at the initial stages of the phase formation depends on the presence of the intrinsic structural defects Si<sup>+</sup> and defects like Si<sup>+</sup> implanted into SiO<sub>2</sub>. The addition of SF<sub>6</sub> to the starting mixture results in the appearance of emission bands due to the Si<sup>+</sup> defects in the radical luminescence spectrum.

#### INTRODUCTION

Combustion processes involving monosilane and its chloro derivatives are of great practical interest in view of the problems of semiconductor technology [1], the chemistry of semiconductor nanoparticles [2], and so on. To control these processes, the kinetics of the oxidation of monosilane and its chloro derivatives by a branched-chain mechanism [3–5] should be known.

To elucidate the nature of the active intermediate species and final reaction products, emission spectroscopy is widely used. The emission bands of OH radicals ( $A^2\Sigma - X^2\Pi$  transition) at 306.4 nm [6–8] and of SiO radicals ( $A^{1}\Pi - X^{1}\Sigma$  transition) in the region 230– 280 nm [7, 8] were identified in the chemiluminescence spectra of the flame of monosilane. The bands of  $SiH_3$ radicals [9] and a broad emission band in the region 350–650 nm [8, 10] were detected in the laser magnetic resonance spectrum (Fig. 1). The superequilibrium concentrations of oxygen atoms [11] were determined in flame by ESR spectroscopy, although van de Weijer and Zwerver [8] failed to detect these atoms in the combustion products by a laser-induced fluorescence technique. The emission of SiH<sub>2</sub> radicals  $(A^1B_1 - X^1A_1 \text{ tran-}$ sition) in the region 550-620 nm [12] and of SiH radicals ( $A^2\Pi - X^2\Pi$  transition) at 413 nm [13, 14] was observed in a rarefied flame in the countercurrent diffusion flows of  $SiH_4$  and molecular oxygen. Similarly, the OH  $(A^2X - X^2\Pi)$  [15], SiO  $(A^1\Pi - X^1\Sigma)$ , and SiCl  $(A^{1}B_{1}-X^{2}A_{1})$  radicals were detected in the spectra of a rarefied flame of dichlorosilane (DCS) with oxygen in the region 300-380 nm [16]. The Cl atoms were detected in the ESR spectra [17]. However, the nature of a broad diffuse band found in the emission spectra of  $SiH_4 + O_2$  and DCS +  $O_2$  flames in the region 350–650 nm [16] with a maximum at ~450 nm is so far unclear and debatable. Emission of this kind with spectra similar to that presented in Fig. 1 was also observed in other oxidation processes with the participation of silicon-containing substances. It was suggested [18] on the basis of the chemiluminescence spectra of the SiH<sub>4</sub> + O<sub>3</sub> reaction that the diffuse emission in the visible region can be attributed to excited H<sub>2</sub>SiO\* or HSiOH\* molecules. It was shown by theoretical calculations [18] that this emission can be due to the  $(A^1A'-X^1A_1)$  transition in the H<sub>2</sub>SiO\* molecule. The emission of the SiH<sub>2</sub> + O<sub>2</sub> reaction in the visible region was attributed [19] to the chemiluminescence of the (SiO<sup>•</sup>)\* radical formed in the process



**Fig. 1.** Chemiluminescence spectra during monosilane oxidation: (1) preliminarily prepared mixture of 3.3%SiH<sub>4</sub> +  $29\%O_2 + 67.7\%$  He; 723 K; 7.6 torr; spectral resolution of 3 nm [10]; (2) separated flows of SiH<sub>4</sub> and O<sub>2</sub> (1 : 3) over the surface of a hot disk (873 K); 1 torr; spectral resolution of 2 nm [8].



**Fig. 2.** Chemiluminescence spectra during the reaction of monosilane and oxygen (5% SiH<sub>4</sub> in  $O_2$ ) under conditions of countercurrent diffusion flows (*1*) without additives and (2) in the presence of inhibitor CF<sub>3</sub>Br (1%) [13]. (3) The spectra of SiH<sub>4</sub> pyrolysis products excited by a CO<sub>2</sub> laser [27] (multiphoton absorption method); 50 torr.

$$SiH_2 + O_2 \longrightarrow (SiO')^* + H_2O + 550 \text{ kJ/mol.}$$
 (I)

However, in the well-known chemical reaction

$$Si + N_2O \longrightarrow N_2 + SiO' + 635 \text{ kJ/mol},$$
 (II)

chemiluminescence at 440 nm [20] was not observed under any conditions. An attempt to explain the nature of the diffuse emission was made by van de Weijer and Zwerver [8, 21], who attributed the above chemiluminescence to the emission of the oxygen molecule in a metastable state. According to data [8], excited oxygen molecules are formed in the gas-phase reaction

$$SiO + O + O_2 \longrightarrow SiO_2 + O_2^* + 4.7 \text{ eV}.$$
 (III)

In this case, energy is transferred to the numerous highest excited vibrational levels of the O<sub>2</sub> molecule in different electron states  $(A^3 \Sigma_u^+, C^3 \Delta_u, \text{ and } C^3 \Sigma_u^-)$ . Tran-

sitions from these states to the ground state  $X^3 \Sigma_g^-$  are accompanied by continuous emission in the region 350-650 nm (Fig. 1). This assumption is based on the findings of Brus and Comac [22], who observed chemiluminescence in the visible region during the interaction of  $O_2$  with the pure Si(111) surface, which occurred several centimeters above the surface. Brus and Comac [22] concluded that this emission belongs to excited oxygen molecules in a metastable state with a lifetime of  $5 \times 10^{-4}$  s. However, they did not rule out that the emission can be caused by the desorption of other particles (likely, SiO<sup>•</sup>) from the surface. Continuous emission in a considerably wider spectral region was observed in some works. For example, Chung et al. [23] found that an orange flame, similar to the emission of solids, can be due to the emission of  $SiO_x$  agglomerate particles rather than SiO<sub>2</sub>. A flame with SiCl<sub>4</sub> additives does not produce such an emission, although only  $SiO_2$  is formed during combustion. The emission of the reaction products in the countercurrent flows of  $O_2 + N_2$ and  $N_2 + H_2$  with SiH<sub>4</sub> or SiCl<sub>4</sub> additives was also considered [23]. Extra pure SiO<sub>2</sub> powder was formed in the flows with SiCl<sub>4</sub> admixtures. It was found [24] that the color of the flame of  $SiH_4 + O_2 + N_2$  mixtures varied from whitish blue to bright orange with the SiH<sub>4</sub> concentration. A mixture of the following composition was used:  $[SiH_4] = 1.6-2.1\%$ ,  $[O_2] = 2.0-24.0\%$ , and the balance N<sub>2</sub> up to a total pressure of 1 atm,  $T_0 = 293$  K. The inhibition effect of N<sub>2</sub>, CO<sub>2</sub>, CF<sub>4</sub>, CF<sub>3</sub>Br, CF<sub>3</sub>H,  $C_2H_4$ , and  $C_6H_6$  gas additives on monosilane combustion in oxygen at countercurrent diffusion flows was studied in [13]. When CF<sub>3</sub>Br was added to the mixture containing 5% SiH<sub>4</sub>, the color of the flame changed from bright orange to whitish blue, which is typical of a flame with a low  $SiH_4$  concentration (Fig. 2). The intensity of flame emission near ~500 nm significantly decreased in the presence of  $CF_3Br$  additives (1%), although the emission intensity of (SiO<sup>'</sup>)\* radicals  $(A^2\Pi - X^2\Pi)$  remained almost unchanged. Assuming that the continuous emission of the flame without  $CF_3Br$  additives near 500 nm is mainly determined by the emission of solid particles, Koda and Fujiwara [13] concluded that a decrease in the emission intensity indicates a considerable decrease in the temperature of the surface of particles formed, and the emission at  $\lambda < 500$  nm (see Figs. 1 and 2) cannot be assigned to a solid. A rough approximation of the intensity of emission at 700 nm according to Planck's law indicates that, in the presence of  $CF_3Br(1\%)$ , the temperature decreased by more than 400 K, although the spatial distribution of aerosol particles remained unchanged. At the same time, the maximum gas temperature measured by a thermocouple decreased by only 60 K relative to a maximal value of 1250 K. These data indicate that the emission spectra of monosilane combustion with oxygen in the visible region, which essentially depend on the experimental conditions and mixture compositions, are difficult to interpret.

It was found [25] that upon the ignition of SiH<sub>4</sub> + O<sub>2</sub> mixtures ([SiH<sub>4</sub>] = 30%; ignition temperature of 373 K) a white powder (SiO<sub>2</sub>) and H<sub>2</sub>O are the main products, whereas in the case of the mixtures with [SiH<sub>4</sub>] > 70%, H<sub>2</sub> and a brown powder consisting of Si, SiO, and a small amount of SiO<sub>2</sub>, are the main reaction products. It was suggested that the kinetic mechanism of SiH<sub>4</sub> oxidation involves elementary reactions corresponding to the thermal decomposition of monosilane. The time of SiH<sub>4</sub> decomposition at 1000 K was estimated at  $3 \times 10^{-3}$  s. It has been found using laser-induced fluorescence [26] that Si atoms are formed from dichlorosilane in the bulk during chemical vapor deposition on a support heated to 1123 K at a total pressure of 625 torr (0.7 torr of DCS in He). The rate of Si formation from SiH<sub>4</sub> in a gas phase is one or two orders of magnitude higher than that from DCS. The possibility of strong thermal radiation on the condensation of Si particles was found [27] in the pyrolysis of monosilane using multiphoton absorption of CO<sub>2</sub> laser radiation for preparing Si particles. At a pressure of 152 torr, only continuous emission due to the heat of Si condensation was observed. However, even at 53 torr, individual emission peaks, which may be attributed to the  $SiH_2^*$ ,  $SiH^*$ , and  $H_2^*$ species, were detected (see Fig. 2, curve 2). Comparison of Figs. 1 and 2 shows that the above emission occurs in the range 350-650 nm and that the emission beyond the range 550–650 nm is likely due to the  $SiO_x$ agglomerates and condensed Si particles. Based on these findings, one can conclude that  $SiO_2$  aerosols, which are the final products of oxidation of monosilane and its derivatives, can be emitters in the range 350-600 nm (Fig. 1). Pure SiO<sub>2</sub> aerosol is known to have no absorption bands near 300 nm [28]. However, in the presence of crystal lattice defects in SiO<sub>2</sub> aerosols, the corresponding external sources of excitation can produce electroluminescence, photoluminescence, triboluminescence, adsorption luminescence, and radicalrecombination luminescence in the visible region of the spectrum [29, 30]. This luminescence is due to the occurrence of  $SiO_2$  defects whose size is no greater than the unit-cell parameter of SiO<sub>2</sub> (a silicon-oxygen tetrahedron), that is, point defects (vacancies, interstitial atoms, bond defects, and so on) [29, 30]. Figure 3 presents the photoluminescence spectra of SiO<sub>2</sub> nanoparticles (10-20 nm in diameter) prepared by the evaporation of polycrystalline silicon with a laser beam in an He + O<sub>2</sub> or Ar + O<sub>2</sub> atmosphere at  $P_{O_2} = 100$  torr and a total pressure of 800 torr [31] and the triboluminescence spectra that appeared upon mechanical grinding of vacuum-hydrogen quartz glass in a vacuum [30]. In this glass, surface  $\equiv$ SiO<sup>•</sup> radicals are luminescence centers in the range 600-750 nm and =Si: radicals are luminescence centers at 440 nm [32].

The aim of this work was to elucidate the nature of continuous emission in the visible region (400–600 nm) during the combustion of monosilane and its chloro derivatives in oxygen, the integral emission in the visible region during combustion, the conductivity of a reacting gas mixture, and the scattering of radiation from a probing light source on a =Si: aerosol. To solve these problems, spectroscopic measurements under static and flow conditions were used.

## **EXPERIMENTAL**

Kinetic measurements were carried out in a vacuum setup, which was described elsewhere [10, 16, 33, 34] under static conditions at 300 K and a total pressure of 0.5 to 10.0 torr. The reaction vessel was a quartz cylinder 120 mm in diameter and height with a removable

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**Fig. 3.** Luminescence spectra: (1) photoluminescence of SiO<sub>2</sub> nanoparticles (10–20 nm in diameter) obtained by evaporation of polycrystalline silicon into an atmosphere of O<sub>2</sub> (100 torr) + He (700 torr) [31]; spectral resolution of 1 nm; (2) triboluminescence on the mechanical grinding of quartz glass in a vacuum [30]; spectral resolution of 15 nm;  $S_{sp} \sim 4 \text{ m}^2/\text{g}$ .

bottom. A prepared combustible mixture was fed into the reactor from a storage tank through a vacuum valve. The mixture was ignited by heating a Nichrome wire 0.3 mm in diameter using a capacitor bank (3000  $\mu$ F). The conductivity of the reacting mixture was measured using a molybdenum rod 40 mm in length and 1 mm in diameter as a single probe. Spectroscopic measurements were carried out in the range 200-680 nm with the use of a BM-25 high-aperture (aperture ratio of 1: 4.5) diffraction monochromator (Germany) equipped with a device for continuous wavelength scanning. An STE-1 spectrograph (aperture ratio of 1 : 12) was used in a number of measurements. In studies of combustion under static conditions, two slits (1 mm) were arranged in a focal plane at the outlet of the STE-1 spectrograph in the calculated spectral regions to monitor chemiluminescence simultaneously at two wavelengths. Two photomultiplier tubes (FEU-71 and FEU-39) were used whose signals were fed to two channels of an S9-6 storage oscilloscope. The UV absorption spectra were recorded with the use of a DVS-25 mercury-hydrogen lamp, which exhibits a continuous emission spectrum in the range 200-320 nm. The lamp radiation was passed through a quartz collimator and a reactor and was focused with a condenser on the inlet slit of the spectrograph. Radiation was detected with the use of an FEU-71 photomultiplier tube. The scattering of light by aerosol particles was analyzed using an LGN-209A helium–neon laser ( $\lambda = 633$  nm) at an angle of 90°; detection was performed with an FEU-39 photomultiplier tube. A quartz reactor (170 cm in length and 0.9 cm in inner diameter) was used to study emission spectra in rarefied flames during the oxidation of SiH<sub>4</sub> and DCS under conditions of flame front propagation. The reactor had optical quartz windows at the ends [10,



**Fig. 4.** Kinetic curves for (1) emission intensity of  $(\text{SiO}^{-})^*(A^1\Pi - X^1\Sigma)$ ; (2) integral emission intensity in the range 400–620 nm; (3) conductivity; (4) light absorption at 220 nm; and (5) radiation scattered by an aerosol at an angle of 90° relative to the direction of a probing beam with  $\lambda = 632.8$  nm. Initiated ignition of 25% DCS in O<sub>2</sub>; 4.1 torr; 300 K.

35]. The emission spectrum of a flame propagating along the reactor after initiated ignition was measured with the use of an OSA-500 optical spectrum analyzer (Germany). The resolution of the optical system was 0.4 nm per channel. The required number of spectrum scans (one scan is equal to 500 channels in 32 ms) was stored in the memory of an OSA-500 computer. The reactor provided a number of scans at which the signalto-noise ratio was >25. In studies of the optical spectra,  $SF_6$  was added to a combustible mixture (up to 10% on a fuel basis). This additive significantly decreased the intensity of continuous emission in the visible region of the spectrum, which resulted from the formation of a solid phase in the reactor volume [16, 33, 36], and allowed us to reveal the structure of the emission. The  $O_2$  and SF<sub>6</sub> gases were of chemically pure grade. The concentration of impurities in monosilane was no higher than 0.1% according to the technical certificate; the purity of DCS was checked by IR spectrophotometry [37].

# **RESULTS AND DISCUSSION**

The kinetic data on DCS oxidation are presented in Fig. 4. As can be seen, a maximum chemiluminescence of  $(SiO')*(A^1\Pi - X^1\Sigma)$  is reached  $5 \times 10^{-4}$  s earlier than



**Fig. 5.** (1) Time taken to reach a maximal intensity of integral chemiluminescence in the range 400–600 nm as a function of pressure (a mixture of 11% DCS in O<sub>2</sub>; 300 K; initiated ignition); (2) the limiting time of deexcitation of a particle (possibly,  $O_2^*$  [8, 21, 22]), which is equal to  $5 \times 10^{-4}$  s.

a maximum of the integral emission in the visible region (curves 1 and 2, respectively). The maximal values of the integral emission (curve 2), conductivity (curve 3), and absorption at  $\lambda = 220$  nm (curve 4) are reached almost simultaneously. The time of reaching these maxima coincides with the moment at which the rate of increase of the intensity of scattering probing radiation with a wavelength of 633 nm by an aerosol (curve 5) formed in the gas phase during the reaction is maximum. Under the experimental conditions specified in Fig. 4, the addition of 10% SF<sub>6</sub> produces a simultaneous decrease in both the conductivity and the intensity of scattered radiation. Hence, the integral emission in the visible region is certainly related to phase formation in the gas phase. This relation is clearly shown in Fig. 5 (curve 1). In addition, curve 2 in Fig. 5 shows the limiting time of deexcitation in the visible region of the spectrum of an excited molecule (likely  $O_2^*$ , for which this time is  $<5 \times 10^{-4}$  s according to [8, 21, 22]). The difference between curves 1 and 2 in Fig. 5 indicates that experimental curve 1 cannot be explained by the deexcitation of excited species (like  $O_2^*$ ). The experimental relationships presented in Fig. 4 (curves 2 and 5) can be explained by the adsorption of atoms and molecules or the recombination of atoms on the freshly formed surface of an SiO<sub>2</sub> aerosol [30, 32, 35]. The recombination of active species formed during combustion on the surface of an SiO<sub>2</sub> aerosol is accompanied by the superequilibrium emission of electrons or ions (Fig. 4, curve 3). This emission is a channel of energy relaxation in an excited solid at which, for example, the energy of excited electrons exceeds the work function of the surface. Radiative relaxation, namely radicalrecombination luminescence, is another manifestation (simultaneous with the above process) of the formation of electronically excited states during recombination in the solid (Fig. 4, curve 2). The adsorption of molecules or atoms (adsorption luminescence) can also produce the emission of photons, electrons, and ions through the interaction of sorbed particles with the point defects of the crystal lattice (for example, on the completion of an oxide lattice or upon the recombination of adsorbed oxygen molecules with surface anionic vacancies). After the occupation of surface sites with great heats of adsorption, adsorption luminescence and adsorption emission stopped, since adsorption at these sites is irreversible (see curves 2, 3, and 5 in Fig. 4). Curve 4 in Fig. 4 also confirms the appearance of a solid  $SiO_2$ phase, which is characterized by an absorption band at 248 nm [29]. The above data indicate that the appearance of a new phase (SiO<sub>2</sub> aerosol) during the oxidation of monosilane or DCS is accompanied by chemiluminescence in the visible region of the spectrum, which is due to the phase itself. A similar mechanism of chemiluminescence was observed [38] in the crystallization of the complex  $Ru(bipy)_3Cl_2 \cdot 6H_2O$  from solutions (acetonitrile and ethanol) in the presence of hydroperoxides. It was found that the reactions of hydroperoxides on the juvenile surface of the crystals formed are responsible for the well-known phenomenon of crystal luminescence [38]. Under these conditions, a metal ion on the juvenile surface of a freshly formed crystal cyclically changes its oxidation number to form an excited state, which is detected by typical chemiluminescence in the red region of the spectrum. The appearance of luminescence on grinding quartz glass and in the contact of various gases with the sample destroyed in a vacuum was studied [30, 32] (see Fig. 2, curve 3). New structural defects (centers) are formed upon grinding the quartz samples, which emit in the range 630-650 nm and at the band with a maximum at 440 nm. These centers were attributed to the intrinsic quartz structure defects  $\equiv$  SiO<sup>•</sup> and = SiO<sup>•</sup>. When a solid is subjected to other impacts, for example, photoexcitation, the appearance of these centers also manifests itself in emission [30, 32]. To examine the possibility of luminescence due to the radiative deactivation of excited oxygen molecules near the surface of mechanically activated quartz powder, the spectrum of a microwave gas discharge in oxygen was compared with the adsorption luminescence spectra of O<sub>2</sub> on magnesium oxide [32]. It was found that luminescence resulted from the solid rather than a gas phase containing O<sub>2</sub> molecules and O atoms in ground and excited states. In addition, the adsorption luminescence spectra and their emission maxima on the surface of MgO and SiO<sub>2</sub> powders differ considerably [30, 32]. Hence, although oxygen molecules in an excited state are formed in the gas phase upon recombination of oxygen atoms on the surface [39], their contribution to the total emission is evidently small because of adsorption luminescence.

We found earlier that, in DCS and monosilane oxidation reactions, the rate of propagation of a flame front, the conductivity, and the absorption intensity of



**Fig. 6.** Emission spectra in the visible region: (1) shape of the emission spectrum of 10% SiH<sub>4</sub> + O<sub>2</sub>, 5.5 torr; (2) shape of the emission spectrum of 20% DCS + O<sub>2</sub>, 5.1 torr; (3) spectrum of a rarefied flame of a mixture of 15.7% SiH<sub>4</sub> + 23.2% SF<sub>6</sub> + O<sub>2</sub>, 5.5 torr; 293 K; initiated ignition; (4) spectrum of a rarefied flame of a mixture of 27.2% DCS + 15% SF<sub>6</sub> + O<sub>2</sub>, 6.0 torr; 293 K; initiated ignition; (5) electroluminescence spectrum of Si–SiO<sub>2</sub> structures doped with terbium; and (6) photoluminescence spectrum of a nanocrystalline (3–5 nm) silicon film [41]; 300 K; excitation at 337 nm; emission maximums at 390, 415, 437, and 466 nm.

probing radiation in the UV region of the spectrum decrease in the presence of  $SF_6$  additives [16, 33, 37, 40]. The kinetic curves of combustion are similar to the corresponding curves in the absence of  $SF_6$  (Fig. 4). It was also found [33, 36] that the  $SF_6$  additives to a combustible mixture lead to a decrease in the intensity of continuous emission in the visible region and to the appearance of structure peculiarities in this region of the emission spectrum. Figure 6 (curves 3, 4) presents the emission spectra measured under static conditions (in the regime of initiated ignition) in the oxidation of monosilane and DCS in the presence of an  $SF_6$  additive. The shapes of the emission spectra for the combustion of monosilane and DCS are shown in Fig. 6 (curves 1 and 2, respectively). The total pattern of the spectrum for monosilane combustion is presented in Fig. 1. The emission spectra of the flame obtained under conditions of flame front propagation are similar in shape to curves 3and 4 in Fig. 6. The emission spectra of intermediates in the reactions of monosilane and DCS with oxygen recorded in the presence of SF<sub>6</sub> are almost identical in the range 400-530 nm. The system of bands in the wavelength range 590-660 nm is observed in the spectrum of a flame of monosilane; it can be attributed to the



**Fig. 7.** Spectrum of (1) a rarefied flame of DCS with  $O_2$  and (2) the photoluminescence spectrum of combustion products in the gas phase 0.5 s after completion of combustion: (1) 22% DCS +  $O_2$  + 6% SF<sub>6</sub>, 10 torr; 300 K; initiated ignition; (2) the same conditions; a DRGS-12 mercury–helium lamp as a source of excitation.

emission of the radical  $(SiH_2)^*$   $(A^1B_1-X^1A_1)$ : (020)– (000), (030)–(010), and (020)–(010) transitions, which correspond to the bands at 580, 589, and 614 nm, respectively [33, 39]. In both cases, the absorption band near 413 nm was assigned to the emission of the radical  $(SiH^{+})^*(A^1\Pi-X^1\Sigma^+)$  [42]. According to calculated data [18], the bands at 432, 467, 486, and 513 nm (see Fig. 6) were attributed to the emission of the electronically excited species H<sub>2</sub>SiO\*( $A^1A'-X^1A_1$ ) [33].

However, according to Figs. 4 and 5, the experimentally identified emission in the visible region is due to phase formation in the course of combustion. Figure 7 presents the emission spectrum of a rarefied flame of DCS with  $O_2$  (curve I) and the photoluminescence spectrum (curve 2) of a SiO<sub>2</sub> aerosol formed in the course of combustion (a DRGS-12 mercury-helium lamp as a probing radiation source; an OSA-500 optical spectrum analyzer; a mixture of 22% DCS +  $O_2$  + 6%  $SF_6$ ; P = 10 torr; T = 300 K; static conditions; initiated ignition), which was measured 0.5 s after the completion of combustion. Note that, 3 s after the completion of combustion, the intensity of this photoluminescence spectrum sharply decreased and became comparable with a noise level of OSA-500. Figure 7 presents the photoluminescence spectrum of a SiO<sub>2</sub> aerosol in the range 450-520 nm, where the effect of the scattered emission lines of the DRGS-12 lamp was minimal. The accordance between the spectra (Fig. 7, curves 1 and 2) confirms the fact that emission observed in the visible region is due to radical luminescence on the formation of dispersed SiO<sub>2</sub> particles in the gas phase. Because of this, the emission spectra of combustion products in the visible region (Fig. 1 and Fig. 2, curve 2) and the photoand triboluminescence spectra of SiO<sub>2</sub> particles (Fig. 3) are almost identical. Emission at ~650 nm (~1.9 eV) (Fig. 3, curve 2), which appears in the emission spectra of the SiH<sub>4</sub> combustion products (Fig. 1, curve 2; Fig. 6, curve 3), is due to the surface defect  $\equiv$ SiO<sup>•</sup> [29, 30]. According to [29], the absorption band at 650 nm is due to the appearance of thermolized electrons in the conduction band of the SiO<sub>2</sub> oxide layer, and the excitation mechanism for this band is caused by the capture of conduction electrons by surface traps, which result from the occurrence and dissociation of silanol groups (Si–O–H) to form a nonbridging oxygen atom in an excited state. The relaxation of this atom to the ground state is accompanied by light emission at 650 nm:

$$\equiv \text{Si-O-H} + e^{-} \longrightarrow (\text{SiO}^{\cdot})^{*} + H$$
(IV)  
$$\implies \equiv \text{SiO}^{\cdot} + H + hv(\sim 1.9 \text{ eV}).$$

This fact indicates that the concentration of the Si-O-H groups on the surface of  $SiO_2$  can be monitored by the band intensity at 650 nm [43]. This conclusion is in agreement with the findings of Ratnov et al. [44], who found by IR spectrophotometry that the SiO<sub>2</sub> films obtained by DCS oxidation contain hydrogen atoms and hydroxyl groups in significantly smaller amounts than in the case of monosilane oxidation. The broad emission band near 440 nm (Figs. 1 and 3) can be assigned to the intrinsic defect of quartz, a two-coordinated silicon atom in the =Si: radical [29–31, 43]. Note that, in a study of the photoluminescence of strongly oxidized films of porous silicon stored in air, a weakly pronounced structure with the maxima at 417, 435, and 465 nm was found in the continuous emission spectrum in the range 400–500 nm [45]. A similar structure was observed in both the blue photoluminescence spectrum of silicon oxide films implanted with silicon [46] and in the photoluminescence spectrum of nanocrystalline silicon films containing no SiH<sub>n</sub>, Si–O–H, and SiO groups (Fig. 6, curve 6) [41]. According to Filippov et al. [45], surface defects of the Si<sup>+</sup> type stabilized not only by trapped free carriers but also by molecular oxygen or water can play an important role in the blue photoluminescence spectra. Thus, it is believed that the manifestation of structure peculiarities in the emission spectra of rarefied flames during oxidation of monosilane and DCS in the presence of  $SF_6$  additives at 432, 457, 481, and 513 nm (Fig. 6, curves 3 and 4) is due to the appearance of Si<sup>+</sup> impurity ions in the SiO<sub>2</sub> aerosol formed. The above spectra are similar to the electroluminescence spectra of quartz glass doped with terbium (Fig. 6, curve 5) [29]. The presence of defects in the structure of SiO<sub>2</sub> formed upon the combustion of monosilane in a threefold excess of oxygen was found [47]; the paramagnetic centers  $\equiv$ Si and centers as anionic vacancies with trapped electrons were detected by ESR spectroscopy. Based on published data and our experimental results, we can conclude that emission in the visible region observed during the combustion of monosilane and DCS is due to adsorption luminescence and radical-recombination luminescence on the surface defects of a dispersed SiO<sub>2</sub> aerosol formed. The fine structure of this spectrum (Fig. 7, curves *1* and *2*) and the character of its time decay depend on local crystal fields, which depend on the surrounding of the Si<sup>+</sup> atom [29], the concentration of electronically excited states on the aerosol surface [48], and the delocalization of electron states in the system of close-packed monodispersed single crystals (the Anderson transition) [49].

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