Detection of SiH_2 from the A^1B_1–X^1A_1 transition in the emission spectrum of the rarified flame in the oxidation of silane

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Silylenes (SiH_2) have been detected by (A^1B_1–X^1A_1) emission in the rarified flame in the oxidation of silane for the first time.

The application of SiO_2 thin films in integrated curcuit processing has evoked increasing interest in the oxidation of silanes. The branching chain nature of these reactions has been established, but the kinetic mechanisms have not been yet assigned. The emission bands of SiO ($A^1\Pi$) and OH ($A^2\Sigma^+$) have been observed in the rarified flame in the oxidation of SiH_4,[1] and OH ($A^2\Sigma^+$) in the oxidation of dichlorosilane (DCS).[2] Evidence for the important role of excited states in chain branching has been obtained, but the chemical nature of these particles has not been clarified.[2]

We have earlier observed a $SiCl_2$ ($^1B_1$–$^1A_1$) emission in the region 300–380 nm in DCS oxidation.[2] Silylenes have been also proposed to play a key role in SiH_4 oxidation,[4,5] however, these radicals have not been observed in the flame of this reaction. The hypothetical kinetic mechanisms proposed are contradictory in many respects. For instance, in ref. 6 the reactions of silylene are not taken into account at $T < 1000$ K. The mechanism proposed in ref. 7 contains about 70 elementary reactions, but includes no reaction of silylene; silylenes only arise from monomolecular decomposition of silane as in ref. 6. It is evident that this reaction cannot offer noticeable concentrations of silylenes (much less, electronically excited) even over the temperature range 800–1000 K.

This work is aimed at the detection of the active intermediates in the emission spectra of rarified flames of SiH_4 and DCS oxidation.

The optical spectrum of SiH_2 (A^1B_1–X^1A_1) lies in the range of 650–480 nm.[8] As for the visible emission spectra of the flames in the oxidation of silanes, a considerable blackbody radiation from the solid aerosol particles occurs.[9] This markedly complicates the detection of the emission bands in this region. It has been established that the application of a constant electrical field reduces the amount of SiO_2 aerosol during the ignition of silane–oxygen mixtures[10] as well as the addition of SF_6.[11] We have used both ways for decreasing the intensity of blackbody radiation to reveal the emission bands in the visible region.

The experiments were carried out under static and flow conditions at 293 K and total pressures in the range of 0.6 to 10 Torr. The static quartz reactor (a tube 170 cm lengthwise and 0.9 cm inner diameter) had inlets for electrical power supply and gas evacuation as well as optical windows placed on the butt-ends. The ignition was provided by a rapidly heated nichrome wire coil placed near the butt-end of the tube. The emission spectrum of the rarified flame propagated initiation was recorded with an optical spectra analyser OSA-500 (Germany). The resolution of the optical system was 0.4 nm per channel. The light emitted during the flame propagation was brought to focus on the entry slit of the OSA-500. The required number of scans (1 scan = 500 channels per 32 ms) was stored in computer memory.

The flow quartz cylindrical reactor (15 cm height, 15 cm in diameter) was used in experiments under discharge conditions only for the purpose of the further verification of the assignment of the emission bands. The reactor had a removable cover and inlets for electrical power supply and gas evacuation as well as optical windows. An instrumental cell consisting of two copper plates ($S = 50$ cm^2, the distance between plates 1 cm) was placed in the reactor. The glow discharge in the SiH_4 (or DCS)–O_2 mixture flow was set up in this cell (electrical field strength 340–380 V cm^{-1}, discharge current 5 μA). The emission spectrum of the glow discharge was recorded in the same way as described above. The reactors were evacuated to 10^{-3} Torr before each experiment. The mixtures of SiH_4 and DCS with O_2 and SF_6 (if necessary) were prepared prior to the experiment.

The static reactor was used only in experiments with the rarified flames of the mixtures containing SF_6 in the absence of discharge. The flow reactor was used in experiments with silane–oxygen mixtures without SF_6 under discharge conditions.

The resulting spectra are shown in Figures 1 and 2. It should be noted that the spectrum obtained under static conditions in the visible region in the absence of SF_6 [dotted line in Figure 1(*b*)] represents the continuous emission both for SiH_4 and DCS oxidation in accordance with refs. 4, 5 and 9. A comparison of the spectrum of the rarified flame of SiH_4 oxidation without discharge [Figure 1(*b*)] and those reported in studies of the optical spectra[8,12,13–16] of SiH_2 strongly suggests that the emission bands observed are due to the transitions $^1B_1(0, v', 0)$–$^1A_1(0, v'', 0)$ of SiH_2 as shown in Figure 1. That the emission is due to excited SiH_2 is in little doubt, since from excited states of other possible transients such as SiH[17] and SiO[18] it lies at wavelengths lower than 420 nm. Moreover, the bands in the spectrum [Figure 1(*b*)] of the rarified flame are also observed in the spectrum obtained under conditions of discharge [Figure 1(*a*)] and yet these bands are missing from the spectra of the oxidation of DCS in discharge as well as in the presence of SF_6 under these conditions. It means that the emitting particles are probably uncharged and contain neither F nor Cl atoms. It should be noted that the $^1B_1(030)$–$^1A_1(010)$ transition of SiH_2 was observed in the emission in the infrared multiphoton decomposition of SiH_4.[15,16] The absence of the intense bands corresponding to the transitions $(0, v_2', 0)$–(000)[14] from the spectra (Figure 1) is due to the different mechanisms of the excitation of SiH_2 in ref. 14 with respect to ref. 16 and

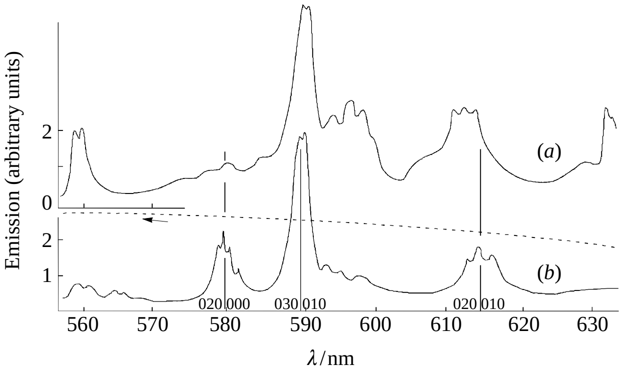

Figure 1 The emission spectra in the visible region of SiH_2 $A^1B_1(0, v', 0)$–$X^1A_1(0, v'', 0)$; (*a*) flow conditions, glow discharge, 400 scans, 10% SiH_4 in O_2, 0.65 Torr; (*b*) static conditions, rarified flame, 40 scans, 10 accumulations, 15.7% SiH_4, 23.2% SF_6 in O_2, 5.5 Torr. The similar spectrum has been also observed under the conditions in Figure 2(*a*). The qualitative spectrum in the absence of SF_6 is shown with the dotted line in arbitrary units in spectrum (*b*), 4 Torr, 10% SiH_4 in O_2.

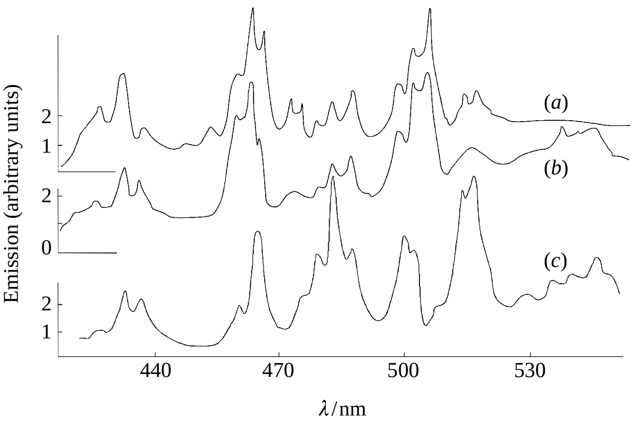

Figure 2 The emission spectrum of hypothetical H_2SiO^*: (*a*) static conditions, rarified flame, 40 scans, 5 accumulations, 11.4% SiH_4, 44.5% SF_6, 10 Torr; (*b*) static conditions, rarified flame, 40 scans, 10 accumulations, 27.2% DCS, 15% SF_6 in O_2, 6 Torr; (*c*) flow conditions, glow discharge, 400 scans, 20% DCS in O_2, 0.7 Torr.

this work. We have analysed only the bending transitions which determine the nature of the states $^1B_1(\angle H–Si–H = 121.2°)$ and $^1A_1(\angle H–Si–H = 92.3°)$[19] similarly to ref. 16. It should be noted that the warming up does not exceed 250 °C under our conditions according to ref. 20, in which the conditions of the oxidation of silane were almost similar. This is due to low pressures and energy dissipation in heterogeneous chain break processes. Therefore, the warming up does not cause the emission observed.

The observation of intense silylene bands evidently shows that the concentration of these radicals is by several orders of magnitude greater than that under thermodynamic equilibrium conditions.

It is known that SiH_2 reacts with almost gas kinetic collision frequency with SiH_4;[15] the reaction of SiH_2 with O_2 also proceeds rapidly leading to SiO^* ($A^1\Pi$).[21] These are the possible basic reactions of SiH_2 in SiH_4 oxidation.

The emission spectra in the region 425–530 nm are shown in Figure 2. The spectrum of the rarified flame of the oxidation of SiH_4 under static conditions appears at $[SF_6] > 40\%$ to total pressure [Figure 2(*a*)]. That for the oxidation of DCS under static conditions appears at $[SF_6] > 10\%$ to total pressure [Figure 2(*b*)]. It is evident that the emission bands in Figures 2(*a*) and 2(*b*) are common to both reactions. Moreover, all emission bands in the spectrum obtained under flow conditions [Figure 2(*c*)] occur also in Figures 2(*a*) and 2(*b*). The difference in intensities is probably due to the different excitation mechanisms. It also means that the emitting particles are probably uncharged and do not contain F or Cl atoms. The emission in this spectral region is possibly caused by electronically excited H_2SiO^* particles in accordance with theoretical calculations predicting the emission in the region 500 nm;[22] in this case these particles are common for the oxidation of SiH_4 as well as of DCS. Furthermore, it is easy to verify that the difference between the wavenumbers of the bands 432, 457, 486, 513 nm, respectively, is ~ 1200 cm^{-1}. On the other hand, the fundamental frequency of Si–O measured for H_2SiO under conditions of matrix isolation is 1202 cm^{-1},[23] *i.e.* close to that obtained from Figures 2(*a*) and 2(*b*). This is an added reason for the assignment of these spectra to H_2SiO^*, however, this assignment is only tentative.

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