STATE-SELECTIVE SPECTROSCOPIC DETECTION OF REACTION PRODUCTS (SiH_2, Si) IN THE IR LASER DECOMPOSITION OF SiH_4

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The decomposition mechanism of $SiH_2(^1B_1)$ formed after IR multiple-photon dissociation of SiH_4 has been investigated by simultaneous acquisition of spontaneous chemiluminescence of SiH_2 radicals and state-selective two-photon laser-induced fluorescence spectra of the atomic silicon produced. Evidence for the opening of an efficient dissociation channel leading to $Si(^1D_2)+H_2(^1\Sigma_g^+)$ from high vibrational levels of the $SiH_2(^1B_1)$ state is presented and discussed.

1. Introduction

It is now well established that silylene (SiH_2) is a key intermediate in a wide range of decomposition processes of silicon hydrides including pyrolysis [1], chemical vapour deposition [2,3], glow discharge [4] and IR laser-induced dissociation [5–7]. It was already suggested [5] that the major feature which differentiates the gas-phase reaction sequences following the initial step

$$SiH_4 \rightarrow SiH_2 + H_2 \qquad (1)$$

is the energy state in which the radical SiH_2 is formed. Whenever silylene is formed in the $^1A_1$ ground state, its insertion into undissociated SiH_4 giving rise to higher silanes is the dominant mechanism following step (1) [1]. Otherwise, silicon formation, followed by particle nucleation and condensation, is observed when SiH_2 is formed in the electronic excited $^1B_1$ state [5]. It was also recently observed [8,9] that the gas-phase reaction dynamics following the primary step (1) changes depending on the degree of vibrational excitation of the $^1B_1$ electronic state. In fact, at $v_2' \leqslant 7$ the $^1B_1$ state may couple to the triplet surface ($^3B_1$) and tunnel through the potential barrier to form $Si(^3P)+H_2$. A more efficient direct dissociation of SiH_2 to $Si(^1D_2)+H_2$ is allowed from $v_2' > 7$ bending vibrational levels of the $^1B_1$ state.

The aim of this paper is to investigate the process of SiH_2 dissociation leading to atomic silicon production after the IR MPD (multiple photon dissociation) of silane. Interest in the subject is primarily due to the importance of silane as starting material for the laser-induced formation of thin silicon films [10] and silicon-containing ceramic powders [11,12].

In order to understand the decomposition dynamics of SiH_2 following IR MPD of silane, we monitored the formation of gas-phase $Si(^3P$ and $^1D_2)$ atoms by laser-induced fluorescence (LIF) and detected the simultaneous visible emission from undissociated electronically excited SiH_2 fragments.

2. Experimental

Silane (99.999% pure, supplied by L'Air Liquide) was excited using a pulsed multimode, line-tunable TEA CO_2 laser (Lumonics model 203). A typical pulse shape consisted of a 150 ns (fwhm) peak followed by a tail of 1.5 μs. Laser energy was monitored by collecting on the surface of a Gen-Tec pyroelectric detector (model PRJ-D) a fraction of the laser beam which was deflected by a 10% reflectivity ZnSe beam splitter. Whenever necessary, the pyroelectric detector was replaced by a fast detector (Molectron model P3) in order to obtain the IR laser pulse time profile. The laser beam was mildly focused in the centre of the cell by a 1.5 m focal length spherical copper mirror which produced a collimated region of radiation

along the cell axis. The beam cross section, as measured by burnt patterns on thermosensitive paper, was 0.22 cm^2 in the centre of the empty cell. Typical laser fluences were in the range 1–8 J/cm^2.

The cell was a UHV stainless steel six-way cross equipped with two ZnSe windows for CO_2 laser transmission and quartz (suprasil) windows for visible–UV light collection and transmission. Conical light baffles were inserted in the cell in order to minimize scattered dye laser radiation and to prevent CO_2 laser produced powders from reaching (and fogging) the optical windows. A background pressure lower than 10^{-5} Torr was achieved by evacuating the cell with a turbomolecular pump (Elettrorava model ETP 8/450).

State-selective silicon atom detection was accomplished using two-photon LIF. Energy states relevant to the detection of $Si(^3P_{J''})$ and $Si(^1D_2)$ have been reported by Brewer [13]. A LIF signal in the range 250.7–252.8 nm from $^3P^o_J$ states is expected after two-photon excitation of $Si(3\,^3P_{J''}) \rightarrow Si(4\,^3P_{J'})$ transitions in the range 405–412 nm; LIF signals at 243.51 nm (from the $3\,^1D^o_2$ state) and at 288.16 nm (from $4\,^1P^o_1$) follow two-photon excitation of $Si(3\,^1D_2)$ to $Si(4\,^1D_2)$ at 455.67 nm [13]. Silicon transitions were excited by the tunable radiation emitted from a XeCl (Lambda Physik EMG 103 MSC) pumped dye laser (Lambda Physik model FL 2002). The dye laser radiation (2–3 mJ energy/pulse; ≈12 ns pulse duration; ≈0.2 Å bandwidth) entered the cell at right angles to the CO_2 laser beam through a suprasil window after passing a 15 cm focal length quartz lens.

The LIF signal was collected at right angles to both laser beams on a RCA 1P28 photomultiplier tube. Appropriate band-pass filters were used to discriminate Si atom fluorescence signals against the scattered radiation from the dye laser. The LIF signal from the photomultiplier output was fed into an EG&G ORTEC fast preamplifier (model 9301), collected on an EG&G boxcar averager (model 162) combined with an EG&G gated integrator (model 165) and displayed on a strip chart recorder.

Synchronization between the CO_2 and the dye laser was achieved by using a delay generator; a typical delay of 250 ns was used throughout the course of this experiment.

SiH_2 visible luminescence was simultaneously detected (at right angles to the CO_2 laser beam) through an additional quartz window suitably placed at 3 cm from the entrance window of the CO_2 laser. A 12.5 cm focal length quartz lens (5 cm diameter) collected a portion of this radiation and imaged it (with lateral magnification 1) onto the entrance slit of a 0.32 m focal length ISA spectrograph (model HR-320, $f_N=5$) supplied with a 150 grooves/mm grating. An EG&G optical multichannel analyzer (OMA III) was employed for detection of the SiH_2 luminescence spectrum. An intensified silicon photodiode array detector (512 elements) was mounted at the exit of the spectrograph and the luminescence spectrum was acquired with a resolution of ≈5 Å/channel. An EMI 9658R photomultiplier tube replaced the OMA for time analysis of SiH_2 luminescence signals. The photomultiplier output was fed into a TEK 2430 digital oscilloscope (40 MHz bandwidth) for signal acquisition and averaging.

The crystalline structure and composition of the CO_2 laser produced powders were evaluated using X-ray (Cu Kα) diffraction analysis [12].

3. Results and discussion

Silane (at 20 Torr pressure) was irradiated with the output of the TEA CO_2 laser tuned at 994.19 cm^{-1} in the fluence range 1–3 J/cm^3. Over the whole laser fluence interval a powdery silicon deposit is observed inside the cell and a broad spontaneous luminescence spectrum is detected in the wavelength range 400–880 nm (fig. 1). In a previous paper [5], this emission was ascribed to decay from electronic excited states of sylilene radicals formed after the IR MPD of SiH_4.

The band peaking at 720 nm was firmly assigned to the $^1B_1 \rightarrow {}^1A_1$ transition, while a proper spectral analysis of the band peaking at 840 nm was impossible due to the lack of spectroscopic data for other SiH_2 electronic excited states. We note that the intensity of the SiH_2 luminescence increases with laser fluence until a sudden drop (by about a factor of 3) is found when the CO_2 laser fluence ϕ reaches 2.5 J/cm^2, as shown in fig. 1. This decrease in the luminescence spectral intensity is accompanied by a narrowing in the time profile of the emission signal, as shown in fig. 2, and by a relevant increase in the

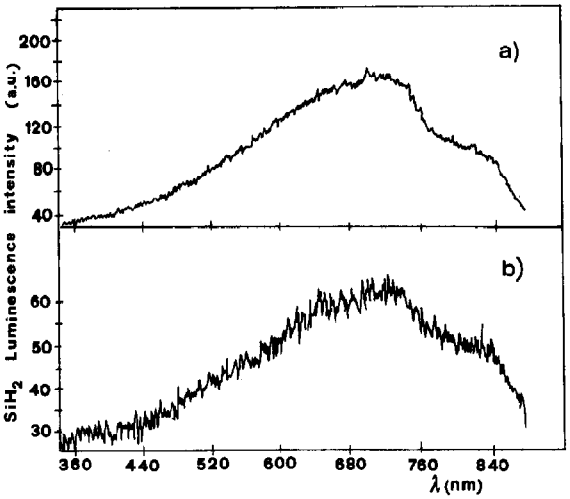

Fig. 1. OMA spectra of SiH_2 fragment emission after the IR MPD of SiH_4 at $p=20$ Torr: (a) $\phi \approx 2.0$ J/cm^2, (b) $\phi \approx 2.6$ J/cm^2.

amount of silicon powder produced during the CO_2 laser irradiation.

Gas phase silicon formation in the ground state has been detected by two-photon LIF exciting the transitions $3\,^3P_{J''}$ ($J''=0, 1, 2$) to $4\,^3P_{J'}$ ($J'=0, 1, 2$) in the range 405–412 nm and observing the group of transitions from $4\,^3P_J^o$ ($J=0, 1, 2$) to $3\,^3P_{J''}$ ($J''=0, 1, 2$) states in the range 250.7–252.8 nm [13,14]. A portion of the LIF excitation spectrum for the Si(^{3}P) atoms, at wavelengths corresponding to the strongest two-photon excitation transitions, is reported in fig. 3. The LIF signal, at 408.45 nm excitation wavelength, is reported in fig. 4 for two different CO_2 laser fluences together with the corresponding SiH_2 spontaneous emission signals. It appears clearly from data shown in fig. 4 that the change in SiH_2 chemiluminescence at CO_2 laser fluences greater than 2.5 J/cm^2 corresponds to a decrease in the LIF signal from Si(^{3}P) atoms.

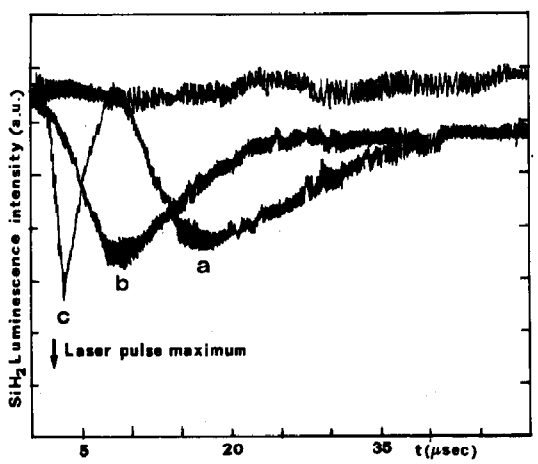

Fig. 2. Time dependence of fragment luminescence at $p(SiH_4)=20$ Torr: (a) $\phi \approx 1.5$ J/cm^2, (b) $\phi \approx 2.0$ J/cm^2, (c) $\phi \approx 2.6$ J/cm^2.

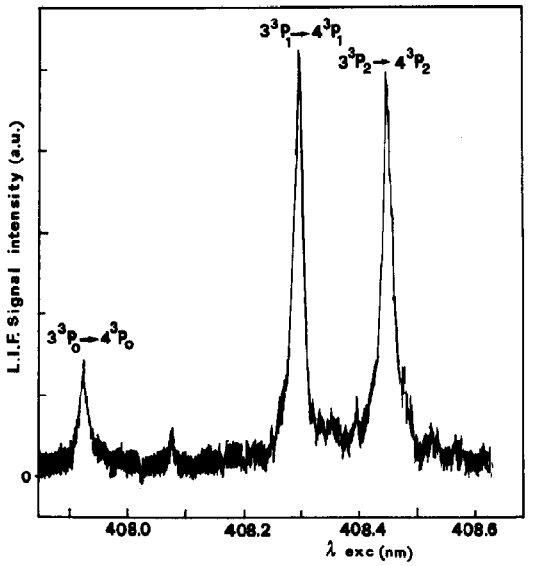

Fig. 3. Two-photon LIF excitation spectrum for Si($^3P_{J''}$) atoms after IR MPD of SiH_4 ($p=20$ Torr) at a CO_2 laser fluence $\phi \approx 2.0$ J/cm^2. Only the strongest transitions ($3\,^3P_{J''} \rightarrow 4\,^3P_{J'}$ with $|J''-J'|=0$) are reported.

Regarding the influence of the CO_2 laser fluence ϕ on the time dependence of SiH_2 spontaneous emission reported in fig. 2, we can observe the following. At $\phi \leqslant 2.5$ J/cm^2, the time profile of SiH_2 luminescence signals is mainly determined by energy pooling [15] between vibrationally excited SiH_4 molecules which provide a continuous source of SiH_2 emitting fragments until vibrational cooling of the parent molecules is achieved by V–T transfer processes [5]. The sudden decrease of the luminescence decay time at $\phi > 2.5$ J/cm^2 is indicative of the onset of a process which rapidly removes a portion of the emitting fragments.

All these experimental findings lead us to hypothize the opening of a new dissociation channel to atomic silicon for SiH_2 excited to high bending vibrational levels of the $^1B_1$ state. This has been confirmed by the detection of a LIF signal, at 288.16 and

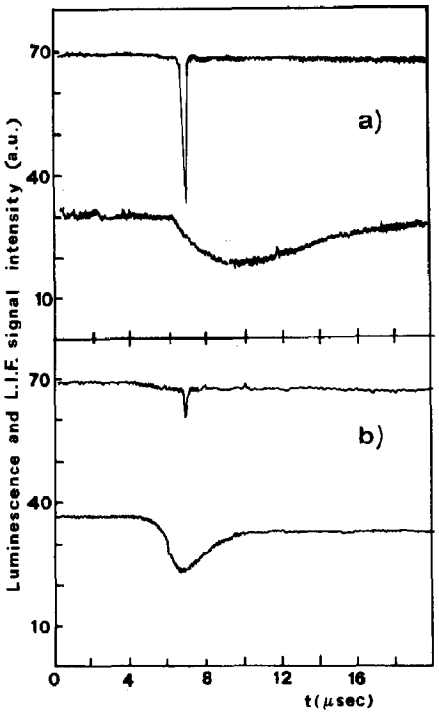

Fig. 4. SiH_2 spontaneous luminescence signals (lower curves) and $Si(^3P)$ LIF signals (upper curves) at two different CO_2 laser fluences: (a) $\phi \approx 2.0$ J/cm^2, (b) $\phi \approx 2.6$ J/cm^2.

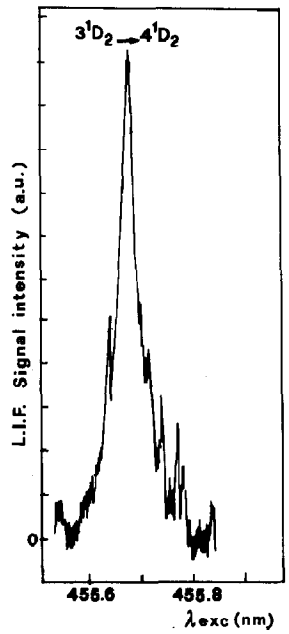

Fig. 5. Two-photon LIF excitation spectrum for $Si(^1D_2)$ atoms after IR MPD of SiH_4 (p=20 Torr) at a CO_2 laser fluence $\phi \approx 2.6$ J/cm^2.

at 243.51 nm (fig. 5), following two-photon excitation of $Si(3\,^1D_2)$ to $Si(4\,^1D_2)$ at CO_2 laser fluences greater than 2.5 J/cm^2.

Keeping in mind the model proposed by Francisco et al. [9] as well as the experiment of Van Zoeren et al. [9], our results are consistent with the following dissociation mechanism for the SiH_2 radicals formed after IR MPD of SiH_4. At a silane pressure of 20 Torr, collision-induced MPD to SiH_2+H_2 takes place at CO_2 laser fluences greater than 1 J/cm^2 [5]. The SiH_2 radicals are formed in the $^1B_1$ electronic state and the initial distribution over rovibronic levels depends on the excess energy available during the SiH_4 dissociation process.

At low CO_2 laser fluences ($1 \leqslant \phi \leqslant 2.5$ J/cm^2) SiH_2 can either decay to the ground state emitting the broad chemiluminescence spectrum reported in fig. 1 or dissociate to $Si(^3P)+H_2$ (figs. 3 and 4). It was shown by Francisco et al. [9] that on symmetry and correlation grounds the $^1B_1$ levels cannot dissociate directly to $Si(^3P)+H_2(^1\Sigma_g^+)$. It is possible that $^1B_1$ levels couple to $^3B_1$ states and tunnel through the potential barrier to form $Si(^3P)+H_2(^1\Sigma_g^+)$. However, the activation energy for this dissociation channel is high (44.7 kcal/mol) [9] and, as a consequence, only a small number of silicon atoms are formed and nucleate in particles.

As the CO_2 laser fluence increases, the initial vibrational distribution of SiH_2 radicals in the $^1B_1$ state is shifted towards higher vibrational quantum numbers. In ref. [9] the opening of the $Si(^1D_2)+H_2(^1\Sigma_g^+)$ dissociation channel is calculated to be 22.3 kcal/mol above the origin of the $SiH_2(^1B_1)$ state; Van Zoeren et al. [8] observed the opening of this channel at $v_2' > 7$.

Present results indicate that at CO_2 laser fluences greater than 2.5 J/cm^2, a substantial fraction of SiH_2 radicals is formed in vibronic levels with $v_2' > 7$ where direct dissociation to $Si(^1D_2)+H_2(^1\Sigma_g^+)$ is allowed. This is fully confirmed by the sudden detection of a $Si(^1D_2)$ LIF signal, as soon as the CO_2 laser fluence reaches 2.5 J/cm^2, as well as the simultaneous increase in silicon powder production. This last result supports the hypothesis that the channel leading to $Si(^1D_2)$ is more efficient than the predissociation to $Si(^3P)+H_2$.

It is worth mentioning that the decrease in the $Si(^3P)$ LIF signal as soon as the $Si(^1D_2)$ LIF signal

starts to appear is related to the long radiative lifetime of the Si($^1D_2$) state ($\tau_{rad} \approx 370$ s) [16]. We can guess that the Si($^1D_2$) atoms deactivate after reaching the cell walls or form clusters in the gas-phase instead of decaying back to the Si(^3P) ground state through a forbidden transition.

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