QUANTUM YIELD STUDIES OF DISILANE PHOTODISSOCIATION AT 193 nm BY INFRARED DIODE LASER SPECTROSCOPY

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Quantum yields for the loss of disilane and the formation of silane in the 193 nm photodissociation of disilane have been measured using time-resolved infrared diode laser absorption spectroscopy under single excimer laser pulse conditions at total pressures of 5 to 10 Torr in helium buffer gas. The total quantum yield for loss of disilane is 0.7 ± 0.1 while the quantum yield for formation of silane is only 0.10 ± 0.03. The results suggest that numerous photodissociation pathways as well as non-photodissociative relaxation pathways exist for disilane excited near its electronic absorption threshold.

1. Introduction

Disilane, Si_2H_6, is the prototypical molecule containing a silicon–silicon single bond. As such, it occupies a central place in silicon hydride chemistry. Its dissociation pathways in the ground electronic state have been studied rather extensively, both experimentally [1] and theoretically [2]. Perhaps equally important, and in stark contrast to hydrocarbons, the silicon–silicon bond in disilane is a useful photochemical chromophore which can be excited with standard photolysis sources such as 185 nm mercury lamps and 193 nm ArF excimer lasers. Disilane is, therefore, one of the simplest readily available silicon hydride molecules which can be used as a photochemical source of silicon hydride radicals for kinetic and spectroscopic studies and as a film growth precursor in the photochemical vapor deposition of silicon containing thin films for photovoltaic and microelectronics applications.

In spite of this, little quantitative information on disilane photochemistry is presently available, especially in the region near the electronic absorption threshold. There have been recent spectroscopic studies of disilane from ≈200 nm well into the vacuum ultraviolet using synchrotron radiation [3], and a recent review article on photochemical vapor deposition [4] lists all possible photodissociation pathways as a function of energy up to the ionization limit. The only quantitative study of disilane photochemistry, excluding mercury sensitized photolysis [5], however, was performed at 147 nm [6]. The photochemistry at 147 nm was studied by observing the loss of disilane and the formation of stable products mass spectrometrically during continuous irradiation of the sample with a xenon resonance lamp. The authors accounted for the observed quantum yields by proposing three primary photodissociation processes out of at total of thirty-nine pathways [4] which are energetically possible at 147 nm (photon energy 194 kcal/mol). The situation at 193 nm (photon energy 148 kcal/mol) is almost completely unexplored. Silylene has been demonstrated to be a primary photoproduct in laser-induced fluorescence [7] and laser resonance absorption studies [8], but some twenty photodissociation pathways are energetically possible [4] since each photon contains enough energy to break any single bond in disilane and numerous combinations of bonds. Some insight into disilane photochemistry at 193 nm is essential in exploiting it as a source of silicon hydride radicals and in understanding its utility as a film growth precursor in photochemical vapor deposition.

In this paper we report the initial results of quantum yield studies of disilane photolysis at 193 nm. The total quantum yield for disilane loss and the

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quantum yield for silane formation have been measured using tunable infrared diode laser flash kinetic spectroscopy with microsecond time resolution. The technique allows measurements to be made under single excimer laser pulse conditions, thereby avoiding complications due to secondary photolysis, detection of disilane and silane are quantitative and unambiguous and the time resolution can provide information on primary photochemical as opposed to secondary radical–molecule chemical processes which consume disilane or produce silane. These features are highly desirable in studying silicon hydride systems, since the chemistry of these molecules is often complex. The results are significantly different from those obtained at 147 nm and suggest that multiple photodissociation pathways as well as non-photodissociative relaxation processes are important. The quantum yield results also provide some insight into why disilane is such an efficient silicon source in photo-CVD processes.

2. Experimental

A schematic of the experimental apparatus is shown in fig. 1. Disilane is admitted to the gas cell under slowly flowing conditions through the inner pair of gas inlets while inert buffer gases are admitted through the outer pair of inlets in order to keep the cell windows well purged. The flow cell, gas handling equipment and pumping system are designed to operate in the 1–100 Torr pressure range at constant total gas flow and constant total pressure. The stainless steel cell is 1 m long and is identical to one which has been described previously in detail [8], except that normal incidence BaF_2 windows are used to transmit the ultraviolet and infrared laser beams. The length between the inner pair of gas inlets, which defines the volume containing disilane and hence the optical pathlengths for the experiment, is 53 cm.

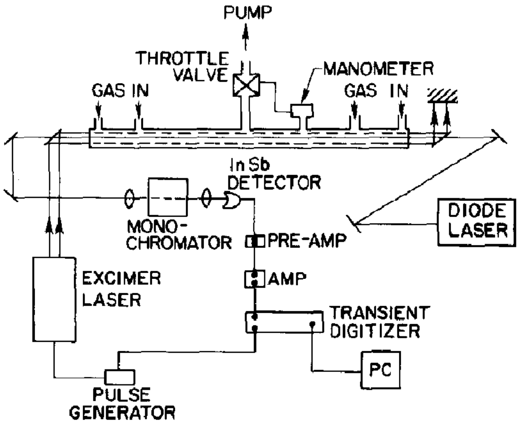

Fig. 1. Schematic of the infrared diode laser flash kinetic spectrometer.

Under typical conditions, 40 to 230 mTorr of disilane in 5 to 10 Torr of helium or carbon tetrafluoride buffer gas at a total flow rate of 200–300 sccm was photolyzed by the unfocused output of an ArF excimer laser (Lambda Physik 102E) operating at a repetition rate of 2 s^{-1}. The gas residence time in the active volume of the cell ranged from 0.7 to 2 s. The incident excimer laser power was measured with a calibrated energy meter and was corrected for measured losses in the optical path and at the cell entrance window. The amount of disilane excited by the excimer laser pulse was calculated from the known pressure of disilane, the known pathlength and the measured absorption cross section for disilane at 193 nm. The absorption cross section was obtained from the slope of a semi-logarithmic plot of transmitted excimer laser power as a function of disilane partial pressure in the cell.

Loss of disilane and formation of silane were detected by transient changes in absorption of the infrared probe beam generated by a tunable lead-salt diode laser (Laser Analytics). The excimer laser beam and the diode laser beam were collinear and counter propagating. In early experiments the mode selection monochromator was placed directly in front of the diode laser while in later experiments the optical arrangement was as shown in fig. 1. In some experiments the excimer laser beam and the diode laser beam diameters were made identical by placing apertures at both ends of the cell while in other experiments the excimer laser beam was not apertured and was much larger than the diode laser beam. These variations in the optical arrangement did not change the quantum yield results. The infrared diode laser was operated in the region around 2150 cm^{-1} where both silane and disilane have infrared vibration–rotation transitions associated with the Si–H bond stretch. Survey spectra were recorded using phase sensitive detection of the mechanically chopped diode laser output. Silane formation after excimer laser photolysis was probed using various lines of the P(6), P(7), P(9) and P(13) multiplets of the ν_3 band. Disilane loss was probed using the strongest features of the spectrum in the same spectral region. Changes in diode laser intensity were detected using a 1 mm^2 InSb detector cooled to liquid nitrogen temperature. Transient absorption curves were averaged and recorded using a transient digitizer. Typically 320 to 640 excimer laser shorts were averaged. The time resolution of the detection electronics was ≈1 μs. Transient difference spectra could also be recorded, by scanning the diode laser and integrating the transient absorption with a dual channel boxcar integrator. One gate was set immediately before and the other gate immediately after the excimer laser pulse.

In order to quantitatively measure the amount of disilane lost and the amount of silane formed, the incident diode laser power, I_0, the transient change in diode laser power, ΔI, and the relevant absorption cross sections must be determined. The value of I_0 was determined before each measurement by chopping the diode laser with a mechanical chopper. The value of ΔI was determined from the maximum change in the transient absorption signal. The absorption cross sections for silane and disilane in the infrared were measured by admitting known quantities of silane and disilane to the cell. Typical peak cross sections were in the range of 0.05 Torr^{-1} cm^{-1} for disilane and 1–12.5 Torr^{-1} cm^{-1} for silane. The cross sections were determined from the slopes of semi-log plots of transmitted infrared power versus partial pressure of silane or disilane, recorded with the diode laser mechanically chopped. In the calibration experiments the cell was operated in both the normal flowing mode at 5 to 10 Torr total pressure with helium buffer gas and in a static mode at low pressure, 1–20 mTorr, with pure silane or disilane. Both calibration procedures gave the same cross sections, demonstrating that the pathlength of interest in the flow cell is well defined and that pressure broadening by helium, especially of the silane lines, is not significant. Severe deviations from linearity in the semi-log plots were observed in pure silane at pressures above 20 mTorr. The experimental changes in silane concentration during quantum yield measurements were less than 10 mTorr.

Disilane (Matheson, 97%), silane (Airco, C.C.D. Grade), propylene (MG Scientific Gases, 99%), and carbon tetrafluoride (Liquid Carbonic) were used as received. Helium (99.999%, Liquid Carbonic) was passed through a cartridge filter purifier to further limit oxygen and water impurities. The major impurity in silane is hydrogen (≈200 ppm) and the major impurities in disilane are hydrogen and silane.

3. Results

We measure an absorption cross section of $(3.4\pm0.3)\times10^{-18}$ cm^2 for disilane excited with 193 nm ArF laser pulses. This value is in good agreement with the value of 4×10^{-18} cm^2 at 190 nm determined by Itoh et al. [3] in a synchrotron radiation absorption study and with the value of $\approx3.5\times10^{-18}$ cm^2 at 193 nm which can be estimated from an older ultraviolet absorption study by Feher [9].

Infrared diode laser spectra of silane and disilane in the region around the P(6) transition of the ν_3 band of silane [10,11] are shown in fig. 2, along with a transient difference spectrum of the same region, obtained while photolyzing disilane at an excimer laser repetition rate of 10 s^{-1}. The strong silane lines are easily seen in the difference spectrum as downward features and some of the strongest disilane lines can be seen as weak upward features. The spectroscopic assignment for silane comes from comparison of the diode laser frequency determined by the mode selection monochromator with the frequency of silane P-branch lines determined by Fourier transform infrared spectroscopy and from comparison of the multiplet pattern with a compilation of diode laser spectra of the ν_3 band of silane [12]. Since the rotational constant of silane is ≈3 cm^{-1}, the assignment is relatively straightforward. The disilane spectrum is not assigned. The ν_5 and ν_7 Si–H stretching bands of disilane overlap in this region [13,14] and a rotational assignment at diode laser resolution is not presently available.

Typical transient loss and formation spectra of disilane and silane are shown in fig. 3 on a milisecond timescale. From ten to twenty independent measurements of the maximum absorption change

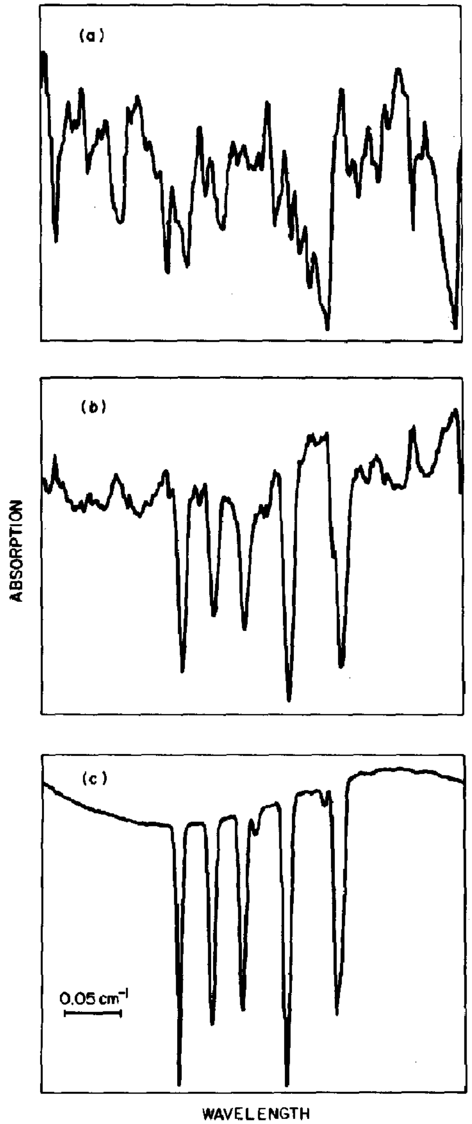

Fig. 2. Diode laser spectra of (a) disilane and (c) silane in the P(6) region of the ν_3 band of silane and (b) transient difference spectrum during excimer laser photolysis.

in these signals at 5 and 10 Torr in helium buffer gas, we find that the quantum yield for disilane loss is 0.7 ± 0.1 while the quantum yield for silane formation is only 0.10 ± 0.03. The errors are one standard deviation. The silane quantum yield does not change, within error, when several Torr of CF_4, a more efficient vibrational relaxer of silane, is added to the gas mixture and the disilane quantum yield does not change when 0.9 Torr of propylene, and efficient silylene scavenger [15], is added to the gas mixture. The peak amplitudes of both the disilane loss and silane formation signals depend linearly on the excimer laser power for more than a factor of two change in photolysis energy. When viewed on faster timescales, fig. 4, the disilane loss signal exhibits a detector limited risetime, while the silane signal rises over 20 to 100 µs depending on total pressure and the nature of the bath gases present. Any slow rise in the disilane signal is too small to be discerned at our present signal to noise levels.

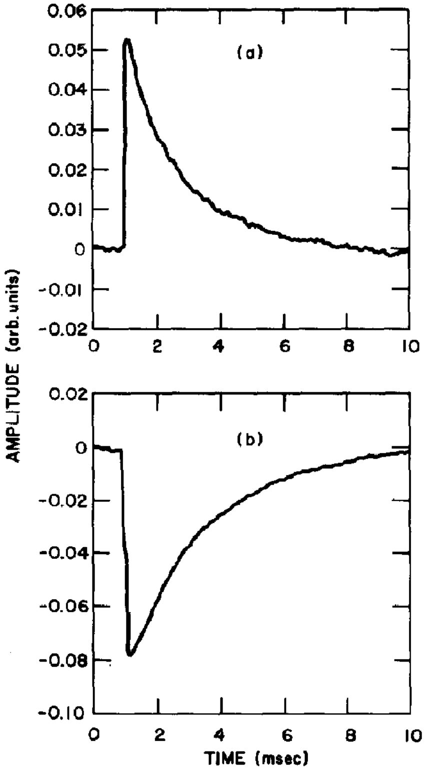

Fig. 3. Typical transient signals for (a) loss of disilane and (b) formation of silane on a millisecond timescale following excimer laser photolysis.

While it is easy to find disilane transitions which are not overlapped by silane lines, the converse is not true. Interference of the disilane spectrum with the silane transient measurement is, however, minimized by the factor of ≈40 difference in peak cross sections and by choosing silane lines which fortui-

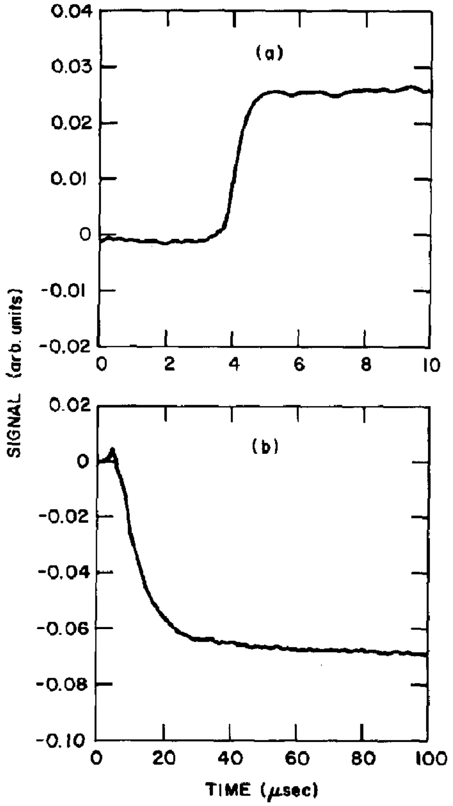

Fig. 4. Transient loss of disilane (a) and formation of silane (b) on microsecond timescales.

tously sit in valleys of the disilane spectrum whenever possible. Corrections to the silane quantum yield due to interference from the disilane spectrum would not significantly change the interpretation of the results.

4. Discussion

Before discussing the quantum yield results, it is useful to consider what electronic state is prepared when disilane is excited at 193 nm. The answer to this question is not entirely clear, since relatively little electronic spectroscopy has been done on disilane and high level ab initio calculations for the excited states have not yet been carried out. The most complete studies of disilane electronic spectroscopy thus far are recent synchrotron absorption [3] and electron energy loss spectroscopy studies [16]. Both studies conclude that the lowest energy transition in the absorption spectrum is a Rydberg transition involving excitation of a $2a_{1g}$ silicon–silicon bonding electron to the 4s Rydberg level. The singlet transition is dipole forbidden and should be weak. A triplet transition involving the same orbitals is expected to lie at slightly lower energy. The electron energy loss study suggests that the lowest valence transition is at 7.6 eV (164 nm). While the low resolution optical spectra near the electronic absorption threshold appear continuous, the EELS spectra show weak vibrational structure. Therefore, based on the current understanding of disilane spectroscopy, we conclude that single photon absorption at 193 nm excites the $4s \leftarrow 2a_{1g}$ transition and that the upper state is not purely dissociative.

In order to interpret the quantum yield results in terms of primary photodissociation pathways, it is necessary to consider the timescale of the experiment. The fastest non-detector limited signal rise rather which should be easily discernible is about 2×10^5 s^{-1}. If such processes were due to radical–molecule reactions between disilane and primary photoproducts, the bimolecular rate constants for the reactions would have to be less than $\approx 10^{-10}$ cm^3 molecule^{-1} s^{-1}, i.e. slower than gas kinetic. The slowest signal rise component to which the apparatus should be sensitive is about 5×10^3 s^{-1}. Processes slower than this will be washed out by diffusion of products out of the probe beam and diffusion of disilane back into the photolysis volume.

These limits provide the key to interpreting the photodissociation process because the expected photoproducts can be divided into two groups, those that are expected to react gas kinetically with disilane and those that react too slowly for the results to be observed in competition with diffusion. Given the possible complexity of the photochemistry alluded to in section 1, it is unreasonable to expect that the measurement of two quantum yields will provide a complete understanding of disilane photodissociation. Nevertheless, a reasonably consistent picture for the types of products generated can be deduced. The twenty energetically allowed photodissociation channels can produce twelve distinct transient chemical species [4], ignoring formation of different electronic states of some of the species. The only stable primary photoproducts are silane and molecular hydrogen. The transient species can be grouped into silylenes and silylidynes, SiH_2, SiH_3SiH, SiH and $SiSiH_2$; silicon monoradicals, SiH_3, Si_2H_5, H_2SiSiH; and closed-shell disilicon species, H_2SiSiH_2 and $Si(H_2)Si$. The remaining possible products are hydrogen atoms, silicon atoms and the diatomic Si_2. Silylene reacts gas kinetically with disilane [8] and with propylene [15]. We assume that the other silylenes exhibit similar kinetic behavior. Silylidyne reacts rapidly with silane [17] and we therefore assume that it will react rapidly with disilane and propylene. Under our concentration conditions, the reactions of the monoradicals and hydrogen atoms with disilane would be too slow to be observed [18]. We assume that the closed-shell species are unreactive with disilane. Nothing is known, experimentally, about the chemistry of these molecules. Silicon atoms and Si_2 are probably relatively unreactive with disilane. They are ground state triplets and would be likely to react by hydrogen abstraction. Abstraction from disilane is strongly endothermic in both cases, however [19,20].

Given these experimental observations and assumptions, the quantum yield data can be interpreted as follows. The prompt loss of disilane represents loss due to photolysis plus any loss due to reaction of disilane with the silylidynes and silylenes generated. Since addition of a fivefold excess of propylene does not change the observed quantum yield, we conclude that the primary dissociation quantum yield is 0.7 ± 0.1 and that production of silylidynes and silylenes accounts for less than 20% of the photoproducts. This leaves 20–40% of the excited disilane to decay without dissociating either by fluorescence or non-radiative processes. Since the total pressure in our experiments is 5–10 Torr, collisional processes may play a role if the excited state has any appreciable (nanosecond) lifetime.

The risetime of the silane signal is dominated by vibrational relaxation to the vibrational ground state. This process is slow because the lowest vibrational frequency of silane is 910 cm^{-1}. Under our conditions the final stages of the vibrational relaxation are dominated by collisions with undissociated disilane and with CF_4 when it is present. Helium is inefficient in removing at least the final quanta of vibrational energy from silane, as evidenced by the fact that the silane signal risetime does not increase noticeably when the helium pressure is increased from 2 to 10 Torr. The risetime does increase when CF_4 is added or when more disilane is present. The quantum yield of silane does not however, increase when the disilane concentration is increased by a factor of five. From these observations, we conclude that we are sensitive only to the primary yield of silane. The quantum yield of 0.10 ± 0.03 is consistent with the conclusion that silylenes and silylidynes account for less than 20% of the dissociation, since the silicon containing products which would be produced in conjunction with silane are SiH_2, SiH and Si.

Our results contrast with the results of Perkins and Lampe at 147 nm [6], in that they propose a primary quantum yield of 1.0 and quantum yields of 0.61 and 0.18 for production of silylene and silylsilylene. The differences may reflect the fact that they are exciting higher Rydberg levels and possibly purely dissociative valence states.

Our interpretation of the quantum yields at 193 nm leads to the conclusion that the majority of photoproducts are reasonably kinetically stable monoradical and/or closed-shell silicon species. This helps to explain why disilane is such an efficient silicon source in photochemical CVD at 193 nm. Very little of the silicon is lost as silane and most of the photoproducts are long enough lived to diffuse to film growth surfaces. Our results also suggest that further direct time-resolved product studies are necessary, since disilane may be a rich photochemical source of silyl radicals and disilicon species for further spectroscopic and kinetic studies. It is important to note that the quantum yield results apply only to conditions where the excimer laser repetition rate is comparable to the gas residence time so that multiple photolysis does not occur. When the excimer laser repetition rate was increased to 20 s^{-1} a strong infrared fluorescence signal was observed. Furthermore, in complementary molecular beam sampling mass spectrometry studies [21], we have observed that the quantum yield for loss of disilane increases from 0.7 at low repetition rates to a value of around 4 at higher repetition rates. These intriguing phenomena are currently under investigation.

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