

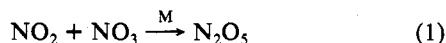
$$K_{1,2} = 1.33 \times 10^{-27} (T/300)^{0.32} e^{11080/T} \text{ cm}^3 \text{ molecule}^{-1} \quad (\text{ref } 4)$$

$$K_{1,2} = 1.77 \times 10^{-27} e^{11001/T} \text{ cm}^3 \text{ molecule}^{-1} \quad (\text{ref } 17)$$

which correspond to an equilibrium constant of  $K_{1,2} = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K.

It can be seen that the present directly determined value of  $K_{1,2}$  at 298 K is a factor of 1.5-1.8 higher than these literature values, though in agreement within the combined likely overall error limits. The reasons for these discrepancies are not known at the present time but, as discussed in the Experimental Section, are probably not due to uncertainties in the  $\text{NO}_3$  radical absorption cross section used in this work.

The present equilibrium constant at 298 K, when combined with the rate constant data for the  $\text{N}_2\text{O}_5$  thermal decomposition,<sup>5,6</sup> as evaluated by Malko and Troe,<sup>4</sup> yields a rate constant for reaction 1 of  $k_1 = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 760-torr



total pressure, with an estimated overall uncertainty of a factor of ~1.5-2.0. This value for  $k_1$  is in good agreement with the experimental value of  $k_1 = (2.0 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined by Fowles et al.<sup>7</sup> at ~80-torr total pressure (although this rate constant is still expected to be in the falloff region between second- and third-order kinetics in this pressure regime<sup>8</sup>). Furthermore, this estimated value of  $k_1$  is in reasonable agreement with, though higher by a factor of ~1.4 than, the rate constant of  $k_1 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  estimated by Kircher et

al.<sup>8</sup> at 298 K and 760-torr total pressure of  $\text{N}_2$  (using the Troe falloff expression) from experimental data obtained over the range 20-700-torr total pressure.

Finally, the use of the present value of  $K_{1,2}$  will result in the values of the room-temperature rate constants for  $\text{NO}_3$  radical reactions with organics determined recently in these laboratories<sup>19-23</sup> being increased by a factor of 1.8.

*Note Added in Proof.* Kircher et al.,<sup>8</sup> using their rate constant data for reaction 1 and the literature data<sup>5,6</sup> for reaction 2, have derived the expression  $K_{1,2} = 3.15 \times 10^{-30} T e^{11350/T} \text{ cm}^3 \text{ molecule}^{-1}$ . This leads to  $K_{1,2} = 3.26 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K, in good agreement with the value determined here.

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*Registry No.*  $\text{NO}_2$ , 10102-44-0;  $\text{NO}_3$ , 12033-49-7.

*Supplementary Material Available:* Table I, listing experimental data for the  $\text{N}_2\text{O}_5$ - $\text{NO}_2$ - $\text{NO}_3$ -air systems (6 pages). Ordering information is available on any current masthead page.

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## Infrared Photochemistry of Alkyl- and Arylsilanes

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The multiple infrared photon decomposition (MIRPD) mechanisms of ethylsilane, *n*-butylsilane, and phenylsilane have been investigated. Elimination of  $\text{SiH}_4$  proceeds via a four-center activated complex involving H atoms  $\beta$  to the Si. When this reaction path is not possible, extensive fragmentation of the organic group may occur. The  $\text{SiH}_4$  eliminated in these reactions may then undergo secondary MIRPD to produce  $:\text{SiH}_2$ , which may in turn deposit on and/or react with adjacent surfaces to produce various forms of amorphous silicon (a:Si-H). The composition and morphology of these deposited films have been investigated.

### Introduction

Much work has been directed toward understanding the kinetics and mechanism of reactions of the simple silanes. It is only recently, however, that the primary dissociation pathways have been established. Secondary reactions have often obscured the primary processes and, as a result, progress in establishing the primary reaction steps in conventional thermal, mercury-sensitized, and photochemical reaction systems has been slow.

The thermal studies of silane, for example, are complicated by a large number of secondary and surface reactions, which has prevented the unambiguous characterization of the primary

photolysis process. Hogness et al.<sup>1</sup> first presented evidence that the primary process in silane is unimolecular and first order; later Purnell and Walsh<sup>2</sup> proposed a mechanism which was not first order, but rather free-radical induced. Since publication of these two preliminary results, several other photochemical experiments have shown that both processes may be important. Thermal-shock-tube studies, on the other hand, have clearly shown the primary process to be unimolecular. In thermal and photochemical studies of other simple silanes, such as  $\text{Si}_2\text{H}_6$ ,  $\text{CH}_3\text{SiH}_3$ , and

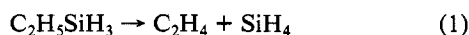
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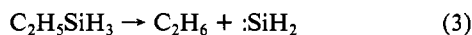
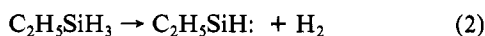
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$C_2H_5SiH_3$ , similar problems arise in attempts to resolve the question of primary dissociation pathways.

The decomposition of ethylsilane has been studied by Simons et al.,<sup>3-5</sup> using chemical activation, but no information on the thermal chemistry of  $RSiH_3$  ( $R > \text{ethyl}$ ) is available. In the Simons work,<sup>5</sup> it was postulated that the primary reaction mechanism was four-center unimolecular elimination of ethylene:



However, this could not be experimentally confirmed because of complications due to secondary reactions between the methylenes which were used to chemically activate ethylsilane. Other primary processes suggested were



In recent years, multiple infrared photon dissociation (MIRPD) has proven to be an effective method for initiating unimolecular reactions and preparing reactive intermediates.<sup>6</sup> This technique possesses several advantages over conventional thermal methods, in that complicated secondary gas-phase and wall reactions may be virtually eliminated. The MIRPD of monosilane has been investigated,<sup>7</sup> but no work on polysilanes or substituted organosilanes has been reported. Both alkylsilanes, such as ethyl- and *n*-butylsilane, and arylsilanes, such as phenylsilane, possess strong infrared absorptions in the 920–950- $cm^{-1}$  region coinciding with the output of the  $CO_2$  laser<sup>8</sup> and thus are suitable for candidates for MIRPD experiments.

A practical motivation for establishing the mechanism of the dissociation process is that silane has been shown to be a good precursor for silicon film formation by chemical vapor deposition (CVD). Knowledge of the reactive species generated is essential for understanding the composition of these films by using various deposition methods, such as rf and dc discharge in monosilane,<sup>9</sup> and CVD,<sup>10</sup> homo-CVD,<sup>11,12</sup> or laser-assisted CVD<sup>13-15</sup> in monosilane or disilane.<sup>16</sup>

Thus, the present work has two principal objectives: first, to establish the primary mode of decomposition of ethyl-, *n*-butyl-, and phenylsilane following MIRPD; second, to identify the reactive species produced which may give rise to the formation of silicon thin films.

## Experimental Section

**Materials.** The reagents, ethylsilane, *n*-butylsilane, and phenylsilane, were obtained from Petrarch Systems, Inc. Each sample was degassed by several freeze (–196 °C)–pump–thaw cycles. Ethylsilane was also distilled by using a pentane/liquid  $N_2$  slush

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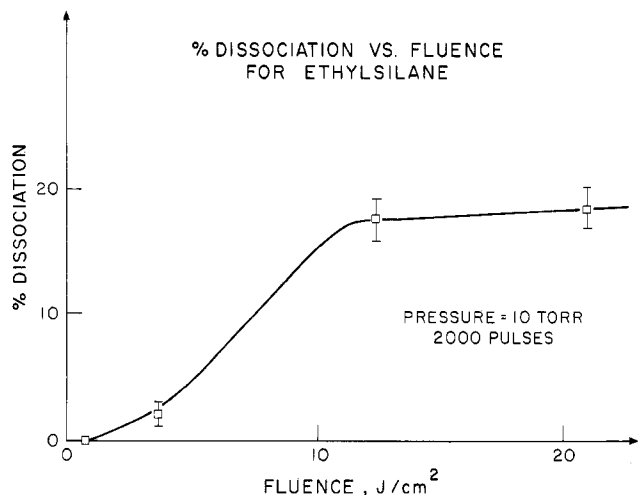


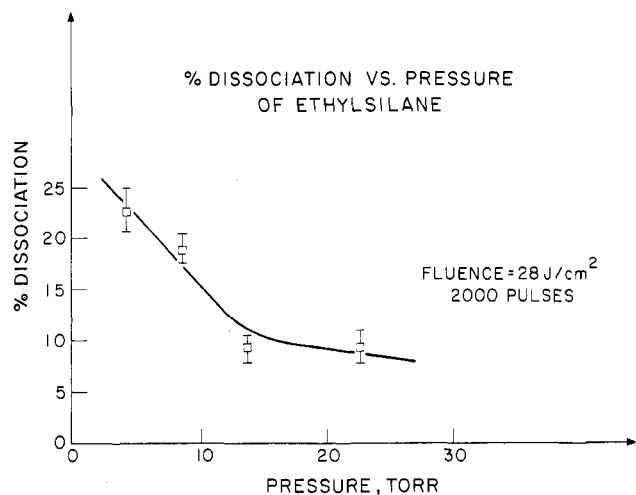
Figure 1. Net dissociation yield for ethylsilane at 10 torr vs. laser fluence (2000 pulses at 10P(20) line).

at –160 °C. The other reagents were degassed several times at room temperature. Research-grade deuterium was obtained from Matheson Co. (stated purity 99.5%) and used without purification. Infrared analysis of the materials showed no detectable impurity. Gas-chromatographic product analyses revealed no traces of silane, disilane, or other traces of products resulting from possible sample decomposition in any of the materials.

**Apparatus and Procedures.** Samples were prepared for irradiation by filling a 2.5 cm diameter × 10 cm long glass cell, equipped with side arm and fitted with NaCl windows, to a specific pressure. The pressure range in these experiments was from 1 to 25 torr. Infrared absorption measurements were taken before and after each sample irradiation by using a Beckman IR spectrometer. The high-resolution Fourier transform infrared (FT-IR) spectrum of each sample was recorded by using a Nicolet 7199 spectrometer, with a resolution of 0.06  $cm^{-1}$ . The FT-IR spectrum revealed several absorption lines of the Si–H deformation mode of these compounds to be coincident with lines from a  $CO_2$  laser. The laser lines used were 10P(20) (944  $cm^{-1}$ ) for ethylsilane and *n*-butylsilane and 10P(32) (933  $cm^{-1}$ ) for phenylsilane. The Tachisto 215G TEA laser was tuned to one of these lines and checked with an Optical Engineering  $CO_2$  spectrum analyzer. Pulse energy was varied from 0.1 to 0.5 J, as measured from the integrated output from a Scientech thermopile. The beam was used either unfocused, slightly collimated, or focused. The beam was collimated by using a telescope consisting of two 27.9 cm fl concave and convex AR Ge lenses. The beam waist was determined by measuring the transmission through an aperture at both ends of the cell. Energy fluences were calculated as described by eq 6 in ref 17. Tighter focusing was achieved by using a 27.9 cm fl Ge lens. The number of laser pulses ranged from 10 to 3500 shots.

**Analytical.** Following each irradiation, the contents of the cells were analyzed by IR and then attached to an injection line of a gas sampling loop in a Perkin-Elmer Model Sigma-3B gas chromatograph with a flame ionization detector connected to a Spectra-Physics Minigrator integration recorder. The GC was equipped with a 6 ft × 1/8 in. o.d. 30/60 mesh silica gel column packed in Teflon tubing and was operated at a column temperature of 80 °C, detector temperature at 125 °C, injector temperature of 60 °C. Prepurified nitrogen was used as the carrier gas, at a column inlet pressure of 38 psi. A typical chromatogram of the cell content after irradiation of ethylsilane showed the peaks to be fully resolved and reproducible. Standard mixtures were prepared to calibrate the gas chromatograph. Identification of products of reaction by GC was based on comparison of product retention time to retention times of standards (ethylene, 1-butene, acetylene, monosilane); a number of uncharacterized peaks were

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**Figure 2.** Net dissociation yield vs. ethylsilane pressure for 2000 pulses at 28 J/cm<sup>2</sup>, 10P(20) line.

observed in phenylsilane photolysis which were characterized only as to retention time and relative GC response. After gas-chromatographic analysis, the cell was evacuated and an IR spectrum of the empty cell was measured. Mass-spectral analyses were carried out at the MIT Spectrometry Laboratory by using a Varian MAT200 mass spectrometer.

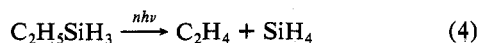
#### Mechanism of Gas-Phase Decomposition

**Results for Ethylsilane.** Mass-spectrometric analysis of 25-torr ethylsilane samples irradiated with a collimated beam (fluence between 0.2 and 0.28 J/cm<sup>2</sup> at the 10P(20) line) revealed the presence of unreacted ethylsilane (*m/e* 60), silane (*m/e* 32), and ethylene (*m/e* 28). Silane and ethylene were corrected for contributions due to the background N<sub>2</sub> (*m/e* 28) and O<sub>2</sub> (*m/e* 32) in the atmosphere. Our analysis showed the absence of Si<sub>2</sub>H<sub>6</sub> (*m/e* 62), Si<sub>3</sub>H<sub>8</sub> (*m/e* 92), and higher molecular weight (i.e., *m/e* > 60) species. Gas-chromatographic analysis of the irradiated ethylsilane sample also gave no evidence for the formation of Si<sub>2</sub>H<sub>6</sub> or Si<sub>3</sub>H<sub>8</sub>. The primary products observed were thus SiH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and a small trace of C<sub>2</sub>H<sub>6</sub> (<1%).

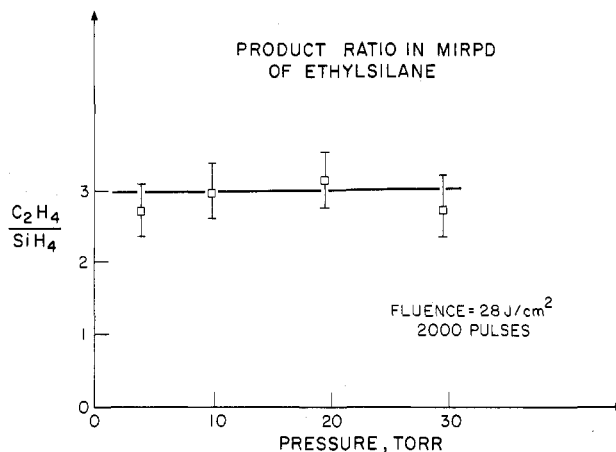
The net dissociation of ethylsilane following 2000 pulses was determined as a function of laser fluence (see Figure 1). There appears to be a threshold for dissociation at a fluence of 0.3 J/cm<sup>2</sup> or less; as the fluence increases, the yield tends to saturate. This behavior has been observed in chemical systems, such as ethyl acetate,<sup>18,19</sup> which exhibit "large-molecule" behavior. The effect of increasing pressure is to decrease the net dissociation yield at a fixed fluence, as shown in Figure 2. This, too, is characteristic of large-molecular behavior.

When the laser beam is focused with a 27.9 cm fl Ge lens, visible luminescence is observed in the focal region. Product analysis of the cell contents following irradiation shows the presence of acetylene. The formation of this product has been shown to result from the secondary multiphoton dissociation of vibrationally hot ethylene under focused-beam conditions.<sup>20</sup> There was no evidence for the formation of Si<sub>2</sub>H<sub>6</sub> or higher silanes under these conditions on the basis of gas-chromatographic and infrared analysis.

There are several possible mechanisms which could explain the presence of the products observed from the photolysis experiments with collimated and uncollimated beams. One such mechanism proposed by Simons et al.<sup>3-5</sup> is the molecular elimination of silane from ethylsilane:

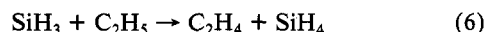
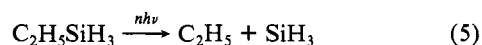


Another possible mechanism is that of C-Si bond fission followed



**Figure 3.** Pressure dependence of ethylene/silane product ratio in IRMPD of ethylsilane (2000 pulses of 10P(20) line at 28 J/cm<sup>2</sup>).

by secondary bimolecular reaction of the intermediate to give silane and ethylene, i.e.

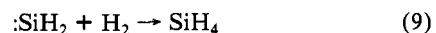
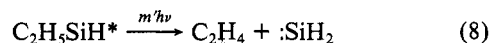
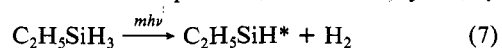


These two primary mechanisms can be distinguished by scavenging experiments.

Deutsch has shown deuterium to be a good scavenger of SiH<sub>3</sub> and SiH<sub>2</sub> radicals in SiH<sub>4</sub>/D<sub>2</sub> irradiation experiments.<sup>7a</sup> We prepared mixtures of 52 torr of 4:1 D<sub>2</sub>:C<sub>2</sub>H<sub>5</sub>SiH<sub>3</sub> and irradiated the mixture for 2000–3000 laser pulses at a fluence of 28 J/cm<sup>2</sup> with a collimated 10P(20) CO<sub>2</sub> laser beam. Mass-spectroscopic analysis of these mixtures shows no evidence for products SiH<sub>3</sub>D, C<sub>2</sub>H<sub>5</sub>D, or SiH<sub>2</sub>D<sub>2</sub>. Moreover, the branching ratio, C<sub>2</sub>H<sub>4</sub>/SiH<sub>4</sub>, for these experiments appeared to be constant.

The results of these experiments suggest that the initial dissociation process is most likely four-center elimination (eq 1), as Simons et al.<sup>3-5</sup> have proposed. This conclusion is not too surprising, because a great number of infrared laser induced reactions tend to proceed via molecular elimination pathways.<sup>21</sup> Other experimental evidence in accord with a four-center unimolecular elimination reaction is the [C<sub>2</sub>H<sub>4</sub>]/[SiH<sub>4</sub>] product ratio dependence on pressure shown in Figure 3. For irradiation by the 10P(20) CO<sub>2</sub> laser line for 2000 pulses and a fluence of 28 J/cm<sup>2</sup>, the product ratio is nearly constant with pressure.

Simons et al.<sup>3-5</sup> found three-center elimination of hydrogen (eq 2) to be another favored reaction pathway in the chemical activation studies. This was also confirmed from chemical activation studies on ethyl-d<sub>3</sub>-silane. In the MIRPD studies, such a pathway could also lead to the observed products, silane and ethylene, by



However, the absence of C<sub>2</sub>H<sub>5</sub>SiHD<sub>2</sub> and SiH<sub>2</sub>D<sub>2</sub> from deuterium-scavenging experiments and the constant [C<sub>2</sub>H<sub>4</sub>]/[SiH<sub>4</sub>] dependence on pressure do not support the above mechanism for IRMPD of ethylsilane.

The kinetics of the four-center elimination mechanism (eq 4) predict a [C<sub>2</sub>H<sub>4</sub>]/[SiH<sub>4</sub>] ratio of unity. The fact that this ratio is closer to 3 (see Figure 3) suggests a loss of SiH<sub>4</sub>. This could result from secondary multiphoton dissociation of SiH<sub>4</sub> (which is most likely vibrationally hot) to give hydrogen and silylene, :SiH<sub>2</sub>. The elimination of H<sub>2</sub> was suggested to be the key decomposition step in the SiF<sub>4</sub>-sensitized MIRPD of silane;<sup>22</sup> in that work Si<sub>2</sub>H<sub>6</sub> was observed as a reaction product, presumably formed

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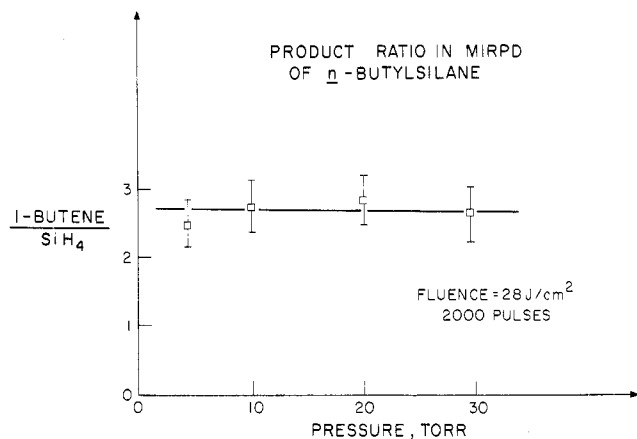


Figure 4. Pressure dependence of 1-butene/silane ratio in IRMPD of *n*-butylsilane (2000 pulses of 10P(20) line at 28 J/cm<sup>2</sup>).

by insertion of :SiH<sub>2</sub> into SiH<sub>4</sub>. The insertion products are not found under our experimental conditions because, in contrast to the SiF<sub>4</sub>-sensitized experiments, all the SiH<sub>4</sub> is vibrationally excited, and thus any such products would tend to decompose. In the multiphoton dissociation of silane itself, Deutsch<sup>7a</sup> has also shown that the dominant reaction channel is the formation of :SiH<sub>2</sub> and H<sub>2</sub>. The :SiH<sub>2</sub> formed would then diffuse to the cell walls and windows to form amorphous silicon (a:Si-H), which was observed as a brownish-yellow deposit with both collimated and focused-beam conditions. The formation of this deposit was not as visibly apparent when the experiments with added D<sub>2</sub> were performed; this can be rationalized in terms of the D<sub>2</sub> collisionally relaxing the vibrationally excited SiH<sub>4</sub> product, thus quenching the secondary IRMPD process and hence the formation of both silylene fragment and deposit. The characterization of these deposits is discussed more fully in the following section; we note here only that :SiH<sub>2</sub> diffusion to and reaction on the walls of the reactor vessel has been long believed to be the origin of surface deposits in reactions of silicon compounds.<sup>2,22-24</sup>

**Results for *n*-Butylsilane.** Butylsilane was chosen in order to investigate further the laser-induced elimination reaction. It is also attractive in that if the primary dissociation processes in alkylsilanes involved free radicals, then it could be clearly distinguished from an elimination process by the difference in products observed.

Photolysis of *n*-butylsilane was carried out over the same pressure and fluence range as with ethylsilane. The dependences of net dissociation on fluence and pressure were similar to those obtained with ethylsilane. Products observed by GC analysis included 1-butene, monosilane, ethylsilane, ethylene, and several small unidentified peaks. Figure 4 shows a plot of [1-C<sub>4</sub>H<sub>8</sub>]/[SiH<sub>4</sub>] showing again a constant ratio over the experimental pressure range. There was no evidence for the formation of *trans*-2-butene, *cis*-2-butene, or disilane on the basis of gas-chromatographic and infrared analysis.

These results are again consistent with the four-center elimination mechanism described previously for ethylsilane. If Si-C bond fission did occur, the resulting species would be silyl radical, SiH<sub>3</sub>, and *n*-butyl radical. Products resulting from *n*-butyl radical decomposition are known to be ethylene and propylene;<sup>25,26</sup> the mechanism of propylene formation is suggested to be either prior rearrangement to 2-butyl radical<sup>25</sup> or a four-center internal H abstraction,<sup>26</sup> but this point has not been resolved. 2-Butene would also be a likely product of subsequent reactions of the 2-butyl radical. In any case, the absence of propylene, 2-butene, or butane<sup>26</sup> in the products indicates the absence of a free-radical

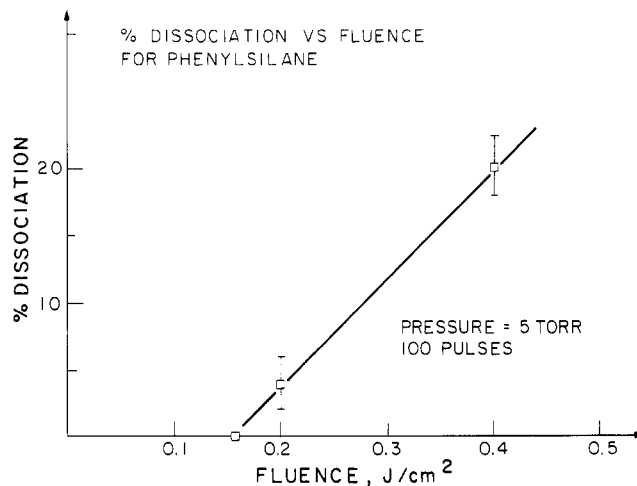
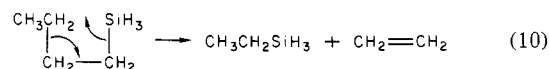


Figure 5. Net dissociation yield for phenylsilane at 5 torr vs. laser fluence (100 pulses at 10P(32) line).

pathway in this reaction. A possible mechanism for the production of the ethylsilane and ethylene products may be a four-center elimination involving transfer of an ethyl group:



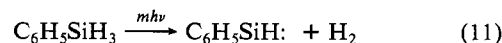
The formation of a brownish-yellow deposit on the walls and windows of the cell was again observed with collimated or focused-beam conditions. Given the fact that the [C<sub>4</sub>H<sub>8</sub>]/[SiH<sub>4</sub>] ratio is greater than unity, we again surmise that secondary multiphoton dissociation is occurring to give :SiH<sub>2</sub> which diffuses to the cell walls to form the observed deposit.

**Results for Phenylsilane.** Ojima et al.<sup>27</sup> have shown that phenylsilane reacts upon heating in the presence of rhodium catalysts to form a phenylsilane intermediate which then gives 1,2-diphenyldisilane and other polysilanes. No other thermal or photochemical dissociation studies of this molecule can be found in the literature.

Photolysis of phenylsilane was observed to be exceedingly more facile than for the alkylsilanes. Figure 5 shows the relationship between percent dissociation and fluence at the 10P(32) line with an apparent threshold for dissociation at a fluence of less than 0.2 J/cm<sup>2</sup> with an unfocused beam. At 0.4 J/cm<sup>2</sup>, 20% dissociation (5 torr) was observed after only 100 pulses; with ethylsilane at the 10P(20) line 2000 pulses at 28 J/cm<sup>2</sup> were required to obtain this dissociation level at 5.5 torr. Under standard conditions, i.e., 10-torr cell pressure, 28 J/cm<sup>2</sup> and 2000 pulses, percent dissociation of ethyl-, *n*-butyl-, and phenylsilane, respectively, was 19%, 14%, and 70%.

Product analysis of photolyzed samples (5–10 torr) of phenylsilane at the 10P(32) line shows the principal product species to be ethylene and acetylene (each ~15% of the total gaseous products), monosilane (~5%), and ethylsilane (1–2%). There were also several other major uncharacterized products and numerous minor products; complete characterization of all the products species was not possible. An analysis of the ratios of [C<sub>2</sub>H<sub>4</sub>]/[SiH<sub>4</sub>], [C<sub>2</sub>H<sub>2</sub>]/[Ph-SiH<sub>3</sub>], and [C<sub>2</sub>H<sub>4</sub>]/[Ph-SiH<sub>3</sub>] in the photolyzed gas mixture showed a direct relation between fluence and ratio, suggesting that there are significant secondary reactions involved in the photolysis of the phenyl radical.

Several mechanisms for the IRMPD may be considered. One would be a three-center molecular elimination process to give phenylsilene



or a free-radical process beginning with the breaking of the C-Si bond

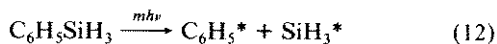
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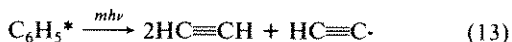
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followed by decomposition of the "hot" phenyl radical



The presence of  $\cdot\text{C}\equiv\text{CH}$  leads to formation of polyacetylenes and, ultimately, production of the soot which, depositing on adjacent surfaces, would account for the carbonaceous content of the observed deposits as described below. A four-center elimination, as in the case of the alkylsilanes, might also occur; this could yield  $\text{SiH}_4$  and benzyne. The benzyne would dimerize with an association rate constant of  $7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , forming biphenylene;<sup>28</sup> condensed biphenylene could also contribute to the carbon content of the observed deposits.

The formation of the brownish-yellow deposit on the cell walls was again observed; even at 0.19 J/pulse (unfocused beam) this deposit was observed after only one or two pulses in a 5-torr phenylsilane atmosphere. On the basis of the XPS analysis of these films (following section), this deposit contains silicon and is probably a form of a:Si-H, although it is heavily contaminated with carbon.

### Characterization of Deposition Products

As noted in the preceding section, a brownish-yellow deposit was formed on the walls and windows of the cell during the photolysis, most copiously with phenylsilane. Initial analysis of this deposit was carried out by simply measuring the infrared transmittance of the deposits on the windows, following prolonged evacuation of the photolysis cell to remove any adsorbed gaseous species. The most prominent features observed were a broad band around  $1020\text{--}1080 \text{ cm}^{-1}$ , and a less intense feature in the  $2100\text{--}2200\text{-cm}^{-1}$  region.

The lower-frequency absorption coincides with that measured by electron energy-loss spectroscopy (EELS) on Si(100) following exposure to  $\text{H}_2\text{O}$  vapor at temperatures above  $280 \text{ }^\circ\text{C}$  and is assigned to a bridging oxygen between to silicon atoms.<sup>29</sup>



Support for this assignment is given by the observation that, if phenylsilane is irradiated in an inadequately evacuated cell, an explosion occurs in the gas (presumably with the residual oxygen in the cell), and the  $1020\text{--}1080\text{-cm}^{-1}$  feature is markedly enhanced in the absorbance of the resulting deposit. The  $2100\text{--}2200\text{-cm}^{-1}$  feature is observed in EELS on Si(100) exposed to  $\text{H}_2\text{O}$  vapor at  $T < 280 \text{ }^\circ\text{C}$ ,<sup>29</sup> and also in the infrared spectrum of amorphous Si deposited by sputtering in a 10%  $\text{H}_2$  atmosphere.<sup>30</sup> This band is assigned as a Si-H stretch, either of a single hydrogen attached to a Si "dangling bond" at the surface<sup>29</sup> or to symmetric and antisymmetric  $\text{SiH}_2$  modes.<sup>30</sup> Both the Si-oxygen and Si-hydrogen structures are consistent with the proposed mechanism, i.e., formation of silylene ( $\text{:SiH}_2$ ) and its migration to the surface, followed by reaction with the monolayer of water chemisorbed on the sodium chloride surface upon which the film is actually observed.

In order to obtain more detailed characterization of these surface deposits, conditions were chosen in which the films formed by MIRPD of either silane, disilane, or phenylsilane could be collected on a suitable substrate and subsequently analyzed. Four substrates were used: silver foil (Ag), molybdenum foil (Mo), glass slips, and fused silicon substrates. The glass and silicon substrates were dipped in concentrated HF and washed with distilled water immediately prior to use. The Ag foil was heated red hot under vacuum ( $10^{-7}$  torr) to remove oxides and stored in methanol. The Mo foil was washed with concentrated  $\text{H}_2\text{SO}_4$  followed by distilled water and stored in methanol.

The substrates were positioned in the cell several millimeters beneath the focal point of the laser beam. The cell was then filled

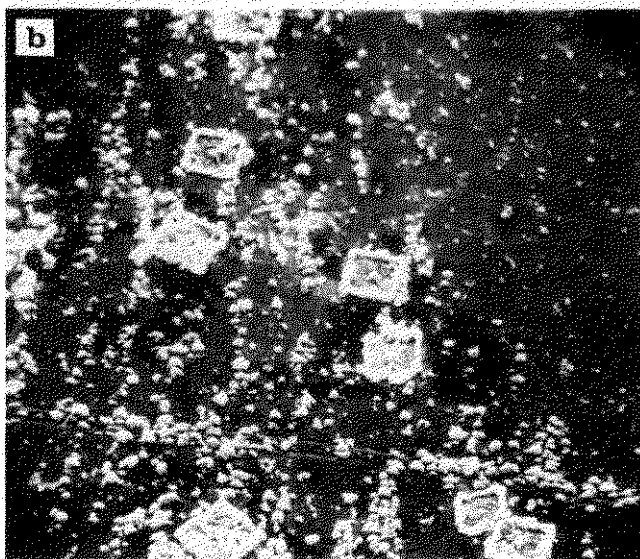
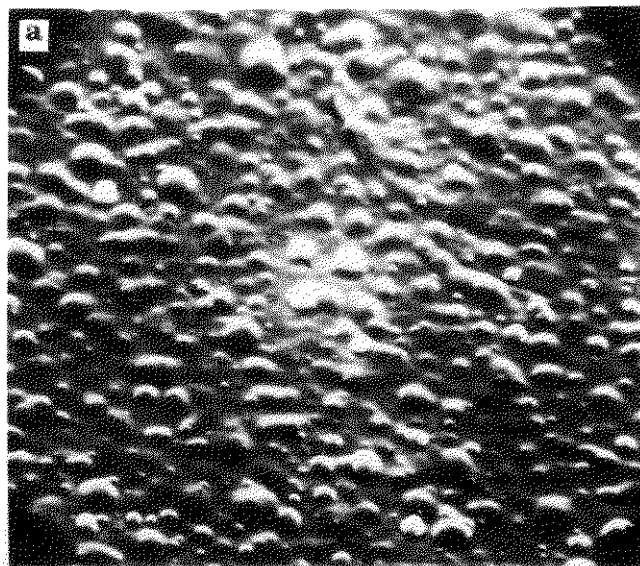


Figure 6. (a) SEM (2000 $\times$ ) of film deposited on Ag substrate by IRMPD of phenylsilane at high infrared fluence. (b) SEM (2000 $\times$ ) of film deposited on Ag substrate by IRMPD of disilane.

with a known pressure of reactant (6–11 torr) and room-temperature photolysis (0.19–0.33 J/pulse) was carried out for a specified number of pulses (10–2000). The beam was unfocused for phenylsilane and disilane; in monosilane-based film formation the beam was focused ( $\sim 28 \text{ J/cm}^2$ ). Some films were formed at elevated temperature ( $110 \text{ }^\circ\text{C}$ ); temperature was maintained by heating tape wrapped around the reaction chamber.

Following film formation, the substrate was removed and stored under vacuum. Samples on the Ag and Mo substrates were analyzed by X-ray photoelectron spectroscopy (XPS) and/or Auger spectroscopy by using a Perkin-Elmer 548 X-ray photoelectron spectrometer or 590A scanning Auger microprobe, respectively. Scanning electron micrographs (SEM's) were obtained with a Cambridge Mark 2A electron microscope. All of these instruments were provided at the Central Facilities for Surface Analysis and Scanning Electron Microscopy of the MIT Center for Materials Science and Engineering.

In the case of silane, a smooth film was deposited on the Ag surface. Auger microprobe analysis showed that this film consists of  $\sim 50$  atom % Si and  $\sim 25$  atom % O (H is not detected). By  $\text{Ar}^+$  sputtering the surface, we found that the film formed is on the order of  $20\text{--}50 \text{ \AA}$  thick (for  $\sim 2000$  laser pulses); beneath this layer, Ag (60 atom %) was seen, indicating about 40% surface coverage by deposited material. In addition, there is a C atom concentration of 20–25%, which must be adventitious, i.e., in-

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produced as contamination either during the deposition or in subsequent handling. This carbon contamination must be taken into account in evaluating the results of these analyses.

Phenylsilane, on the other hand, produced a thick deposit having a nodular appearance (shown in Figure 6a). After a few atomic layers of oxidized material are stripped away by Ar<sup>+</sup> sputtering, an average film composition of ~75 atom % C, ~18 atom % Si, and ~7 atom % O was encountered, which extended uniformly to a depth of many hundreds, perhaps even thousands, of angstroms. Ag was barely seen, even after extensive Ar<sup>+</sup> sputtering, indicating nearly complete surface coverage.

The deposit from MIRPD of phenylsilane was not entirely uniform, however. X-ray fluorescence analysis of the material shown in Figure 6a establishes that the lumps of nodules which were observed are silicon-rich material, while the "valleys" between the nodules are poorer in Si and richer in C. A similar nodular appearance, but on a much larger scale, has been observed in products of CW laser heating of SiCl<sub>4</sub><sup>31</sup> or of silane/ammonia mixtures.<sup>32</sup> Breiland et al. have observed<sup>33</sup> formation of gaseous Si<sub>2</sub> during silane CVD; these dimers could presumably go on to form silicon clusters prior to deposition. An extreme case of nonuniform deposition is illustrated in Figure 6b, which is an SEM of material deposited on Ag by MIRPD of disilane. In this case, the material has deposited as discrete nodules directly on the Ag surface: presumably, the square symmetric structures result from preferential nucleation at grain boundaries of Ag crystallites.

### Conclusions and Discussion

In this work, we have shown that the laser-induced unimolecular decomposition of alkylsilanes proceeds via a four-center elimination

mechanism involving H atoms β to the Si. In the case of phenylsilane, extensive fragmentation of the organic group may also occur. The more facile decomposition of the aryl species, as compared with the alkylsilanes, suggests that the multiple infrared photon excitation cross sections are appreciably larger for the latter system; a complete characterization of the MIRPD excitation process would require extensive analysis,<sup>34</sup> which was not carried out for these systems.

The SiH<sub>4</sub> eliminated in the reaction may undergo secondary MIRPD to produce :SiH<sub>2</sub>, which may then deposit on and/or react with nearby surfaces to produce various forms of amorphous silicon. The precise control over the identity and concentrations of the reactive species generated in the vapor phase, which is afforded by MIRPD initiation, makes this technique highly suitable for carrying out detailed investigations of the mechanism of the CVD process. In this connection, it would be very desirable to have a method available for direct observation of the postulated :SiH<sub>2</sub> intermediate; we are currently investigating the possibility of laser-induced fluorescence detection, using the  $\tilde{A}^1B_1-(\tilde{X})^1A_1$  transition,<sup>35</sup> as such a method.

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**Registry No.** Ethylsilane, 2814-79-1; n-butylsilane, 1600-29-9; phenylsilane, 694-53-1.

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## Stabilization of n-Type Silicon Photoanodes in Aqueous Solution by Electrostatic Binding of Redox Ions into Charged Polymers

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Electrostatic binding of redox-active ions into a polymer-coated electrode is demonstrated to be an effective method of improving photoelectrode stability. Pt and n-type Si electrodes have been coated with poly([4,4'-bipyridinium]-1,1'-diylmethylene-1,2-phenylenemethylene dibromide) (poly-oXV<sup>2+</sup>) and other viologen-based polymer films. The poly-oXV<sup>2+/+</sup> system is insoluble in aqueous solutions containing large anions such as ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and Fe(CN)<sub>6</sub><sup>4-</sup>. Cyclic voltmetry of modified electrodes in aqueous 1.0 M NaClO<sub>4</sub> shows behavior consistent with a reversibly electroactive, surface-confined species, E<sup>o</sup>/ (poly-oXV<sup>2+/+</sup>) = -0.45 V vs. SCE. In the presence of electroactive anions, n-type Si electrodes coated with poly-oXV<sup>2+</sup> show substantial improvements in photocurrent stability compared to naked n-Si electrodes. Negative ions from solution are sorbed by the positively charged poly-oXV<sup>2+</sup> units, providing efficient scavenging of photogenerated holes at the semiconductor surface. No improvement in stability is observed with positively charged solution ions, such as Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>. Variation in coverage of the polymer coating causes changes in the observed stabilization of photocurrent. The method may provide a useful framework for design of improved coatings for the stabilization of aqueous semiconductor/liquid interfaces.

We describe a novel approach to the stabilization of n-type semiconductor photoanodes. Most small band gap semiconductors undergo photocorrosion reactions in aqueous solutions which prevent them from sustaining conversion of light into electrical energy or fuels.<sup>1-3</sup> In certain instances, these decomposition

reactions can be suppressed by addition of high concentrations of solution redox reagents.<sup>4-10</sup> However, most redox additives

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