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Preliminary communication

ArF laser photolysis of tetraethyl- and tetravinyl-silane

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Abstract

The ArF laser-induced photolysis of tetraethyl- and tetravinyl-silane $(C_2H_n)_4Si$, ($n = 3$ and 5), affords C_2H_{n-1} unsaturates and a silicon-containing deposit. The reactions are suitable for use in low-temperature chemical vapour deposition of Si/C materials.

Keywords: Silicon; Silicon carbide; Laser photolysis; Tetraethylsilane; Tetravinylsilane

Tetraalkylsilanes show UV absorption maxima at < 200 nm, while those for tetraalkenylsilanes are red-shifted to wavelengths > 200 nm. Only the saturated silanes have been studied by UV photolysis in the gas phase; vacuum UV photolysis of $(CH_3)_nSiR_{4-n}$ (R = alkyl) affords a number of products resulting from a variety of primary photochemical processes [1], which become possible because the absorption of photons delivers energy higher than that needed for the cleavage of the Si–C and C–H bonds.

We have initiated studies on an excimer laser photolysis of R_4Si silanes, where R is an alkyl or alkenyl group, consisting of at least two carbons. In this communication, we report on ArF laser photolysis of tetraethyl- and tetravinyl-silane, showing that these reactions follow a single pathway, and demonstrating their suitability for use in chemical vapour deposition (CVD) of Si/C materials.

Tetraethylsilane (I) and tetravinylsilane (II), possessing absorptivity at 193.3 nm of 86 and 320×10^{-3} kPa^{-1} cm^{-1}, respectively, were laser-photolysed at vapour pressures 0.45 (I) and 0.9 (II) kPa I + II. Both photolyses were terminated at ca. 30% conversion. The dependence of the photolysis progress upon the time of irradiation (Fig. 1) reveals that (II) decomposes faster, evidently because of its higher absorptivity. Gaseous products and their quantities indicate that the

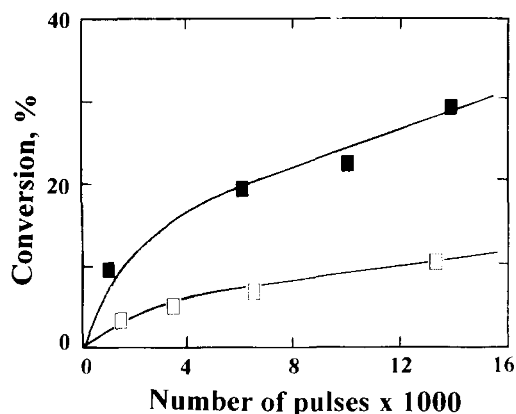

Fig. 1. The progress of the photolysis of $(C_2H_5)_4Si$ (□) and $(C_2H_3)_4Si$ (■).

Table 1
Quantities of products in photolysis of $(C_2H_n)_4Si$ [a]

n	Conversion, %	$(C_2H_n)_3SiH$, kPa	C_2H_{n-1}, kPa
3	14	0.03	0.45
	19	0.03	0.65
	29	0.04	0.90
5	15	0.03	0.20
	25	0.05	0.30
	33	0.08	0.40

[a] The observed products account for 94–100% decomposition of the parent compounds.

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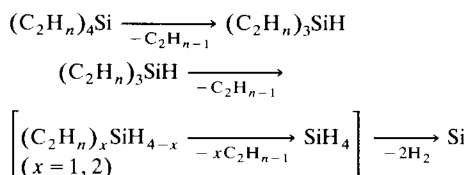


Scheme 1. Stepwise elimination process for ArF laser photolysis of silanes $C_2H_n)_4Si$, $n = 3, 5$.

only pathway for the photolytic decomposition is the elimination of ethene from (I) and of ethyne from (II) (Table 1). In both cases, triorganylsilanes $(C_2H_n)_3SiH$ ($n = 3, 5$) were observed, and can be considered as intermediate products. These facts suggest that both photolyses proceed by the same process, involving a sequence of the elimination of C_2H_4 and C_2H_2 and resulting in the formation of silicon (Scheme 1).

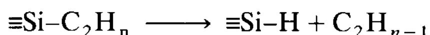
Neither of the other presumed intermediate $(C_2H_n)_xSiH_{4-x}$ ($x = 0$–2) compounds was detected by FTIR spectroscopy, even though they give a very strong absorption band in the region of ν_{Si-H} vibration. (Detection limit of $(C_2H_n)_xSiH_{4-x}$ ($x = 0$–2) compounds by FTIR spectroscopy is $\sim 3 \times 10^{-3}$ kPa.)

We are unaware of any other studies of ArF laser photolysis of R_4SiH_{4-n} ($n = 0$–4, R = alkyl or alkenyl). Similar photolysis of phenylsilanes [2,3] involves [4] a two-channel process, yielding PhSiH + H_2 and SiH_2 + PhH. It is clear that the presumed $(C_2H_n)_xSiH_{4-x}$ intermediates cannot follow either of these pathways and that they prefer to undergo the elimination of the C_2H_{n-1} molecules. Silane has a very small absorption cross-section [4,5] at 193 nm, so the photolytic decomposition rate using ArF lasers is very slow. This hazardous compound, used under a variety of conditions as a precursor for CVD of silicon, appears to be very efficiently produced from precursors (I) and (II) and to decompose to a silicon-containing material.

A grey solid deposit was, indeed, formed over the whole of the inside of the reactor during both photolyses. FTIR spectra of these materials on a KBr plate housed in the reactor during photolysis show absorption bands at the following wavenumbers: 730 (m), 1009, 1050 (both vs), 1242, 1415, 1450 (all w), 2115 (w), 2875, 2911, 2954, (all s) cm^{-1} [deposit from (I)]; 801 (vw), 1079 (vs), 1261, 1385, 1404 (vw) cm^{-1} [deposit obtained from (II)]. The broad absorption of the materials at $\sim$1000–1100 cm^{-1} is assignable to the Si–O stretch, and is attributed to the reaction of some intermediate species with traces of water tenaciously adsorbed on the KBr plate [6]. These spectra reveal that the deposited materials contain some carbon and hydrogen. The high yields of C_2H_4 and C_2H_2 (Table 1) accord with the fact that carbon moieties are very efficiently expelled into the gas phase during photolyses, and that the carbon content in both materials cannot be higher than $\sim$5–10%. We note that UV photolysis of organosilanes containing CH_3 groups bonded to the silicon yields polymeric material originating from $>Si{=}CH_2$ intermediates [1,7].

A brief comment on the suggested reaction scheme is appropriate. The energy of the photon at 193 nm corresponds to $\sim$620 kJ mol^{-1}, which is much greater than the energy needed to cleave the Si–C (360–370 kJ mol^{-1}) bond. The reaction sequence can occur as a photolytic pathway initiated by a direct absorption in the ground state of the $(C_2H_n)_xSiH_{4-x}$ ($x = 1$–4) molecules, or as a thermal route initiated by a fast E–V relaxation and sustained by exothermicity of the individual expulsions of C_2H_{n-1} molecules. The absence of the Si–C chromophores in SiH_4 results in this compound having absorptivity at 193 nm of only 0.2×10^{-3} kPa^{-1} cm^{-1}, which should lower its photolytic reactivity. The fact that silane is not accumulated in the system implies that this compound decomposes by the thermal mechanism [8]. The low absorptivity of $(C_2H_5)_xSiH_{4-x}$: [0.8 ($x = 1$), 1.2 ($x = 2$), 16 ($x = 3$) $\times 10^{-3}$ kPa^{-1} cm^{-1}], and relatively high absorptivity of $(C_2H_3)_xSiH_{4-x}$ [280 ($x = 1$), 230 ($x = 2$), 290 ($x = 3$) $\times 10^{-3}$ kPa^{-1} cm^{-1}] at 193 nm suggest a higher feasibility of photolytic decomposition of the latter intermediates. Low absorptivities of ethene and ethyne (0.5 and 3×10^{-3} kPa^{-1} cm^{-1}, respectively), and the shape of the curve showing the dependence on the degree of conversion on the number of pulses (Fig. 1), indicate that neither of these photolytic products acts as photolytic sensitizer.

The formation of only C_2H_4 from $(C_2H_5)_4Si$ and of only C_2H_2 from $(C_2H_3)_4Si$ reveals that the mode of the elimination



$$\equiv Si{-}C_2H_n \longrightarrow \equiv Si{-}H + C_2H_{n-1}$$

must be intramolecular. This assumption is supported by the absence of hydrocarbons that could have been formed by a sequence of homolysis of the Si–C bond and radical reactions (recombination, disproportionation, H-abstraction). (For example, methane and ethane are produced in the pyrolysis of (I) and (II) [9], and ethene is a product of the infrared multiphoton decomposition of (II) [10]). Preliminary results imply that the laser photolysis of both $(C_2H_n)_4Si$ compounds, and perhaps also of other R_4Si compounds, ($R \neq CH_3$), can be used in CVD of silicon or of Si/C materials with a very low carbon content, which are needed in microelectronics. Compounds can be tailor-made to possess high absorptivity at the wavelength of ArF lasers, making them more efficient precursors for silicon deposition than silane or polysilanes (see for example, Refs. [11–14]). No Si/C materials with a low carbon content have been produced so far by CVD, despite efforts [9,15,16] to use organosilicon precursors with weak Si–C bonds. These photolytic results appear

to be equally promising for CVD of Si or Si/C materials on thermally unstable substrates.

Experimental section

Laser irradiation experiments were carried out under the conditions (energy fluence 150 mJ, repetition frequency 20 Hz) and reactor described previously [17]. The progress of the photolyses was monitored with an FTIR (Perkin-Elmer 1710) spectrometer. The disappearance of (I) and (II) was monitored by use of the absorption bands at 735 and 1597 cm^{-1}, respectively. The amounts of triethylsilane, trivinylsilane, ethene and ethyne were monitored at 2100, 2138, 950, and 3308 cm^{-1}, respectively. The absorption coefficients at these wavenumbers were measured with authentic samples. The UV absorbances of $(C_2H_5)_xSiH_{4-x}$, $(C_2H_3)_xSiH_{4-x}$ ($x = 1$–4), SiH_4, C_2H_4 and C_2H_2 were recorded by using a Philips PU 8720 UV/VIS scanning spectrometer. The organosilicon compounds were prepared by reported procedures [18].

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