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UV-Laser-Induced Photolysis of Trimethyl(vinyloxy)silane for Chemical Vapour Deposition of Polysiloxane Films

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The UV-induced photolysis of trimethyl(vinyloxy)silane (TMVSi) induced by ArF laser, affording a multitude of unsaturated hydrocarbons and a solid polydimethylsiloxane, represents a convenient process of chemical vapour deposition in which the silicon of the parent is almost completely utilized for the formation of the solid phase and in which the morphology and composition of the films is affected by the configuration of the substrate and laser beam. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Silicon oxycarbides are of increasing interest in various fields of applied research (e.g. Refs. 1–4) and find use in ceramic sensors for oxygen detection in high-temperature corrosive conditions and in photodetectors and solar cells.[5,6] Different kinds of these Si/C/O and Si/C/H/O materials are known: black glasses have been prepared by pyrolysis of polysiloxane gels (e.g. Refs. 7–9), nanosized particles have been synthesized by pyrolytic laser–aerosol interaction[10–12] and solid films have been plasma-[13–15] or IR laser-chemical-vapour-deposited by pyrolysis of gaseous organosilicon monomers.[16–20]

Of the IR-laser gas-phase thermally decomposed organosilicon monomers hexamethyldisiloxane,[10–12,18,19] (methoxy)methylsilanes,[19] (ethoxy)-methylsilanes[11,12] and 1,1,3,3-tetramethyldisiloxane[20] have been reported. We have recently shown[21] that trimethyl(2-propynyloxy)silane, $(CH_3)_3SiOCH_2C{\equiv}CH$, undergoes UV laser-induced polymerization in the gas phase and affords polytrimethylsiloxy-substituted, partly unsaturated, polyhydrocarbons. This reaction represents a unique way for chemical vapour deposition (CVD) of polytrialkylsiloxy-substituted macromolecules.

Here we report on UV laser-induced gas-phase photolysis of trimethyl(vinyloxy)silane, $(CH_3)_3SiOCH{=}CH_2$ (TMVSi), and show that photolytically induced polymerization at the double bond of this compound does not occur, but an efficient cleavage of all but the Si–O bonds of this molecule do take place instead and results in CVD of solid polysiloxane films.

EXPERIMENTAL

The laser photolysis experiments were carried out in a reactor which consisted of two orthogonally positioned Pyrex tubes, one fitted with two quartz windows and the other furnished with two NaCl windows. TMVSi (30 Torr) was irradiated at a repetition frequency of 10 Hz by pulses from an ArF (Lambda Physik LPX 200) laser at an incident energy of 50 mJ effective over an area of 1.4 cm^2. The progress of the photolysis was monitored by FTIR spectroscopy (with a Shimadzu FTIR 4000

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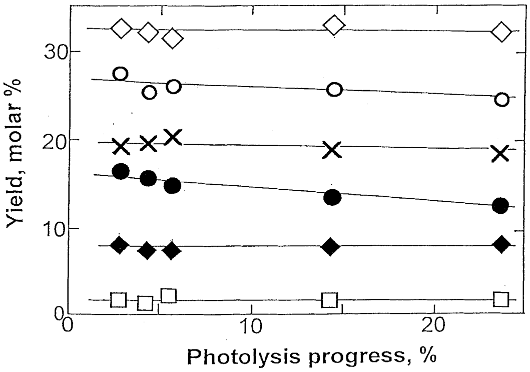

Figure 1 Product yield (mol%) at different stages of the photolysis progress of TMVSi: ◇C_2H_2; ○, CH_4; ×, C_2H_4; ●, C_2H_6; ◆, C_3H_6; □, C_4H_6.

spectrometer) using the absorption band of TMVSi at 1330 cm^{-1}, and by gas chromatography on a Gasukuro Kogyo 370 chromatograph (programmed temperature 30–150 °C, 60 m Neutra Bond-1 capillary and 2 m SUS Unipak S columns) connected with a Shimadzu CR 5A Chromatopac data processor. Identification of gaseous products was accomplished by means of gas chromatography and GC/MS techniques (Shimadzu QP-1000 mass spectrometer). Properties of the deposits on NaCl, quartz and nickel substrates, which were accommodated in the reactor, were measured by FTIR spectroscopy, XP spectroscopy (XPS) (with a VG ESCA 3 Mk II electron spectrometer) and scanning electron microscopy (SEM) (a Tesla BS 350 ultrahigh-vacuum instrument).

RESULTS AND DISCUSSION

ArF laser irradiation of TMVSi results in TMVSi depletion and the formation of volatile hydrocarbons (in mol/mol of decomposed TMVSi × 100): methane (25–27), ethene (19–21), ethane (13–17), propene (7–9) and buta-1,3-diene (2–3), propane (<1), and traces (<0.5) of trimethylsilane and tetramethylsilane. The formation of these products is accompanied by deposition of thin transparent films on the inside of the entire reactor. The relative amounts of the gaseous products are virtually independent of photolysis progress (Fig. 1) and are in line with combination (Eqn [3]), disproportionation (Eqn [4]), cross-disproportionation (Eqn [5]) and hydrogen-abstraction reactions (Eqn [6]) of $H_2C{=}CH^{\cdot}$ and $CH_3^{\cdot}$ radicals produced upon cleavage of the CH_3–Si (Eqn [1]) and O–CH (Eqn [2]) bond of TMVSi (Scheme 1). Another plausible route is subsequent decay (β-cleavage, Eqn [7]) of radical **I** yielding very reactive dimethylsilanone, which is known[22] to polymerize (Eqn [8]). These plausible steps are shown in Scheme 1, Eqns [1]–[8].

Insignificant amounts of trimethylsilane and tetramethylsilane can be explained by very minor cleavage of the Si–O bond and consecutive

$$(CH_3)_3SiOCH{=}CH_2 \longrightarrow CH_3^{\cdot} + {}^{\cdot}Si(CH_3)_2OCH{=}CH_2 \quad [1]$$

$$\mathbf{I}$$

$$\longrightarrow H_2C{=}CH^{\cdot} + {}^{\cdot}OSi(CH_3)_3 \quad [2]$$

$$2R^{\cdot} \longrightarrow CH_3{-}CH_3, CH_3 - CH{=}CH_2, H_2C{=}CH{-}CH{=}CH_2 \quad [3]$$

$$2H_2C{=}CH^{\cdot} \longrightarrow H_2C{=}CH_2 + HC{\equiv}CH \quad [4]$$

$$CH_3^{\cdot} + H_2C{=}CH^{\cdot} \longrightarrow CH_4 + HC{\equiv}CH \quad [5]$$

$$R^{\cdot} + (CH_3)_3SiOCH{=}CH_2 \rightarrow RH(R = CH_3, C_2H_3) + {}^{\cdot}H_2C(CH_3)_2SiOCH{=}CH_2 \quad [6]$$

$${}^{\cdot}Si(CH_3)_2OCH{=}CH_2 \xrightarrow{\beta\text{-cleavage}} H_2C{=}CH^{\cdot} + (CH_3)_2Si{=}O \quad [7]$$

$$n(CH_3)_2Si{=}O \longrightarrow /(CH_3)_2SiO/_n \quad [8]$$

Scheme 1

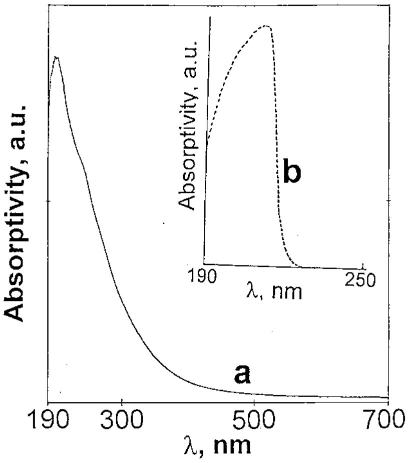

Figure 2 Absorption UV/Vis spectrum of TMVSi (b) and thin films produced by CVD (a).

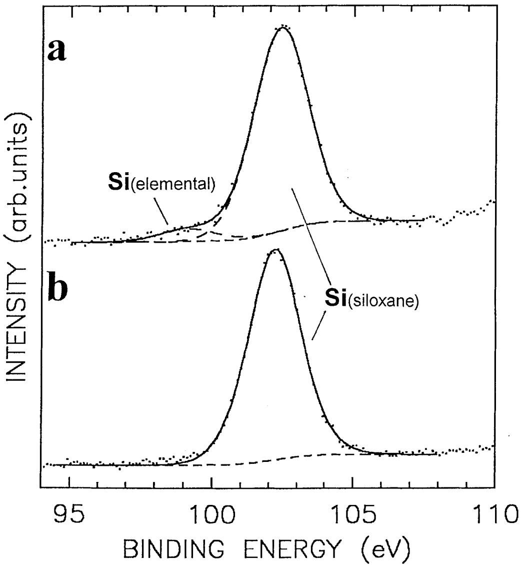

Figure 3 The Si (2p) core level spectra of films deposited onto substrate positioned (a) outside the laser beam, and (b) facing the laser beam.

hydrogen-abstraction by the $(CH_3)_3Si^{\cdot}$ radical,[23] and by recombination of $CH_3^{\cdot}$ and $(CH_3)_3Si^{\cdot}$ radicals, respectively.

We have observed that the yield of methane can be increased by 5–8 mol% at the expense of that of ethyne by using a higher flux [90 mJ/effective area ($1.4\,cm^2$)]. This phenomenon is in line[24] with molecular expulsion of methane at higher fluxes. Other examples of these reactions have been observed (e.g. Refs. 25–27) and methane molecular expulsion from TMVSi affords reactive methyl(ethenoxy)silene.

The final products detected indicate that TMVSi is depleted by a blend of monomolecular decomposition and consecutive hydrogen-abstraction reactions of TMVSi with radicals (Eqn [6]) producing an unstable unsaturate which can be expected to split off a methyl radical and yield silene **II** (Eqn [9]).

$$^{\cdot}H_2C(CH_3)_2SiOCH{=}CH_2 \longrightarrow CH_3^{\cdot} + H_2C{=}Si(CH_3)OCH{=}CH_2 \quad [9]$$

$$\mathbf{II}$$

The assumed steps thus produce very reactive products which can undergo a multitude of reactions, such as further cleavages and polymerizations.[28] The complex reaction scheme and the occurrence of thermal radical chain reactions is supported by the estimated number of TMVSi molecules depleated with one 193 nm photon. Within less than 5% photolysis progress, this value ranges between 4 and 5.

The films deposited onto the substrates accommodated in the reactor show an IR absorption spectrum [wavenumber/cm^{-1} (normalized absorptivity)]—806 (0.35), 845 (0.42), 1040 (1.00), 1260 (0.41), 2853 (0.10), 2926 (0.23) and 2962 (0.14)—which is the same regardless of substrate positioning and which can be assigned, in the given order, to ν (Si–C), ρ (CH_3Si), ν (SiO), δ (CH_3Si) and ν (C–H) vibrations. The absence of absorption bands belonging to C=C bonds (above $3000\,cm^{-1}$) indicates that the deposits can be described as a completely saturated polysiloxane.

The UV spectrum of these films, together with that of TMVSi, is given in Fig. 2: the films possess a maximum at *ca* 204 nm, while TMVSi itself shows, due to a blend of contributions of both chromophore $H_2C{=}CH$ and Si-O-C groups, a bathochromic shift (maximum at 212 nm). The films, being opaque to 193 nm radiation, are detrimental to photolytic progress. Indeed, laser irradiation with 500 pulses drove photolysis to *ca* 5% conversion, while that with as many as 4000 pulses resulted only in photolysis progress of *ca* 9%. Higher photolysis progress can thus be achieved only by irradiating TMVSi through the one and then the other quartz window.

XPS analysis of two kinds of films is presented. The films deposited on the bottom of the reactor, which is outside the laser beam, possess stoichio-

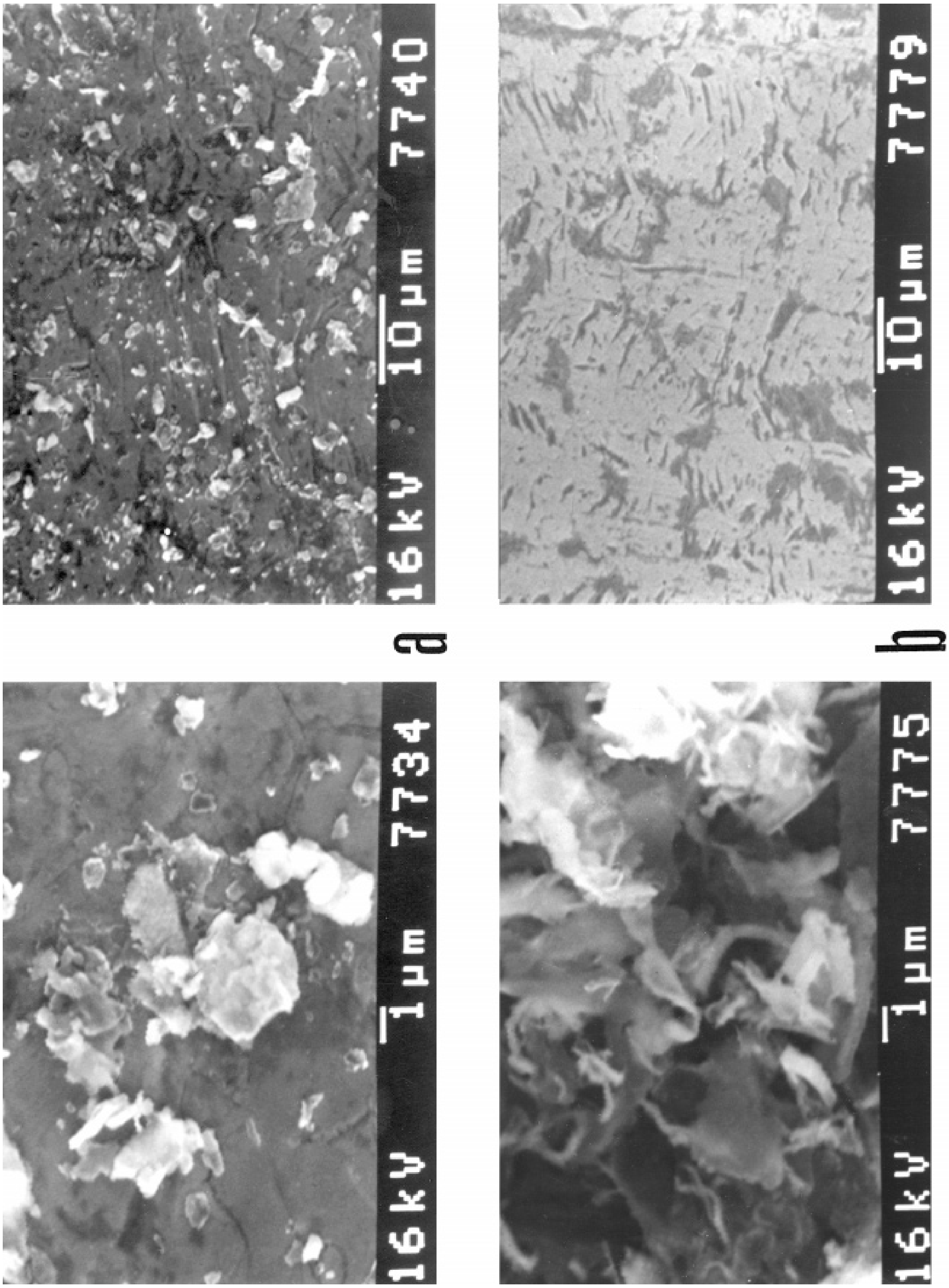

Figure 4 SEM of films deposited on substrate (a) placed on reactor bottom outside the laser beam, and (b) exposed to the laser beam behind the quartz window.

metry $Si^{\alpha}_{0.1}$ $Si^{\beta}_{1.0}$ $C_{4.5}$ $O_{1.0}$, while those deposited on the substrates fixed several millimetres behind the entrance quartz window, and facing the laser beam, show stoichiometry $Si^{\beta}_{1.0}$ $C_{3.3}$ $O_{1.0}$. The Si^{α} relates to elemental silicon and Si^{β} to silicon in the organosiloxane polymer, respectively. The organosiloxane silicon prevails highly in the former and is the only form of silicon in the latter (Fig. 3). This assignment is in line with the spectrum of Si(2p) electrons of both films, which is dominated by the peak located at 102 ± 0.2 eV. It is also supported by the values obtained of the modified Auger parameter, 1711.9 ± 0.2 eV, and the separation between O(1s) and Si(2p) photoemission lines, 430.4 ± 0.2 eV, both of which are characteristic of organosiloxane polymers.[29,30]

SEM images of the two kinds of films differ significantly. Those of the films deposited on the reactor bottom show particulate structure and consist of well-separated agglomerates, the size of which ranges to below 10 μm (Fig. 4a). Very interestingly, those films deposited onto substrates facing the laser beam behind the entrance window reveal discrete continuous structures (Fig. 4b) which can be taken as evidence of laser-induced formation of reactive centres in the deposit. A lower content of carbon in the latter films is in line with additional removal of carbon-containing fragments from once-deposited films. The once-deposited particles apparently increase their size through reactions of their reactive centres with gaseous unsaturated fragments which are not rich in carbon. A similar reactivity of deposited solid particles was observed in laser evaporation of some solid organosilicon polymers.[31]

These results thus stress that the morphology and composition, but not the UV and IR spectra of the deposited polysiloxane films, are strongly affected by substrate and laser-beam configuration.

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