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IR Laser-induced Decomposition of Disiloxane for Chemical Vapour Deposition of Poly(hydridosiloxane) Films

Josef Pola,[1]* Markéta Urbanová,[1] Vladislav Dřínek,[1] Jan Šubrt[2] and Helmut Beckers[3]
[1]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic
[2]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25 068 Řež, near Prague, Czech Republic
[3]Anorganische Chemie, FB 9, Universität-GH, D-42097 Wuppertal, Germany

Continuous-wave CO_2-laser-induced gas-phase decomposition of $H_3SiOSiH_3$, dominated by elimination and polymerization of transient silanone $H_2Si{=}O$ and yielding silane and hydrogen as side-products, represents a convenient process for chemical vapour deposition of poly(hydridosiloxane) films. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

The synthesis and physical properties of disiloxane, $H_3SiOSiH_3$ (DSO), have been known for a long time,[1–7] but its chemistry has been little explored:[8–10] it involves insertion of difluorocarbene into the Si–H bond and cleavage with metal hydrides and ammonia. Thermal decomposition of DSO has not yet been examined, although studies on the thermal decomposition of polydimethylsiloxanes are plentiful. It is well established that (i) polydimethylsiloxanes thermally degrade in conventional (hot-wall) pyrolytic reactors via cleavage of the thermodynamically stable Si–O bond (e.g. Refs. 11–13), and that (ii) IR laser-induced thermolysis of hexamethyldisiloxane[14,15] occurring strictly in the gas phase (with no contribution from the cold reactor surface) is controlled by cleavage of the Si–C bond. These findings can only be explained by an enhancement of Si–O cleavage via heterogeneous steps on the hot reactor surface. Our recent observation of both Si–C and Si–O bond cleavages in the IR laser-induced homogeneous decomposition of 1,1,3,3-tetramethyldisiloxane[16] is, however, indicative of a feasible split of the Si–O bond in disiloxanes possessing Si–H bonds, and suggests that the ease of the Si–O bond cleavage is enhanced by H-substitution at the silicon.

We now report that IR laser-induced decomposition of DSO is dominated by cleavage of the Si–O bond and that this homogeneous decomposition is a convenient process for chemical vapour deposition of silicon suboxide-based films (e.g. Refs. 17–19), which are promising materials for microelectronics.

EXPERIMENTAL

The experiments were carried out using a continuous-wave (cw) CO_2 laser operating in the range 934–952 cm^{-1} by procedures reported previously.[20–22] DSO (3 kPa) or DSO (3 kPa)–SF_6 (0.2–7 kPa)–N_2 (7 kPa) mixtures were irradiated with an output power of 5–12 W in a Pyrex reactor fitted with KBr windows, a port for a pressure transducer, two PTFE valves and a sleeve with a rubber septum. The progress of the DSO decomposition was monitored by GC–MS and GC techniques (silicon elastomer, Porapak and carbo-

* Correspondence to: Josef Pola, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague 6, Czech Republic.
E-mail: pola@icpf.cas.cz
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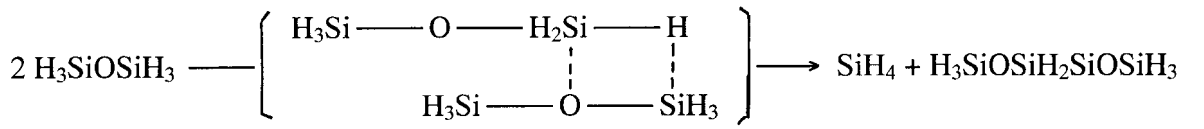
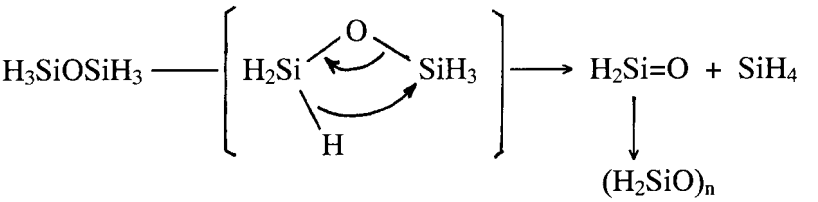


Scheme 1



Scheme 2

sieve columns) as well as by FTIR spectroscopy using the absorption band of DSO at 2169 cm^{-1} and that of silane at 908 cm^{-1}.

RESULTS AND DISCUSSION

The absorption of laser radiation in the $\delta(H_3Si)$ mode[23] of DSO and the ν(S–F) mode[24,25] of SF_6 results in decomposition of DSO, formation of gaseous silane and hydrogen and deposition of a solid material manifesting itself as thin transparent films or thicker yellowish layers. The yield of silane is within the 30–70% decomposition range 0.75–0.90 mol per mol of DSO decomposed. This value, being lower than 1, can be rationalized in terms of minor silane decomposition[26–29] into H_2 and a solid Si/H or silicon(0) material.

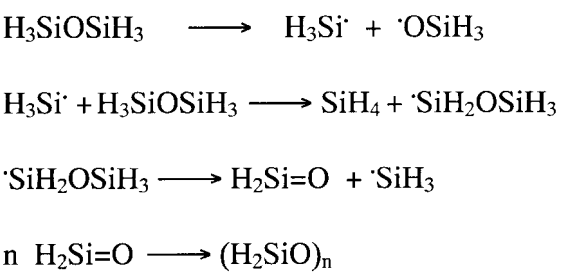
Photoelectron spectroscopy of the films reveals that the O/Si ratio in all the deposits is close to 1. The IR spectra of the deposited films show a very strong and broad band due to the ν(Si–O–Si) mode at approximately 1086 cm^{-1} and several minor bands assignable to vibrations of $H_nSi(O)$ moieties at 803, 870, 980, 2183 and 2250 cm^{-1}. The bands observed at 2183 and 2250 cm^{-1} can be unambiguously assigned[30–35] to the $H_2Si(O)$ structural unit; the lack of bands at *ca* 2100 and 2000 cm^{-1} is indicative of an absence of $(SiH_2)_n$ and $(SiH)_n$ structures[36,37] in which the Si–H bond is isolated from oxygen by at least two silicon atoms.

The observed volatile products can, in principle, be formed by three different mechanisms. These are:

(a) bimolecular formation of a four-centre intermediate depicted for the primary reaction stage by Scheme 1;
(b) monomolecular cleavage via a four-centre transition state (Scheme 2); and
(c) a radical process similar to that reported for decomposition of dimethyl ether (Scheme 3).[38,39]

To discern between these decomposition modes is difficult. Neither scavenging experiments, nor experiments with isotopomeric precursors, proved helpful: silanone trapping with alkoxysilanes was unsuccessful, and the irradiation of DSO–DSO-d_6–SF_6 mixtures afforded all the H_nSiD_{4-n} isotopomers. The latter fact cannot, however, be taken as evidence for radical chains, since the SiH_4 and SiD_4, once produced by molecular elimination, could undergo H/D scrambling.

Irradiation of DSO (0.7 kPa) and cyclohexene (chemical thermometer,[40] 0.7 kPa) in the presence of SF_6 (0.7–2 kPa) and in an excess of nitrogen



Scheme 3

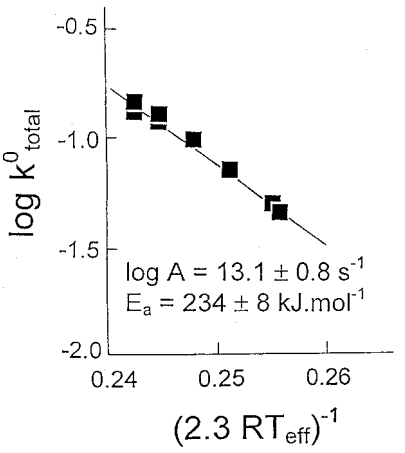


Figure 1 The Arrhenius plot of log k^{o}_{total} vs T_{eff}^{-1} for cw CO_2-laser-photosensitized (SF_6) decomposition of DSO using cyclohexene as marker.

(7.5 kPa), using incident energy in the range of 10–100 W cm^{-2}, was carried out to determine initial rates of depletion of both compounds. The depletion was monitored by FTIR spectroscopy using absorptivities at 759 cm^{-1} (DSO) and 2931 cm^{-1} (cyclohexene). This procedure for non-interfering systems[40] allowed us to estimate the Arrhenius parameters of the decomposition of DSO as log A = 13.1 ± 0.8 s^{-1} and E_a = 234 ± 8 kJ mol^{-1} (Fig. 1), which are in keeping with the suggested four-centre cyclic transition state of the unimolecular decomposition depicted in Scheme 2. Considering that the activation energy of the overall dimethyl ether decomposition[38,39] corresponds essentially to the C–O bond energy (approximately 300 kJ mol^{-1}), the operation of the analogous radical chains in the DSO decomposition would lead to a much higher activation energy, reflecting the dissociation energy of the Si–O bond (*ca* 500 kJ mol^{-1}).

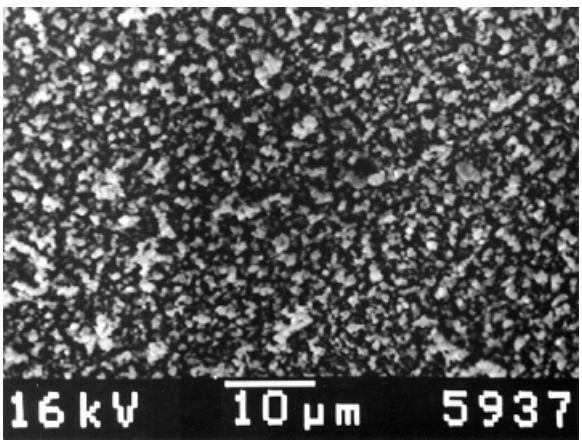


Figure 2 SEM of the Si/H/O deposit obtained.

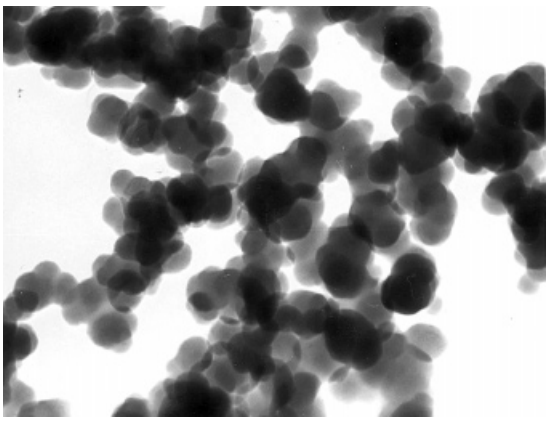


Figure 3 TEM of the Si/H/O deposit. Magnification: ×70 000.

The transient occurrence of silanone $H_2Si{=}O$ is supported by a very minor formation of trisiloxane, cyclotrisiloxane, tetrasiloxane and cyclotetrasiloxane, all of which were identified by a GC–MS technique. These products can only be rationalized in terms of $H_2Si{=}O$ insertion into DSO, or of $H_2Si{=}O$ cyclotrimerization and cyclotetramerization.

Scanning electron microscopy analysis reveals that the films consist of agglomerates which have continuous structures (Fig. 2). Transmission electron microscopy analysis confirms this and shows small particles *ca* 100 nm in size which are bonded together (Fig. 3). These features are consistent with residual activity of depositing agglomerates which increase their size not only in the gas phase but also after their deposition on the reactor surface.

A remark about the fragmentation of DSO under electron impact is pertinent. The mass spectrum of DSO [*m/z* (relative intensity) = 78 (30), 77 (100), 76 (49), 75 (68), 74 (20), 73 (53), 72 (23)] consists of signals corresponding to the loss of 1–6 H atoms. It is thus apparent that the elimination of SiH_4 molecules taking place in the IR laser-induced thermal process is prohibited for the $DSO^{+\cdot}$ ion.

We conclude that DSO decomposes to yield silane and solid poly(hydridosiloxane) films, which are reported for the first time as being produced by IR laser-induced gas-phase decomposition of DSO. The procedure represents a convenient alternative

to formation of Si/O phases achieved through gas-phase oxidation of hazardous silane.

More work using radiation from pulsed TEA CO_2 and ArF lases is in progress.

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