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Journal of Photochemistry and Photobiology A: Chemistry 146 (2002) 141–147

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Chemical reactivity of vinyltrimethoxysilane in aerosol particle formation with acrolein under two-photon excitation

Katsuhiko Semba, Hiroshi Morita*

Graduate School of Science and Technology, Chiba University, Yayoi-cho, Inage-ku, Chiba 263 8522, Japan

Received 21 June 2001; received in revised form 7 September 2001; accepted 1 October 2001

Abstract

Under irradiation with N_2 laser light, a gaseous mixture of vinyltrimethoxysilane (VTMSi) and acrolein (AC) produced sedimentary aerosol particles with a mean diameter of 1.2 μm. From chemical analysis of the product by XPS and FT-IR spectroscopy, VTMSi was found to be incorporated into the sedimentary particles of polyacrolein as polysiloxane. Gas-phase chemical reaction between VTMSi and AC under irradiation with N_2 laser light was investigated from the analysis of volatile products by GC/MS. Identification of cyclic polysiloxane in the gas phase strongly suggested that VTMSi molecules were cleaved at vinyl–Si bond and at O–CH_3 bond by a two-photon process of N_2 laser light, and produced dimethoxysilanone as an intermediate. The nucleation process of the aerosol particles was studied by measuring monitor (He–Ne laser) light intensity scattered by the aerosol particles as formed under irradiation with N_2 laser light. With increasing partial pressure of VTMSi, the nucleation reaction of aerosol particles was accelerated due to the additional production of reactive species from VTMSi molecules. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aerosol particle formation; Two-photon excitation; Vinyltrimethoxysilane; Acrolein

1. Introduction

Photochemical reactions of gaseous organosilicon compounds play an important role in synthesizing novel materials of organosilicon compounds. Among them, gas-phase deposition of alkoxysilanes by chemical vapor deposition (CVD) techniques were investigated extensively to synthesize silicon oxide which showed thermally and chemically stable insulating properties [1–9].

From gaseous mixtures of acrolein (2-propenal) (AC) and some organosilicon compounds such as allyltrimethylsilane and trimethyl(2-propynyloxy)silane, we have succeeded to synthesize aerosol particles under UV light irradiation [10,11], and found that organosilicon compounds were involved in the aerosol particles as several different chemical species depending on the chemical reactivity of the parent molecules. In a preliminary experiment, we have reported that a gaseous mixture of ethenyltrimethoxysilane (vinyltrimethoxysilane) (VTMSi) and AC produced sedimentary aerosol particles which involved Si–O bond under irradiation with N_2 laser light as revealed from X-ray photoelectron spectrum (XPS) [12].

In order to investigate chemical processes of Si–O bond formation in aerosol particles produced from a gaseous mixture of VTMSi and AC, nucleation process of aerosol particles has been studied in the present paper by measuring FT-IR spectra of the gaseous mixture and by measuring monitor light (He–Ne laser) intensity scattered by aerosol particles as formed under light irradiation with a medium pressure mercury lamp and with N_2 laser. Chemical structure of the sedimentary aerosol particles was analyzed from FT-IR and XPS spectra, special attention being paid to a two-photon excitation of VTMSi molecules by N_2 laser light.

2. Experimental

AC (Merck, 95%, stabilized with 0.2% hydroquinone) and VTMSi (Tokyo Kasei, 99%, E.P. grade) were stored in a refrigerator below 10 °C to prevent polymerization. Each of the AC and VTMSi liquid was degassed by freeze–pump–thaw cycles and distilled under the vacuum immediately before use. In order to prepare a gaseous mixture of VTMSi and AC, a fixed amount of VTMSi vapor and then another fixed amount of AC vapor were successively introduced into a cross-shaped irradiation cell with four optical quartz windows (inner diameter and length of

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* Corresponding author. Tel.: +81-43-290-3471; fax: +81-43-290-3490.
E-mail address: hmorita@image.tp.chiba-u.ac.jp (H. Morita).

PII: S1010-6030(01)00610-4

long arm: 35 and 155 mm; inner diameter and length of short arm: 20 and 80 mm) through a vacuum line equipped with a capacitance manometer (Edwards Barocel Type 600). The background pressure of the irradiation cell was less than 8×10^{-5} Torr (1 Torr $=$ 133.3 Pa) and the leakage into the evacuated cell from the atmosphere was carefully controlled to result in pressure increase lower than 1 Torr in a day. The actual partial pressure of AC in the irradiation cell was determined from UV absorption at 350 nm measured with Shimadzu UV-2100S spectrometer. Gaseous samples were irradiated with collimated light of a medium pressure mercury lamp (Ushio UM-452, 450 W) through a UV-29 and a UVD33S filters or with N_2 laser light (Lumonics HE-440, 337.1 nm, pulse width 10 ns) without any focusing lens with a repetition rate of 12 Hz. Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-5121B). FT-IR spectra of the gaseous mixtures were measured with a Nicolet NEXAS 670 FT-IR spectrometer using the cross-shaped irradiation cell equipped with two optical KBr and two optical quartz windows. GC/MS spectra of the gaseous mixtures were measured with a Shimadzu QP 5000 quadrupole mass spectrometer equipped with a column DB-1 (0.25 mm $\times$ 20 m) by mixing the gaseous sample with pure helium gas in order to transfer the sample into GC/MS spectrometer. Monitor (He–Ne laser) light intensity scattered by the aerosol particles floating in the cell was measured with a combination of photomultiplier tube (EMI 6256S) and a lock-in amplifier (SRS SR-530) by chopping and synchronizing monitor light. SEM images of sedimentary aerosol particles were taken with a Topcon ABT-32 scanning electron microscope. XPS was measured with a KRATOS XSAM800 electron spectrometer employing a Mg Kα X-ray.

3. Results and discussion

Under light irradiation with a medium pressure mercury lamp through a UV-29 and a UVD33S filters at an energy of 6.1 mJ cm^{-2} s^{-1} for 1 h, a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) deposited sedimentary aerosol particles (yield 0.1 mg) on a glass plate which was placed at the bottom of the irradiation cell. The reproducible sedimentary pattern due to the convection of the gaseous mixture was formed, indicating that the sedimentary particles were produced in the gas phase. SEM image of the sedimentary aerosol particles (Fig. 1) showed that the sedimentary particles were spherical with a mean diameter of 0.81 μm.

VTMSi molecule has the longest wavelength absorption band at shorter than 200 nm, and its absorption tail extended up to 230 nm. VTMSi does not absorb light under irradiation with a mercury lamp through a UV-29 and a UVD33S filters, and actually, VTMSi vapor (9 Torr) did not produce any deposits under light irradiation for 4 h. On the other hand, AC could dissociate into C_2H_3 and CHO radicals which could initiate polymerization reaction to form aerosol particles [10,13]. Hence, the aerosol particle formation from the gaseous mixture of VTMSi and AC was initiated through the photochemical reaction of AC molecules.

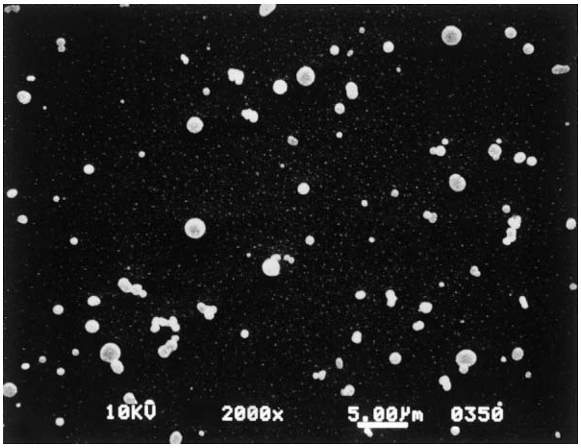

Fig. 1. SEM image of sedimentary aerosol particles deposited from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under light irradiation with a medium pressure mercury lamp at an energy of 6.1 mJ cm^{-2} s^{-1} for 1 h. Original magnification of SEM, 2000×.

The nucleation process in aerosol particle formation was studied by monitoring the He–Ne laser light intensity scattered by the aerosol particles (Fig. 2). In the case of pure AC vapor (41 Torr) (curve a in Fig. 2), scattered light was detected under light irradiation for 3 min, and scattered light intensity reached its maximum in 16 min. With increasing partial pressure of VTMSi, induction period to detect the scattered light and the time to reach the maximum intensity became longer (by 3 and 6 min, respectively, at a partial pressure of 8 Torr). This indicated that the efficiency of nucleation reaction decreased with increasing partial pressure of VTMSi, showing that incorporation of electronically unexcited VTMSi molecules into the nucleation reaction

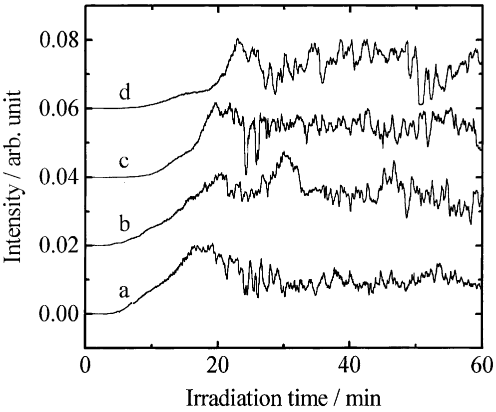

Fig. 2. He–Ne laser light intensity scattered by the aerosol particles produced from a gaseous mixture of VTMSi and AC (41 Torr) under light irradiation with a medium pressure mercury lamp through a UV-29 and a UVD33S filters at an energy of 6.1 mJ cm^{-2} s^{-1}. The partial pressure of VTMSi was: (a) 0, (b) 3, (c) 5 and (d) 8 Torr. The ordinates are shifted consecutively by 0.02 from (a) to (b), (c) and (d).

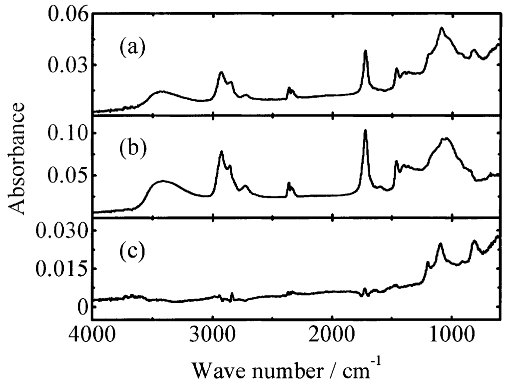

Fig. 3. FT-IR spectra of sedimentary aerosol particles deposited from: (a) a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr), (b) pure gaseous AC (41 Torr) under light irradiation with a medium pressure mercury lamp through a UV-29 and a UVD33S filters for 4 h, (c) difference spectrum between (a) and (b).

decelerated chemical reactions in the nucleation process due to its lower chemical reactivity than the one of AC.

In order to study the chemical structure of the products, FT-IR spectrum was measured with a KBr pellet of the sedimentary aerosol particles produced from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under light irradiation with a medium pressure mercury lamp for 4 h (Fig. 3(a)), compared with the spectrum of sedimentary aerosol particles deposited from pure AC vapor (Fig. 3(b)). The sedimentary particles deposited from the gaseous mixture showed the bands at 2841, 1456, 1186, 1080 and 808 cm^{-1}, besides the bands ascribed to polyacrolein as the difference spectrum between curves (a) and (b) clearly showed. Absorption bands at 2841, 1456 and 1186 cm^{-1} were assigned to symmetric stretching, asymmetric deformation, and rocking vibrations of CH_3 in Si–O–CH_3, while the bands at 1080 and 808 cm^{-1} were assigned to Si–O and C–O stretching vibrations, respectively [14–17], showing the existence of methoxysilyl structural unit. Disappearance of C=C stretching band of VTMSi at 1603 cm^{-1} indicated that VTMSi molecules were polymerized at C=C bond in the particles.

Under irradiation with N_2 laser light at an energy of 1.8 mJ/pulse (i.e., 0.3 mJ cm^{-2} pulse^{-1} under the present experimental conditions) for 3 h, a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) produced sedimentary aerosol particles which were spherical with a mean diameter of 1.2 μm (Fig. 4). Nucleation process of aerosol particle formation was also studied by measuring He–Ne laser light intensity scattered by the aerosol particles (Fig. 5). In the case of pure AC vapor (41 Torr), scattered light was detected under irradiation for 13 min, and scattered light intensity reached its maximum at 47 min (Fig. 5(a)). With increasing partial pressure of VTMSi, the induction period became shorter and the peak intensity became stronger, in contrast to the case under light irradiation with the mercury lamp (Fig. 2). The result indicated that VTMSi accelerated the nucleation reaction by producing reactive chemical species through photodecomposition by a two-photon process of N_2 laser light. The acceleration of nucleation reaction and incorporation into the propagating reactions may be responsible for the larger mean diameter (1.2 μm) of sedimentary particles than the one (0.81 μm) of Fig. 1, where VTMSi was not electronically excited.

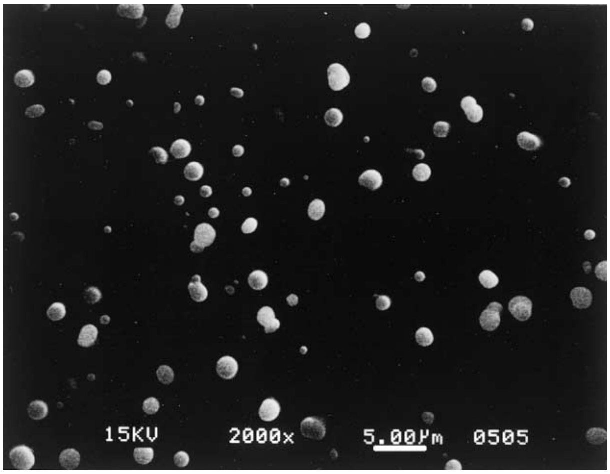

Fig. 4. SEM image of sedimentary aerosol particles deposited from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under irradiation with N_2 laser light at an energy of 0.3 mJ cm^{-2} pulse^{-1} for 3 h. Original magnification of SEM, 2000×.

In order to study photochemical behavior of the gaseous molecules, FT-IR spectra were measured with pure AC vapor (41 Torr), pure VTMSi vapor (8 Torr), and a gaseous mixture of them under light irradiation with a medium pressure mercury lamp. The results for the gaseous mixture are shown in Fig. 6. FT-IR spectrum of the gaseous mixture before light irradiation coincided with the superposition of the spectra of pure AC and pure VTMSi, indicating that chemical reaction between VTMSi and AC did not proceed in the dark. Under UV light irradiation for 4 h (Fig. 6(b)),

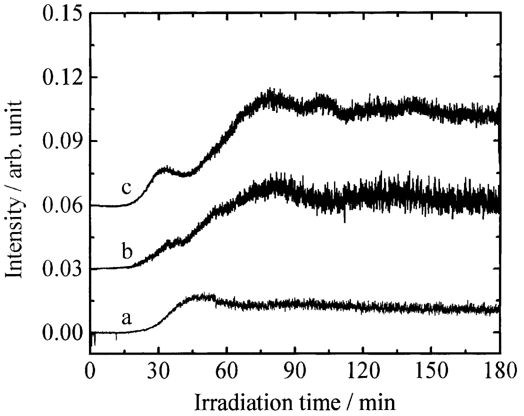

Fig. 5. He–Ne laser light intensity scattered by the aerosol particles produced from a gaseous mixture of VTMSi and AC (41 Torr) under irradiation with N_2 laser light at an energy of 0.3 mJ cm^{-2} pulse^{-1}. The partial pressure of VTMSi was: (a) 0, (b) 5 and (c) 8 Torr. The ordinates are shifted consecutively by 0.03 from (a) to (b) and (c).

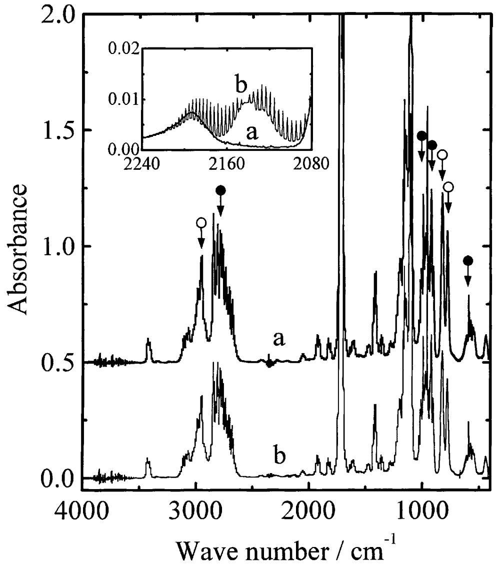

Fig. 6. FT-IR spectra of a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) before (a) and after (b) light irradiation with a medium pressure mercury lamp for 4 h (exposure dose 88 J/cm^2). The ordinate of spectrum (a) is shifted by 0.5. The bands of AC at 2809, 993, 920, and 593 cm^{-1} were indicated by ●, and the bands of VTMSi at 2953, 824, and 778 cm^{-1} by ○.

all the bands ascribed to AC decreased their intensities by 17%, and those ascribed to VTMSi by 25%, due to the depletion of both VTMSi and AC molecules, and a very weak band ascribed to carbon monoxide appeared, showing that AC molecules decomposed into C_2H_4 and CO as a major process. Homolytic cleavage to produce C_2H_3 and CHO radicals which could initiate polymerization reactions and lead to nucleation reaction of aerosol particles was a minor process as reported previously [12,13]. The depletion of AC and VTMSi molecules under light irradiation with a mercury lamp was analyzed from the intensity change of FT-IR bands following Eqs. (1)–(6).

$$\mathrm{AC} + h\nu \xrightarrow{I_a} \mathrm{AC}^* \tag{1}$$

$$\mathrm{AC}^* \xrightarrow{k_1} \mathrm{C_2H_4} + \mathrm{CO} \tag{2}$$

$$\mathrm{AC}^* \xrightarrow{k_2} {}^\bullet\mathrm{C_2H_3} + {}^\bullet\mathrm{CHO} \quad (\text{radicals, } \mathrm{R_1}^\bullet) \tag{3}$$

$$\mathrm{AC}^* \xrightarrow{k_3} \mathrm{AC} \tag{4}$$

$$\mathrm{R_1}^\bullet + \mathrm{AC} \xrightarrow{k_4} \text{polymerization} \tag{5}$$

$$\mathrm{R_1}^\bullet + \mathrm{VTMSi} \xrightarrow{k_5} \text{polymerization} \tag{6}$$

Considering that the product yield of sedimentary aerosol particles from pure AC vapor was less than 0.5% of the total amount of the gaseous reactant, contribution of Eq. (5) to the depletion of AC may be regarded to be negligibly small.

Under irradiation with N_2 laser light, Eqs. (7)–(11) also contributed to the photochemical processes in addition to Eqs. (1)–(6).

$$\mathrm{VTMSi} \xrightarrow{I_b} \mathrm{VTMSi}^* \tag{7}$$

$$\mathrm{VTMSi}^* \xrightarrow{k_6} \mathrm{R_2}^\bullet \tag{8}$$

$$\mathrm{VTMSi}^* \xrightarrow{k_7} \mathrm{VTMSi} \tag{9}$$

$$\mathrm{R_2}^\bullet + \mathrm{AC} \xrightarrow{k_8} \text{polymerization} \tag{10}$$

$$\mathrm{R_2}^\bullet + \mathrm{VTMSi} \xrightarrow{k_9} \text{polymerization} \tag{11}$$

Under the present experimental conditions, gaseous AC and VTMSi were adsorbed significantly (by 12 and 16 %, respectively, after 4 h) on the wall of irradiation cell. The decrease of partial pressures of both AC and VTMSi vapors was measured in the dark, and the depletion rates by adsorption of AC and VTMSi, $d_{\mathrm{AC}}(t)$ and $d_{\mathrm{VTMSi}}(t)$, were determined experimentally. Taking $d_{\mathrm{AC}}(t)$ into account, Eqs. (1)–(4) give

$$-\frac{\mathrm{d[AC]}}{\mathrm{d}t} = k_{\mathrm{AC}}[\mathrm{AC}] + d_{\mathrm{AC}}(t) \tag{12}$$

where

$$k_{\mathrm{AC}} = \frac{I_a(k_1 + k_2)}{k_1 + k_2 + k_3}$$

Integrating Eq. (12) gives

$$-\ln\left(\frac{[\mathrm{AC}]}{[\mathrm{AC}]_0}\right) - \int_0^t \left(\frac{1}{[\mathrm{AC}]} d_{\mathrm{AC}}(t)\right) \mathrm{d}t = k_{\mathrm{AC}}t \tag{13}$$

where $[\mathrm{AC}]_0$ was the initial pressure of AC, and [AC] was determined from the band intensity of FT-IR spectrum under light irradiation. The value of the left-hand side in Eq. (13), $-\ln[\mathrm{AC}]_{\mathrm{cor}}$, was calculated for the 920 cm^{-1} band and plotted against irradiation time, t, in Fig. 7. A good linear relationship holds, and from the slope of the straight line, the first-order rate constant, k_{AC}, was determined under light irradiation with a mercury lamp at an exposure energy

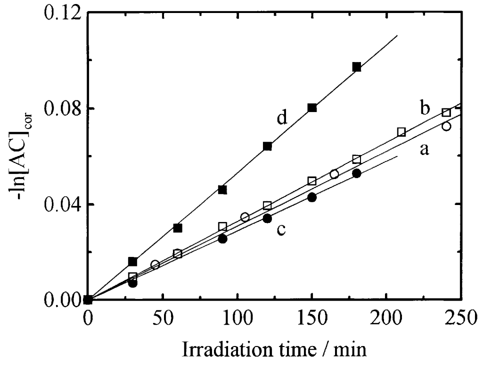

Fig. 7. Irradiation time dependence of $-\ln[\mathrm{AC}]_{\mathrm{cor}}$ evaluated from 920 cm^{-1} band intensity of FT-IR spectrum measured with (a) pure AC vapor (41 Torr) and (b) a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under light irradiation with a medium pressure mercury lamp (at an exposure dose of 22 J cm^{-2} h^{-1}), (c) pure AC vapor (41 Torr) and (d) a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under irradiation with N_2 laser light (at an exposure dose of 13 J cm^{-2} h^{-1} at a repetition rate of 12 Hz).

Table 1
Depletion rate constant of AC vapor, k_{AC}, under light irradiation with N_2 laser at an energy of $0.3\,mJ\,cm^{-2}\,pulse^{-1}$ and with a medium pressure mercury lamp at an energy of $6.1\,mJ\,cm^{-2}\,s^{-1}$

Gaseous sample	Light source	k_{AC}/min^{-1}
AC (41 Torr)	Hg lamp	3.1×10^{-4}
AC (41 Torr) + VTMSi (8 Torr)	Hg lamp	3.3×10^{-4}
AC (41 Torr)	N_2 laser	2.9×10^{-4}
AC (41 Torr) + VTMSi (8 Torr)	N_2 laser	5.3×10^{-4}

of $6.1\,mJ\,cm^{-2}\,s^{-1}$ and with N_2 laser at an exposure energy of $0.3\,mJ\,cm^{-2}\,pulse^{-1}$ with a repetition rate of 12 Hz; the results are tabulated in Table 1. k_{AC} values were also evaluated for several other bands at 2809, 993, and 593 cm^{-1}. The analysis gave the same results as in Table 1. In the case of light irradiation with a medium pressure mercury lamp, k_{AC} value was not significantly influenced by the presence of VTMSi vapor, indicating that VTMSi did not decompose by one-photon absorption of UV light. Hence, the increasing induction period with increasing partial pressure of VTMSi in Fig. 2 can be attributed to lower chemical reactivity of VTMSi than the reactivity of AC in the polymerization reaction. On the other hand, under irradiation with N_2 laser light, k_{AC} value for the gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) was significantly higher ($5.3 \times 10^{-4}\,min^{-1}$) than the one of pure AC (41 Torr) ($2.9 \times 10^{-4}\,min^{-1}$). This clearly showed that VTMSi was decomposed by a two-photon process of N_2 laser light (Eqs. (7) and (8)) and Eq. (10) became effective. Photodecomposition rate of VTMSi under irradiation with N_2 laser light was estimated from the intensity change of FT-IR band at 824 cm^{-1} of pure VTMSi (8 Torr) following Eqs. (7)–(9) and (11). Because pure VTMSi vapor did not produce any deposits under irradiation with N_2 laser light, contribution of Eq. (11) to the depletion of VTMSi may be regarded to be negligibly small. Taking the adsorption of VTMSi, d_{VTMSi}, into account, Eqs. (7)–(9) give

$$-\frac{d[\mathrm{VTMSi}]}{dt} = k_{\mathrm{VTMSi}}[\mathrm{VTMSi}] + d_{\mathrm{VTMSi}}(t) \qquad (14)$$

where

$$k_{\mathrm{VTMSi}} = \frac{I_b k_6}{k_6 + k_7}$$

$$-\ln\left(\frac{[\mathrm{VTMSi}]}{[\mathrm{VTMSi}]_0}\right) - \int_0^t \left(\frac{1}{[\mathrm{VTMSi}]} d_{\mathrm{VTMSi}}(t)\right) dt = k_{\mathrm{VTMSi}} t \qquad (15)$$

Calculated value of the left-hand side of Eq. (15) gave a linear relationship against irradiation time, t, and the first-order rate constant, k_{VTMSi}, was evaluated to be 4.5×10^{-4} min^{-1}. Radicals produced from VTMSi can initiate chemical reactions with AC (Eq. (10)) to result in consumption of AC molecules leading to increase in the efficiency of aerosol particle formation. Under the present experimental conditions, consumption of AC molecules due to a two-photon decomposition of VTMSi ($k \simeq 2.4 \times 10^{-4}\,min^{-1}$) was comparable to the one due to direct decomposition of AC ($k_{AC} = 2.9 \times 10^{-4}\,min^{-1}$).

Table 2
Volatile products in a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) identified by GC/MS under light irradiation with N_2 laser and with a medium pressure mercury lamp

Product	Retention time/min	
	N_2 laser	Hg lamp
Acetaldehyde	1.100	1.117
AC	1.180	1.180
Vinyl acrylate or methyl acrylate	1.600	1.600
Hydrocarbon	2.400	2.400
Alcohol or ketone	2.658	2.658
VTMSi	4.017	4.017
Hexamethylcyclotrisiloxane	4.833	–
AC dimer	5.200	5.250
Octamethylcyclotetrasiloxane	8.475	–

Photodecomposition process was further investigated by GC/MS spectroscopy. Volatile products from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under irradiation with N_2 laser light were identified to be acetaldehyde, hydrocarbon, alcohol or ketone, and organosilicon compounds such as hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane in addition to AC and VTMSi (Table 2). Under light irradiation with a medium pressure mercury lamp, all the above compounds except cyclic siloxanes were identified. Thus, the formation of cyclic siloxanes may be attributed to a two-photon process of N_2 laser light. Under irradiation with N_2 laser light, VTMSi can cleave Si–C bond much easier than Si–O bond as was evidenced from electron impact dissociation of some organosilicon compounds [18] and cleave SiO–C bond as was reported in tetramethoxysilane and tetraethoxysilane [2,5].

$$\mathrm{H_2C{=}CHSi(OCH_3)_3} + 2h\nu\ (\lambda = 337.1\,\mathrm{nm}) \rightarrow {}^{\bullet}\mathrm{C_2H_3} + {}^{\bullet}\mathrm{Si(OCH_3)_3} \qquad (16)$$

$$\mathrm{H_2C{=}CHSi(OCH_3)_3} + 2h\nu\ (\lambda = 337.1\,\mathrm{nm}) \rightarrow \mathrm{H_2C{=}CHSi(OCH_3)_2O^{\bullet}} + {}^{\bullet}\mathrm{CH_3} \qquad (17)$$

These radicals may produce cyclic siloxanes in GC/MS analysis.

Chemical structure of the sedimentary aerosol particles deposited from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under irradiation with N_2 laser light for 3 h was investigated by measuring FT-IR spectrum of deposits in KBr pellet; the result is shown in Fig. 8. Besides the bands ascribed to polyacrolein, IR bands were observed at 2852, 1601, 1406, 1190, 1108 and 790 cm^{-1} as clearly seen in difference spectrum (curve (b)) between the spectrum (a) and the spectrum of polyacrolein particles. The IR bands at 2852 and 1190 cm^{-1} were assigned to C–H symmetric stretching and CH_3 rocking vibrations in Si–O–CH_3. The Si–O stretching band and C–O stretching band in Si–O–CH_3 group which

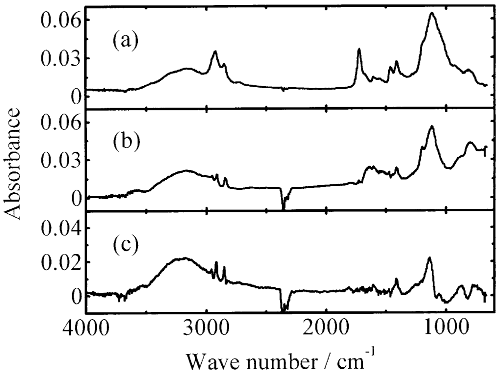

Fig. 8. (a) FT-IR spectrum of sedimentary aerosol particles produced from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under irradiation with N_2 laser light for 3 h, (b) difference spectrum between the spectrum (a) and the spectrum of polyacrolein particles produced under irradiation with N_2 laser light for 3 h, and (c) difference spectrum between (b) and the spectrum of Fig. 3(c).

were observed at 1080 and 808 cm^{-1} in Fig. 3 were shifted to 1108 and 790 cm^{-1}. Fig. 8(c) showed the difference between the spectrum in Fig. 8(b) and Fig. 3(c). The band observed at 1051 cm^{-1} was assigned to Si–O stretching vibration in Si–O–Si structure, indicating that the sedimentary aerosol particles deposited under irradiation with N_2 laser light contain siloxane units in chemical structure. The bands at 1601 and 1406 cm^{-1} could be assigned to C=C stretching vibration and CH deformation vibration in $H_2C{=}CH$– group, respectively. These chemical species may come from the cleavage of CH_3 group (Eq. (17)). Photolytic product of $^{\bullet}O{-}Si(OCH_3)_2CH{=}CH_2$ may rearrange to $O{=}SiR_1R_2$ (R_1, R_2: methoxy or vinyl group), and the silanone are well known to produce cyclic polysiloxane [2] in accordance with the experimental results by GC/MS and FT-IR spectroscopy.

In a previous paper [12], we have reported on XPS spectrum of sedimentary aerosol particles deposited from a gaseous mixture of VTMSi and AC under irradiation with N_2 laser light. The result showed that Si atoms were incorporated into the aerosol particles as three different chemical species, i.e., elemental silicon (Si^{α} assigned to 99.0 eV band), organosilicon polymer bonded with oxygen atoms (Si^{β} assigned to 102.1 eV band) and $(SiO)_n$ or $(SiO_2)_n$ polymer (Si^{γ} assigned to 103.3 eV band) [5,11,19]. The stoichiometry of atoms in the sedimentary aerosol particles was $Si^{\alpha}_{0.05}Si^{\beta}_{0.05}Si^{\gamma}_{0.90}C^{\alpha}_{5.81}C^{\beta}_{1.08}C^{\gamma}_{0.46}C^{\delta}_{0.15}$. These results indicated that polysiloxane is the major chemical species of Si atoms, supporting that Eq. (17) took place by a two-photon process of N_2 laser light and the resulting silanones produced polysiloxane.

Photochemical processes of VTMSi under light irradiation with a medium pressure mercury lamp were investigated by measuring XPS of the sedimentary aerosol particles deposited from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr). The results for C 1s and Si 2p core levels are shown in Fig. 9. C 1s band could be resolved into four

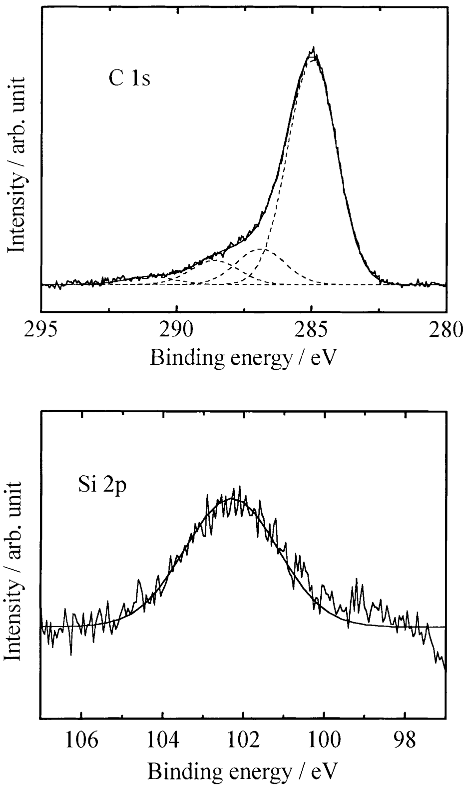

Fig. 9. XPS spectra of C 1s and Si 2p core levels in the sedimentary aerosol particles deposited from a gaseous mixture of VTMSi (8 Torr) and AC (41 Torr) under light irradiation with a medium pressure mercury lamp through a UV-29 and a UVD33S filters for 4 h.

kinds of carbon (α, β, γ and δ) at 285.0, 286.6, 288.7 and 291.0 eV. These were assigned to carbon in hydrocarbon, carbon in C–O bond, carbon bonded to two oxygen (i.e., –O–C–O–), and carbon bonded to more oxygen (i.e., –O–CO–O–), respectively [20,21]. Si 2p band was observed at 102.3 eV which could be assigned to an oxygen-rich silicon, i.e., silicon in trimethoxysilyl group, suggesting that VTMSi was polymerized into polyacrolein through the polymerization reaction of vinyl group of VTMSi. The stoichiometry of atoms was $Si^{\beta}_{1.00}C^{\alpha}_{7.91}C^{\beta}_{1.54}C^{\gamma}_{0.90}C^{\delta}_{0.28}$. It is clear that VTMSi was involved more (∼1.4 times) in the aerosol particles under light irradiation with N_2 laser than with a mercury lamp. This is mainly due to the contribution of photochemical process of Eq. (10).

XPS spectrum of the deposits produced from pure gaseous AC under irradiation with a medium pressure mercury lamp was also measured. C 1s band was resolved into four components as in the case of Fig. 9. The existence of four kinds of carbon atoms supported a proposed chemical structure of polyacrolein [22] which is highly crosslinked with cyclic acetal and hemiacetal structural units. The stoichiometry of C atom in polyacrolein was $C^{\alpha}_{0.77}C^{\beta}_{0.13}C^{\gamma}_{0.07}C^{\delta}_{0.03}$. In the sedimentary aerosol particles deposited from a gaseous mixture of VTMSi and AC, relative abundance of C^{β} atom (which is bonded to one oxygen) is a little higher than the one from pure AC, supporting that the trimethoxysilyl group was involved in the aerosol particles.

In conclusion, a gaseous mixture of VTMSi and AC produced sedimentary aerosol particles under UV light irradiation. Under irradiation with N_2 laser light, two-photon process initiated photodissociation reactions of both AC and VTMSi molecules and produced reactive species which could initiate polymerization reactions between AC and VTMSi, resulting in acceleration of nucleation reaction and leading to the formation of cyclic polysiloxane. Under light irradiation with a medium pressure mercury lamp, nucleation process in aerosol particle formation was initiated only by one-photon process of AC molecules and VTMSi molecules contributed to the particle growth through the vinyl polymerization.

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