Laser-induced aerosol particle formation from a gaseous mixture of trimethyl(2-propynyloxy)silane and acrolein

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Abstract

Upon exposure to N_2 laser light, a gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and acrolein (AC) produced sedimentary spherical aerosol particles with a mean diameter of ≈ 0.5 μm. The IR spectrum of the sedimentary aerosol particles showed bands characteristic of polyacrolein, and XPS showed two Si 2p bands assignable to elemental silicon and silicon bonded in an organosilicon polymer, indicating that TMPSi was incorporated into the parent aerosol particles of polyacrolein, and cleavage of Si–C and Si–O bonds took place in the aerosol particles. The nucleation process of the aerosol particles was investigated by measuring He–Ne laser light intensity scattered by the aerosol particles as formed under irradiation with N_2 laser light.   © 1998 Elsevier Science S.A. All rights reserved.

Keywords: N_2 laser-induced nucleation; Sedimentary aerosol particles; Trimethyl(2-propynyloxy)silane; Acrolein

1. Introduction

UV laser-induced aerosol particle formation and a thin film deposition from gaseous organic molecules can afford a unique way to produce noble materials. Under irradiation with N_2 laser light, acrolein (2-propenal) (AC) produced sedimentary aerosol particles of polyacrolein and methyl acrylate (2-propenoic acid methyl ester) (MA) produced a thin polymeric film by two photon process [1,2]. AC molecules were highly reactive to other molecules such as MA and carbon disulfide during nucleation reaction under UV laser light irradiation, and aerosol particles of polyacrolein involved these gaseous molecules as polymerized species to form composite aerosol particles [1,3]. This result suggested that the aerosol particles of polyacrolein which are growing in the gas phase under UV laser light irradiation can be used as a reaction field with a size ranging from several nm to 1 μm to produce composite particles. By utilizing the reactivity of polyacrolein particles, we have tried to incorporate an organosilicon compound into the parent particles of polyacrolein.

Laser-induced polymerization of organosilicon compounds in the gas phase has recently been studied and it presented a unique technique for chemical vapor deposition

of thin films of organosilicon polymers on substrates of choice kept at ambient temperature [4,5]. Thus, upon exposure to IR laser light, polycarbosilanes were prepared from silacycles as silacyclobutanes, silacyclohexane and disilacyclobutane $R_2Si(CH_2)_nMR_2$ ($R = H, CH_3, H_2C=CH, HC\equiv C$; $n = 2, 4$; $M = C$, Si) via thermal generation of the short-lived and efficiently polymerizing $RSi=CH_2$ silenes [6–10], and upon exposure to ArF excimer laser light (193 nm), polyoxocarbosilanes were prepared from trimethyl(2-propynyloxy)silane (TMPSi) [11].

In the present paper, TMPSi which possesses a $C\equiv C$ bond was chosen as a reactive organosilicon compound, and a gaseous mixture of TMPSi and AC was irradiated with N_2 laser light with the aim to synthesize composite aerosol particles which involve both components. Sedimentary aerosol particles obtained therefrom were characterized by IR spectrum and X-ray photoelectron spectrum (XPS). Furthermore, to understand the nucleation process in aerosol particle formation, a monitor (He–Ne laser) light intensity scattered by the aerosol particles which were formed under irradiation with N_2 laser light was measured.

2. Experimental details

TMPSi was prepared by refluxing a mixture of 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Kasei, GR grade, 96%) and

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2-propyn-1-ol (Wako, EP grade, 98%) for 12 h under nitrogen atmosphere followed by fractional distillation. Fraction at 110°C was used as a pure sample after checking its purity by gas chromatography. TMPSi was stored in a deaerated pyrex glass tube below 10°C to prevent polymerization. AC (Merck, 95%, stabilized with 0.2% hydroquinone) was also stored in a refrigerator below 10°C to prevent polymerization. The TMPSi and AC liquids were distilled under vacuum and degassed by freeze-pump-thaw cycles immediately before use. To prepare a gaseous mixture of TMPSi and AC, a fixed amount of AC vapor which was introduced into a specific region of a vacuum line with a mercury manometer was collected into a glass tube by freezing with liquid nitrogen, and then another fixed amount of TMPSi vapor was introduced into a cylindrical cell (inner diameter: 35 mm, length: 155 mm) or a cross-shaped cell (inner diameter: 35 mm, long arm: 165 mm, short arm: 135 mm) furnished with quartz optical windows on each end. After AC liquid in the glass tube was vaporized, it was introduced into the cell (which was already filled with TMPSi) to prepare a gaseous mixture of TMPSi and AC. The partial pressure of AC vapor in the cell was determined from the analysis of UV absorption spectrum. The background pressure of the vacuum system was 4×10^{-5} Torr (1 Torr = 133.3 Pa). The leakage into the evacuated cell from the atmosphere was checked to be less than 0.5 Torr in a day. The gaseous samples were irradiated with nitrogen gas laser light (Molectron UV24, 337.1 nm) through the optical quartz window with a repetition rate of 12 Hz for 2–8 h. Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-5121B). IR spectrum of the sedimentary aerosol particles was measured with a Hitachi 260-10 IR spectrophotometer, and scanning electron microscope (SEM) images were taken with a Topcon ABT-32 scanning electron microscope. Light intensity scattered perpendicularly to the incident monitor (He–Ne laser) light by the aerosol particles floating in the cell was measured with a combination of a photomultiplier tube (EMI 6256S) and a lock-in amplifier (SRS SR-530) by chopping and synchronizing monitor light with exciting N_2 laser light pulses using a delay and pulse generator (SRS DG535). XPS was measured with a VG ESCA 3MKII electron spectrometer employing Al $K\alpha$ X-ray.

3. Results and discussion

Upon exposure to N_2 laser light at an energy of 2.7–4.4 mJ/pulse for 5 h, a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) deposited sedimentary aerosol particles of brownish white color on a glass plate which was placed at the bottom of the irradiation cell in order not to be directly exposed to the incident laser light. The product yield of the sedimentary aerosol particles was less than 0.1 mg (<0.3%). TMPSi has absorption peak at a wavelength shorter than 200 nm, and it does not absorb the light at 337.1 nm, whereas

AC molecule has n–π^* absorption band in 330 nm region [12,13]. In order to check whether TMPSi can initiate nucleation reaction by two-photon process, pure TMPSi vapor (18 Torr) was irradiated with N_2 laser light for 5 h; we could obtain neither deposit on the optical window, nor sedimentary aerosol particles. Hence, under the present experimental conditions, nucleation reaction of the gaseous mixture of TMPSi and AC was induced through the chemical reaction of AC as discussed previously [3]. Aerosol particles deposited from the gaseous mixture fell down on the glass plate with a reproducible sedimentary pattern due to convection of the gaseous mixture. Fig. 1a shows a SEM image of the sedimentary aerosol particles deposited from the gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) under irradiation with N_2 laser light at an energy of 2.7 mJ/pulse for 8 h. Aerosol particles were spherical, and their particle sizes distributed over a wide range (0.2–3 μm) with a peak around ≈ 0.5 μm and shoulder in 1–2 μm region as shown in Fig. 1b. TMPSi has a tendency to stick on glass surface of the irradiation cell. During long irradiation with UV laser light, partial pressure of TMPSi may decrease more rapidly than that of AC due to adsorption, resulting in earlier consumption of TMPSi than AC in the vapor phase. Residual AC molecules could interact with floating aerosol particles to propagate polyacrolein sphere resulting in the formation of large particles. The shoulder observed in 1 – 2 μm region in Fig. 1b may be due to this process. Thus, a mean diameter of the composite particles which were produced from the initial composition of the gaseous mixture was estimated to be ≈ 0.5 μm.
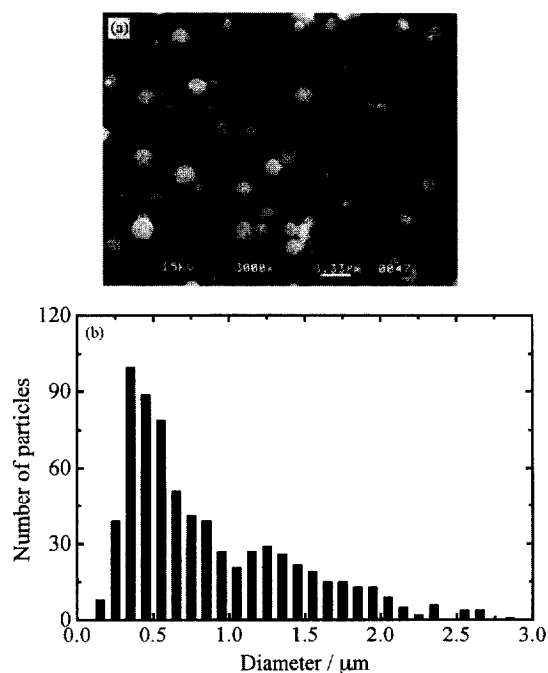

Fig. 1. (a) SEM image of sedimentary aerosol particles deposited from a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) under irradiation with N_2 laser light at an energy of 2.7 mJ/pulse for 8 h, and (b) particle size distribution therefrom. Original magnification of SEM, 3000×.
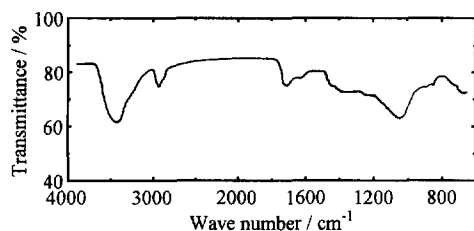
Fig. 2. IR spectrum of the aerosol particles deposited from a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) under irradiation with N_2 laser light.

To characterize properties of the aerosol particles, IR spectrum and XPS were measured with the sedimentary aerosol particles deposited from a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr). In Fig. 2, IR bands characteristic of AC monomer were not observed, but those of polyacrolein were observed in 800–1800 cm^{-1} region (i.e., at 1063, 1155, (1275), and 1430 cm^{-1}) and in 3500 cm^{-1} region [14,15]. TMPSi monomer has a C–H stretching band in CH≡C–group at 3320 cm^{-1} [11], but this band was not observed with the sedimentary aerosol particles. These results showed that TMPSi was not involved as monomeric species in the sedimentary aerosol particles and that polyacrolein was a major component of the particles.

XPS of the sedimentary aerosol particles were measured with Si 2p, C 1s, and O 1s bands. The results are shown in Fig. 3. Si 2p band in Fig. 3a could be resolved into two (α and β) bands with bonding energies at 99.3 and 101.7 eV. These bands can be assigned to elemental silicon and silicon bonded in an organosilicon polymer, respectively. In Fig. 3b, three kinds of carbon (α, β, and γ) were detected at 284.8, 287.2, and 288.8 eV. These bands can be assigned to carbon in hydrocarbons, carbon in C–O bond, and carbon bonded to two oxygen (i.e., –CO–O–). This result partly supported a proposed structure for polyacrolein of highly crosslinked polymer with cyclic acetal and hemiacetal structural units [14]. For oxygen, O 1s band was observed at 532.6 eV, assigned to oxygen bonded in organosilicon and other polymers. The stoichiometry of the atoms in the aerosol particles was determined to be $Si_{0.45}{}^{\alpha}\ Si_{0.55}{}^{\beta}\ C_{13.2}{}^{\alpha}\ C_{3.3}{}^{\beta}\ C_{1.8}{}^{\gamma}\ O_{6.5}$. An abundance of Si bonded in an organosilicon polymer clearly showed that TMPSi was incorporated into the aerosol particles as polymerized species. It is noteworthy that considerable amount of elemental silicon was detected in the aerosol particles. Elemental silicon was also detected in the sedimentary aerosol particles deposited from a gaseous mixture of vinyltrimethoxysilane and AC under irradiation with N_2 laser light [16], but its abundance is much less (5%) compared to the case of TMPSi/AC (45%), indicating that the cleavage of Si–C bond is much easier than that of Si–O bond. From these results, it was suggested that under irradiation with N_2 laser light, cleavage of Si–C bonds of TMPSi molecules which were incorporated into the aerosol particles took place to form Si–Si bond between neighboring TMPSi molecules, followed by cleavage of some Si–O bonds adjacent to Si–Si bonds eventually to produce elemental silicon in the aerosol parti-
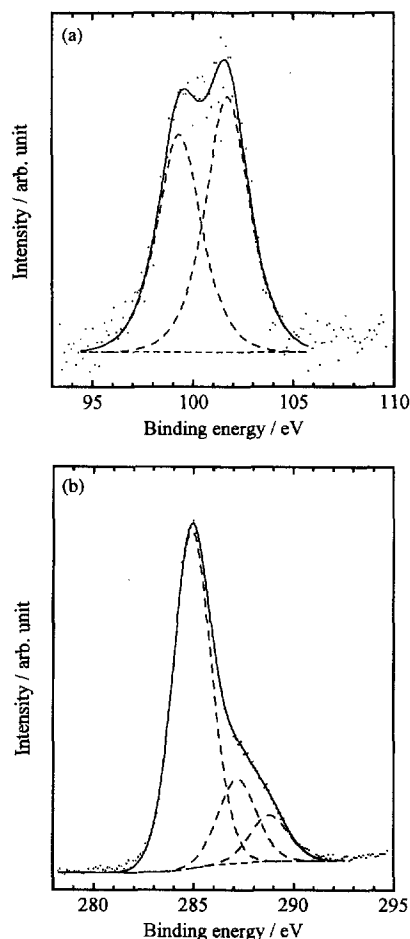

Fig. 3. XPS of (a) Si 2p and (b) C 1s bands measured with the aerosol particles deposited from a gaseous mixture of TMPSi (17 Torr) and AC (38 Torr) under irradiation with N_2 laser light at an energy of 4.1 mJ/pulse for 6 h. Observed spectrum (represented by dots) was resolved into two bands (broken lines) for Si 2p and into three bands for C 1s. The simulated spectrum was denoted by a solid line.

cles. Thus, the elemental silicon may be widely distributed in the polymeric matrix of the aerosol particles with amorphous structure. Although contamination from air produced C^{α} and O atoms on the substrate, the stoichiometry showed that contribution of AC is much more than expected from the initial composition of the gaseous mixture. This also supported that due to adsorption of TMPSi on glass wall, residual AC molecules propagated polymerization to form polyacrolein under prolonged (8 h) irradiation with N_2 laser light.

Nucleation process of a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) was studied by measuring the intensity of He–Ne laser light scattered by the aerosol particles which were produced under irradiation with N_2 laser light. The results are shown in Figs. 4 and 5. Under irradiation with N_2 laser light at an energy of 2.7 mJ/pulse (Fig. 4a), scattered light intensity began to increase gradually at $\approx$ 15 min, and then increased more rapidly at 150 min. After reaching to its maximum at $\approx$ 210 min, scattered light intensity became almost constant until 482 min at which N_2 laser light was shut down. Immediately after the laser was shut down (Fig. 4b),
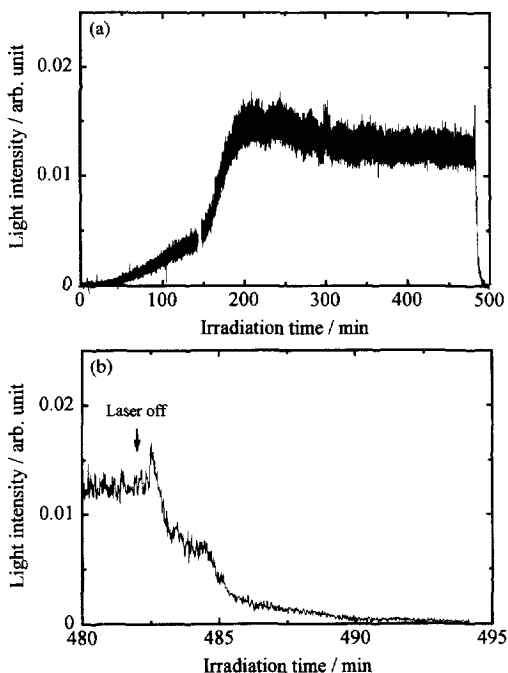
Fig. 4. Light intensity scattered by the aerosol particles produced from a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) (a) under irradiation with N_2 laser light at an energy of 2.7 mJ/pulse, and (b) after the laser light was shut off.

the scattered light intensity increased for a short while (≈ 20 s) and then decayed almost completely in 10 min, accompanied with intensity fluctuation due to convection and sedimentation of the aerosol particles as in the cases of AC/CS_2 and MA/CS_2 [3,17]. The increase of scattered light intensity immediately after the last laser shot reflected photochemical propagation of the aerosol particle formation. In Fig. 5A, the scattered light intensity was measured by varying N_2 laser intensity. With increasing laser intensity, the induction period for detecting the scattered light became shorter and the scattered light intensity became stronger. When the laser intensity decreased to 2.2 mJ/pulse, we could not detect any formation of the aerosol particles. In Fig. 5B, increasing rate of the scattered light intensity (R_s) was evaluated at the first slope by extrapolating a straight line. If we simply assume that the scattered light intensity at the initial stage of aerosol particle formation is proportional to the number of nucleation, then the R_s value is proportional to the number of initiating radicals newly formed from AC in a unit time under irradiation with N_2 laser light. In Fig. 5B, $(R_s)^{1/2}$ value is also plotted against N_2 laser intensity, showing that a linear relationship holds between $(R_s)^{1/2}$ and the laser intensity. This result supported that the nucleation process was initiated by two-photon process, and AC molecule was responsible to initiate nucleation reaction [16].

The product yield of the sedimentary aerosol particles from the gaseous mixture was very low (less than 0.1 mg). If we assume that the integrated scattered light intensity is a measure of the product yield, then we can derive the laser intensity dependence of the product yield. The scattered light intensity

integrated for the first 100 min was plotted against laser intensity in Fig. 6. The result showed that the product yield increased quadratically to the laser intensity over a threshold energy, implying that the propagation process of the aerosol particle formation proceeded by two-photon process.

In conclusion, it is confirmed that the nucleation reaction was initiated by two-photon process of AC, and TMPSi was incorporated into the propagation reaction in aerosol particle formation. Under irradiation with N_2 laser light, cleavage of Si–C bonds of TMPSi molecules which were incorporated into the aerosol particles took place to form Si–Si bond between neighboring TMPSi molecules, followed by cleavage of some Si–O bonds adjacent to Si–Si bonds eventually to produce the elemental silicon.
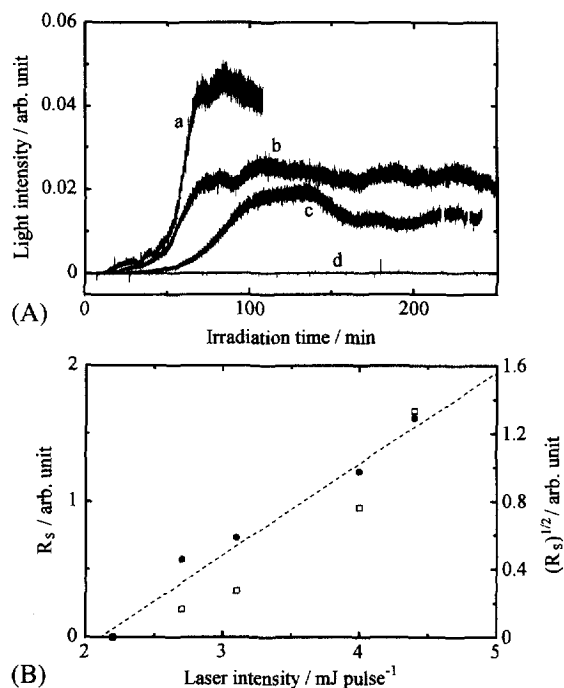

Fig. 5. (A) Light intensity scattered by the aerosol particles produced from a gaseous mixture of TMPSi (20 Torr) and AC (33 Torr) under irradiation with N_2 laser light at an energy of (a) 4.4, (b) 4.1, (c) 3.1, and (d) 2.2 mJ/pulse. (B) Dependence of the R_s value (i.e., increasing rate of the scattered light intensity) ($\square$) and $(R_s)^{1/2}$ value ($\bullet$) on the intensity of N_2 laser light.
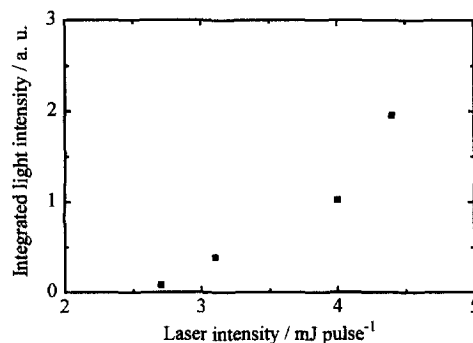

Fig. 6. Laser intensity dependence of the scattered light intensity integrated for the first 100 min under N_2 laser light irradiation.

Acknowledgements

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