

Detection of deposition rate of plasma-polymerized silicon-containing films by quartz crystal microbalance

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Abstract

The deposition rates of plasma-polymerized (pp-) films of vinyltriethoxysilane, vinyltrimethylsilane, tetravinylsilane, diallyldimethylsilane, allyltrimethylsilane, 1,3-divinyltetramethyldisiloxane and 1,1,3,3-tetramethyl-1,3-divinyldisilazane were determined by the quartz crystal microbalance (QCM) technique. Using the same polymerization conditions (100 W RF and 100 Pa vapor pressure) for the various monomers, it was found that the deposition rates were proportional to the polymerization time. The average deposition rate of pp-vinyltrimethylsilane was 2.44 $\mu\text{g}/\text{min}$. The average deposition rate of pp-1,3-divinyltetramethyldisiloxane was five-fold higher and that of pp-tetravinylsilane was 13.5-fold higher than that of pp-vinyltrimethylsilane. The average deposition rate of pp-allyltrimethylsilane was 3.43 $\mu\text{g}/\text{min}$. The average deposition rate of pp-diallyldimethylsilane was 0.8-fold higher. The average deposition rate depended on the chemical structure of the monomer, giving rise to different mechanisms of polymerization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma processing and deposition; Quartz crystal microbalance; Coatings; Polymers

1. Introduction

It is well known that new lower dielectric-constant films are required for future generation integrated circuits (ICs). These materials are required to lower the RC time constants between interconnects, thus improving the overall IC response speeds. As future sizes are reduced below the 0.25 μm level, the need for lower dielectric constant materials becomes increasingly important. This reflects the fact that the interconnect delay times become increasingly dominant relative to gate-to-gate delays as the feature size is decreased [1,2].

Plasma polymerization has been widely used to fabricate thin films of a variety of volatile compounds.

These films firmly adhere to most substrates and are highly resistant to chemical and physical treatment. The plasma polymerization technique has also been conventionally employed to fabricate thin functional films that facilitate the surface modification of materials [3,4]. Such films are expected to be useful as low dielectric-constant films rigidly fixed on the IC [5–7]. Silicon-containing compounds are candidates for low dielectric-constant materials. For the IC fabrication technology, control of the deposition rate of thin film is an important problem. The deposition rates in plasma polymerization have been determined with a balance or by in situ measurement of the film thickness with a multi-interference thickness meter [8–12]. These methods cannot, however, detect the deposition rates of ultrathin films. Piezoelectric quartz crystal is widely recognized as a useful microbalance (quartz crystal microbalance, QCM). Adsorption of material on the

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surface of a crystal changes its oscillation frequency. When an AT-cut quartz crystal with a fundamental oscillation frequency of 9 MHz is used, adsorption of approximately 1 ng of material decreases the oscillation frequency by 1 Hz [13–15]. Many attempts have been made to use these highly sensitive, convenient and portable devices as chemical sensors and immunosensors [16–20]. The QCM has also been used to monitor the thickness of films during vapor deposition and plasma processes. Those reports used only one QCM settled in the vacuum chamber. The deposition rates of gaseous monomers in plasma polymerization have been thoroughly investigated [6–10], whereas those of liquid monomers have not yet been reported. It is well known that a liquid monomer with a high boiling point is easily liquefied in the reaction chamber. Therefore, the plasma polymerization of liquid monomers has not been reported.

In this study, plasma polymerized films were prepared from seven monomers: allyltrimethylsilane; vinyltrimethylsilane; vinyltriethoxysilane; 1,3-divinyltetramethyldisiloxane; 1,1,3,3-tetramethyl-1,3-divinyldisilazane; tetravinylsilane; and diallyldimethylsilane. Each of these monomers was polymerized under conditions of 100 W RF and 100 Pa of vapor pressure. The present work is a preliminary study in using a QCM sensor array to detect the deposition rates of plasma-polymerized films in order to gain an understanding of the deposition mechanism of silicon-containing monomers.

2. Experimental

The monomers used in this experiment were all of analytical or guaranteed grade and were purchased from Wako Pure Chemical Industries Ltd (Osaka, Japan) or Kanto Chemical Co Inc (Tokyo, Japan) and used without further purification. For plasma polymerization, Samco International Co (Kyoto, Japan) equipment, model BP-1, was used [20,21]. Fig. 1a shows a schematic diagram of the plasma polymerization equipment. The deposition rates of the pp-films were measured in situ with a QCM during the polymerization process. The QCM had silver electrodes on both of its surfaces (AT-cut of 9 MHz; $8 \times 8 \times 0.15$ mm) and was purchased from Seywa Crystal Co (Chiba, Japan). The pp-films were deposited on one side of the QCM. The deposition rate of a plasma-polymerized film is not dependent on the positioning of the substrate. Therefore, seven or five QCMs were placed on the lower electrode (diameter 100 mm) for the glow discharge. The position settings of the seven QCMs on the lower electrode are denoted in Fig. 1b, and the five QCMs on the lower electrode are denoted in Fig. 1c. Prior to plasma polymerization, the seven or five QCMs were treated by plasma sputtering for 5 s under 100 W RF power and 100 Pa of He pressure.

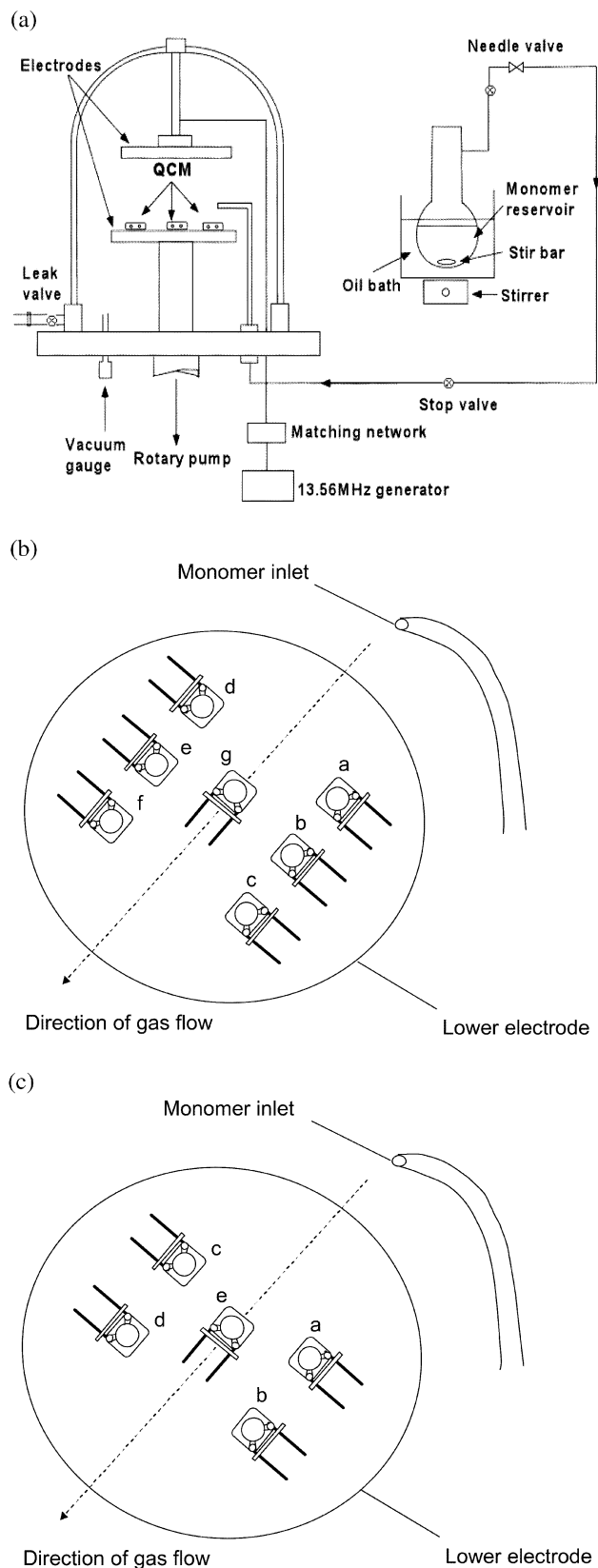


Fig. 1. (a) Schematic diagram of plasma-polymerization equipment. (b) Position settings (a–g) of seven QCMs on the lower electrode. (c) Position settings (a–e) of five QCMs on the lower electrode.

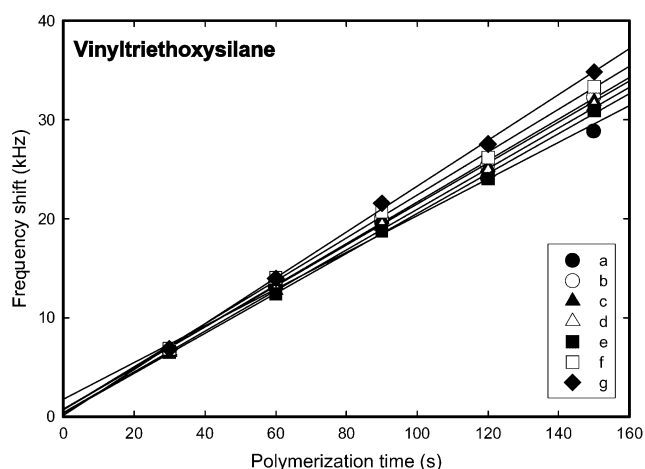


Fig. 2. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-vinyltriethoxysilane.

The plasma polymerization conditions were controlled by two parameters: the vapor pressure of the monomer and the power of the glow discharge. We used the same polymerization conditions for all seven monomers: a vapor pressure of 100 Pa and an RF power of 100 W. The monomers were vaporized at a constant liquid temperature, which was maintained by an oil bath, and under controlled vacuum. The distance between the electrodes was 6.0 cm and the power of the glow discharge was set at 100 W. The plasma polymerization was performed for 30–150 s at 30 s intervals and for 60–300 s at 60 s intervals. We obtained optimum polymer films under these conditions.

The apparatus and procedure for determining the deposition rate have been previously described [22,23]. The oscillating frequency of the QCM was measured with a universal counter (Iwatsu SC7201, Tokyo, Japan) using data stored in a microcomputer (NEC PC9821, Tokyo, Japan). The laboratory-made transistor–transistor logic (TTL) electronic circuit used is described in [15] (circuit II). The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz [22,23]. All of the experiments were carried out at 25 ± 2 °C. The chemical structure of silicon-containing pp-films was measured by FT-IR, X-ray photoelectron spectroscopy (XPS) and the contact angle. These results are published elsewhere [24].

3. Results and discussion

The rate of deposition of the pp-films onto the QCM was directly measured by the shift in the oscillation frequency. Fig. 2 shows the relationship between the deposition rate of pp-vinyltriethoxysilane for the seven positions (a–g) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 150 s. The regression of the

Table 1
Deposition rates of pp-vinyltriethoxysilane

Position	Slope (kHz/s)	Intercept (kHz)	Correlation coefficient
a	0.185	1.780	0.996
b	0.210	0.691	0.999
c	0.207	0.733	0.999
d	0.205	0.403	1.000
e	0.202	0.368	0.999
f	0.217	0.696	0.999
g	0.232	0.092	0.999

polymerization time response for positions a–g is summarized in Table 1. The correlation coefficient of each line is almost 1.000. We define the individual deposition rate for plasma-polymerized films using the slope of lines a–g for each sample. The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. The average deposition rate for the pp-vinyltriethoxysilane film is 0.056 kHz/s ($12.5 \mu\text{g}/\text{min}$). The value of the standard deviation (σ) and the coefficient of variation (C.V.) of pp-vinyltriethoxysilane are $0.85 \mu\text{g}/\text{min}$ and 6.8%, respectively. The reproducibility of the deposition rate is high; in three independent experiments, the C.V. was within 8% (data not shown). This confirms the accuracy of this technique.

Figs. 3–8 show the same relationship for pp-allyltrimethylsilane, pp-vinyltrimethylsilane, pp-vinyltriethoxysilane, pp-1,3-divinyltetramethyldisiloxane, pp-1,1,3,3-tetramethyl-1,3-divinyldisilazane, pp-tetravinylsilane, and pp-diallyldimethylsilane, respectively. The linearity range is also included. Outside this range, or above the thickness formed, the QCM does not work as a microbalance.

Table 2 summarizes the average deposition rates for the seven monomers at a 30 s polymerization time

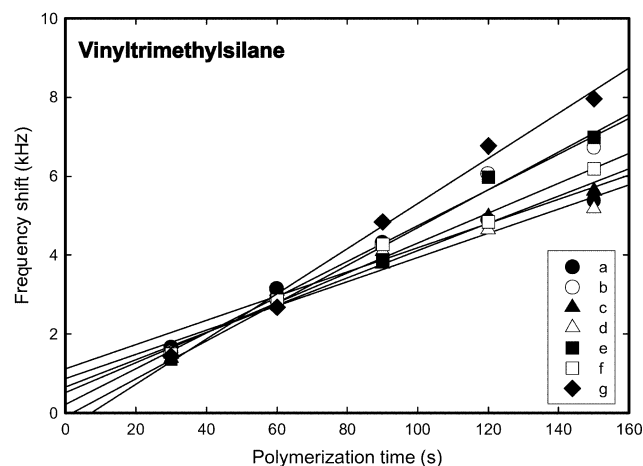


Fig. 3. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-vinyltrimethylsilane.

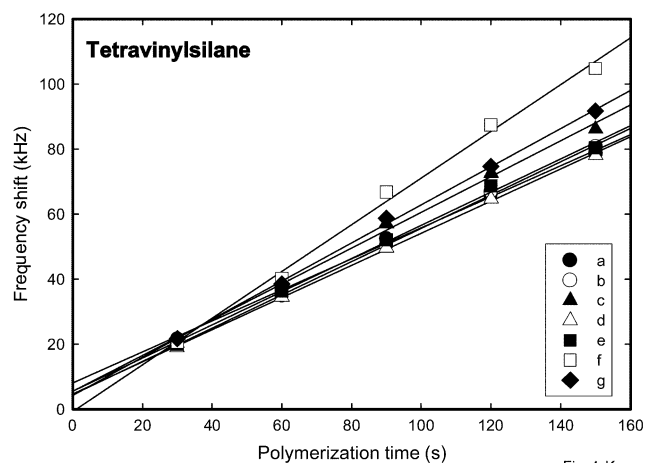


Fig. 4. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-tetravinylsilane.

interval. The values are in the order of tetravinylsilane > vinyltriethoxysilane > 1,3-divinyltetramethyldisiloxane > 1,1,3,3-teramethyl-1,3-divinyldisilazane > allyltrimethylsilane > diallyldimethylsilane > vinyltrimethylsilane.

Table 3 summarizes the averaged deposition rates for the seven monomers at a 60-s polymerization time interval. The values are in the order of tetravinylsilane > vinyltriethoxysilane > 1,1,3,3-teramethyl-1,3-divinyldisilazane > 1,3-divinyltetramethyldisiloxane > vinyltrimethylsilane > diallyldimethylsilane > allyltrimethylsilane. The difference in the order of deposition rate occurred for small deposition values.

The average deposition rate for a 300-s polymerization time interval for tetravinylsilane is 22.00 $\mu\text{g}/\text{min}$, and for diallyldimethylsilane, is 1.34 $\mu\text{g}/\text{min}$. Thus, the polymerization time interval affects the average deposi-

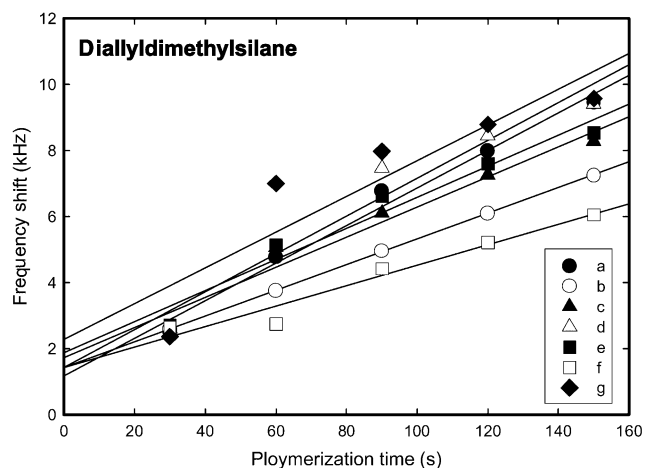


Fig. 5. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-diallyldimethylsilane.

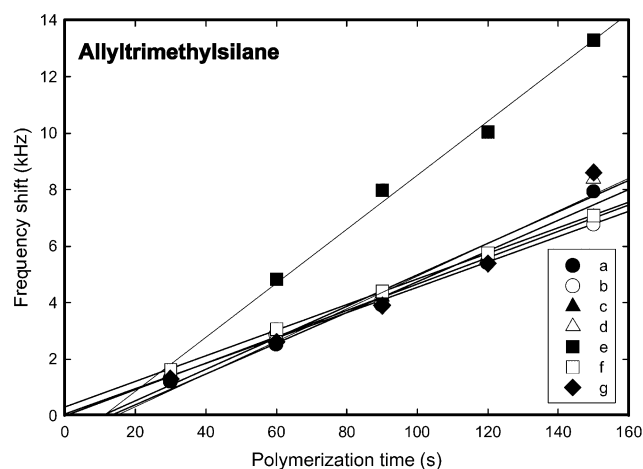


Fig. 6. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-allyltrimethylsilane.

tion rate of pp-films. It is worth noting that for a high deposition rate, a very short polymerization time interval should be selected to detect the deposition rate of the pp-film. Accordingly, the deposition rate of the pp-films is affected by the chemical structure of the monomer, and hence the reaction mechanism.

All the polymerizations were conducted under identical equipment settings, which led to a higher gas-phase concentration of the monomers with lower boiling points. The reaction pathway of the different monomers, however, often canceled this concentration effect. Polymerization is assumed to proceed via a free-radical mechanism initiated through the collision of an electron with a monomer molecule [Eq. (1)]. Dissociation of this molecule results in the formation of free radicals,

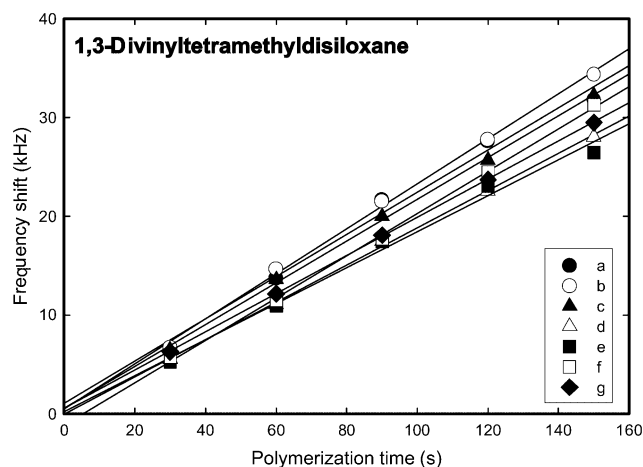


Fig. 7. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-1,3-divinyltetramethyldisiloxane.

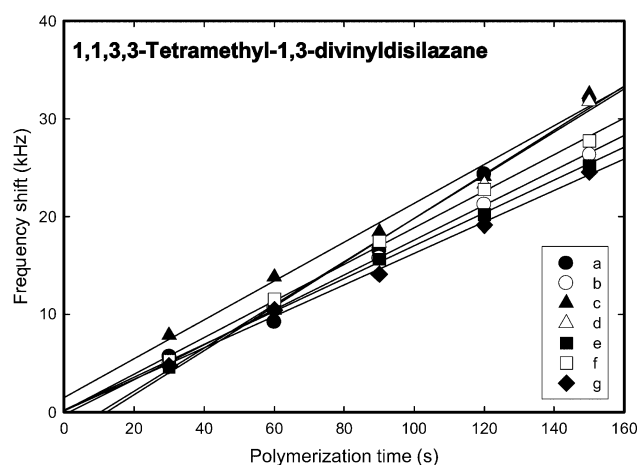


Fig. 8. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-1,1,3,3-tetramethyl-1,3-divinyldisilazane.

which may add to intact monomers [Eq. (2)]; this is denoted as the initiation.



Polymerization [Eq. (3)] then proceeds in the gas phase and on the surface.



Finally, collision between two radicals leads to termination of the reaction [Eq. (4)] by radical–radical coupling or disproportionation, as in the case of standard free-radical polymerization.



If the monomers are polymerizable by conventional free-radical polymerization, plasma polymerization may simultaneously proceed with plasma-induced polymerization, resulting in high deposition rates. In our study, tetravinylsilane, 1,3-divinyldimethylsiloxane and 1,1,3,3-tetramethyl-1,3-divinyldisilazane were deposited at higher rates. The deposition rate of allyltrimethylsilane and diallyldimethylsilane, however, was not higher than the deposition rates of monomers containing allylic hydrogens. The monomers containing allylic protons, i.e. allyltrimethylsilane and diallyldimethylsilane, did not exhibit any significant plasma-induced polymerization. In this case, radical transfer to the allylic position

Table 2

Average of deposition rates of pp-films coated with 30 s of time intervals for the plasma-polymerization

Monomer	Deposition rate ($\mu\text{g}/\text{min}$)	σ ($\mu\text{g}/\text{min}$)	C.V. $\times 10^2$ (%)
Vinyltriethoxysilane	12.49	0.85	6.8
Vinyltrimethylsilane	2.44	0.59	24.4
Tetravinylsilane	33.02	4.96	15.0
Diallyldimethylsilane	2.84	0.59	20.7
Allyltrimethylsilane	3.43	1.06	30.9
1,3-Divinyltetramethyldisiloxane	12.26	0.99	8.1
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	11.48	1.50	13.1

The average deposition rates of the pp-films were calculated from the slope of the seven lines (a–g) in the figures. σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

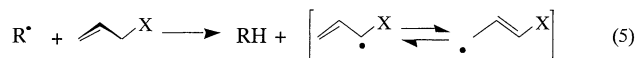
Table 3

Average deposition rates of pp-films coated with 60-s time interval for the plasma polymerization

Monomer	Deposition rate ($\mu\text{g}/\text{min}$)	σ ($\mu\text{g}/\text{min}$)	C.V. $\times 10^2$ (%)
Vinyltriethoxysilane	11.14	2.39	21.4
Vinyltrimethylsilane	1.41	0.33	23.2
Tetravinylsilane	29.65	10.36	35.0
Diallyldimethylsilane	1.34	0.46	34.2
Allyltrimethylsilane	1.07	0.49	46.1
1,3-Divinyltetramethyldisiloxane	4.50	0.57	12.8
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	6.55	1.73	26.4

The average deposition rates of the pp-films were calculated from the slope of the five lines (a–e) in the figures (data not shown). σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

[Eq. 5] was followed by radical–radical coupling [Eq. 6].



The reaction in Eq. 5 may be considered an ‘initiation’ that is promptly followed by termination [Eq. 6] without any intermediate steps of propagation. A unique feature of the plasma polymerization of ‘normal’ monomers is that the system may become starved of monomers. We assume that the rate of polymerization is mainly determined by the rate of initiation k_i and not by the rate of propagation [25,26]. The termination of growing chains is suppressed by the immobility of the plasma-polymerized layer, making the termination rate k_t low.

We are well aware that although the proposed reaction pathway and rate-determining steps are supported by the experimental findings, the results do not provide direct proof of these mechanisms. Additional experimental support may be obtained by in situ determination of the reactive species in the plasma and in the gas phase, as well as the volatile products formed. Precise characterization of the cross-linked film would also be a useful investigation.

Acknowledgments

This work has been supported in part by the Special Funds for ‘Study of Molecular Conversion Technology for Greenhouse Gases’ for the New Sunshine Project, National Institute of Advanced Industrial Science and Technology (AIST), Japan, and Japan International Co-operation Agency (JICA). One of the authors, Z.A. Talib, would like to express his gratitude to JICA for sponsoring his stay in Japan and to Universiti Putra Malaysia for granting leave of absence from his academic duties.

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