

New Synthesis Method of Poly(diphenylsilylenemethylene) Thin Films

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Poly(silylenemethylene)s (PSMs) have been studied for nearly 3 decades, largely due to their thermal and mechanical and pyrolytic properties.¹ Among the PSM family, poly(diphenylsilylenemethylene) (PDPHSM) is of particular interest because of its high thermal stability (over 670 K).² Recently, some unique light emission properties of PDPHSM induced by UV laser irradiation were observed.³ These properties show promise for applications such as polymer-based optical devices. However, thin films of PDPHSM are difficult to synthesize because PDPHSM is insoluble in most solvents and has a high melting point. We have developed a simple, new and unique method for fabricating PDPHSM thin films, for which the thermal polymerization is activated by adding metal nanosized particles.

1,1,3,3-Tetraphenyl-1,3-disilacyclobutane (TPDC) was prepared according to the method of Auner et al.⁴ and purified by recrystallization from chloroform/ethanol before use. The fabrication process of the PDPHSM thin films and of the patterned films, schematically illustrated in Figure 1, includes the following stages.

First Stage: Monomer Deposition. TPDC films were formed on c-Si wafers by a vacuum evaporation technique under a pressure of 1 Pa and a constant temperature of 400 K, to provide of 10 μm thick films at a deposition rate of 1 $\mu\text{m}/\text{min}$. Since the FT-IR spectra of the TPDC films were identical to that of the TPDC before evaporation, TPDC did not degrade during the vacuum evaporation process.

Second Stage: Preparation of the Polymerization Catalysts. Fine metal particles were deposited onto the surface of TPDC films with a conventional sputtering apparatus (JEOL, JFC-1100) in air or argon plasma for 4 min. Patterned depositions were also carried out using masks. For all types of metallic targets, such as Pt/Pd (80/20 in weight ratio), Pt, Cu, Au, or Ag, constant voltage (500 V) and current (8 mA)

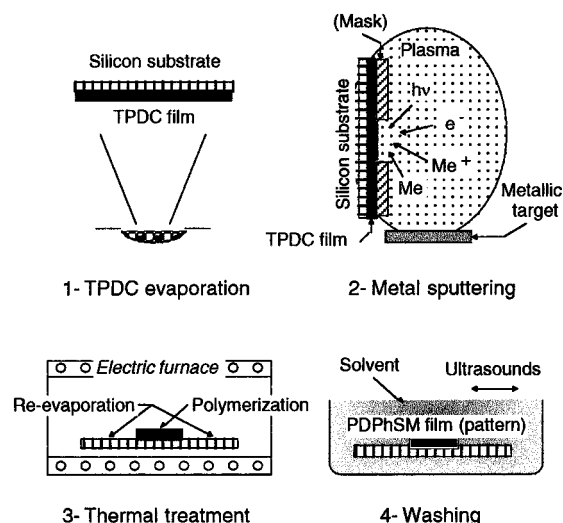


Figure 1. Fabrication process of PDPHSM thin films and patterns.

were employed for the plasma discharge. TEM images of deposited metals (Figure 2) show that the metal particles were discontinuously scattered on TPDC film surfaces. The average diameters of the metal particles are listed in Table 1. The smallest particles were obtained with Pt or Pt/Pd alloy (about 2.5 nm). The FT-IR spectra of the TPDC films did not change with metal sputtering.

Third Stage: Thermal Polymerization. Metal/TPDC/Si-wafer composites were heated in an electric furnace in an air or argon atmosphere to polymerize the TPDC. All the samples were heated at a temperature in the range of 400–550 K from 10 min to 20 h. This temperature range lies between the melting point of TPDC and PDPHSM. For the heat treatments conducted in air, the samples were directly introduced in the furnace at the polymerization temperature. For those conducted in argon, a temperature increase of 20 K/min was applied before reaching the polymerization temperature. In both cases, samples were cooled at 30 K/min and taken out of the furnace after they had cooled to below 370 K. The parts of the initial TPDC films where metal sputtering had not been carried out before the heat treatment were entirely re-evaporated. However, continuous PDPHSM thin films were formed where the film was covered by metal particles, allowing the fabrication of millimetric polymer patterns with complex shapes. By adjusting the heating condition, it was possible to form polymer films with any type of metal particles. The polymerization was mainly confirmed by FT-IR. A broad absorption peak centered around 1060 cm^{-1} and characteristic of the polymer structure was observed (Figure 3b). At the same time, the absorption at 937 cm^{-1} , characteristic of the TPDC structure, disappeared. Generally, Si–O and O–Si–O absorptions appear around 1050 cm^{-1} and the Si–C stretch appears near 850 cm^{-1} .⁵ It is unlikely that the absorptions around 1060 cm^{-1} come from Si–O or O–Si–O because

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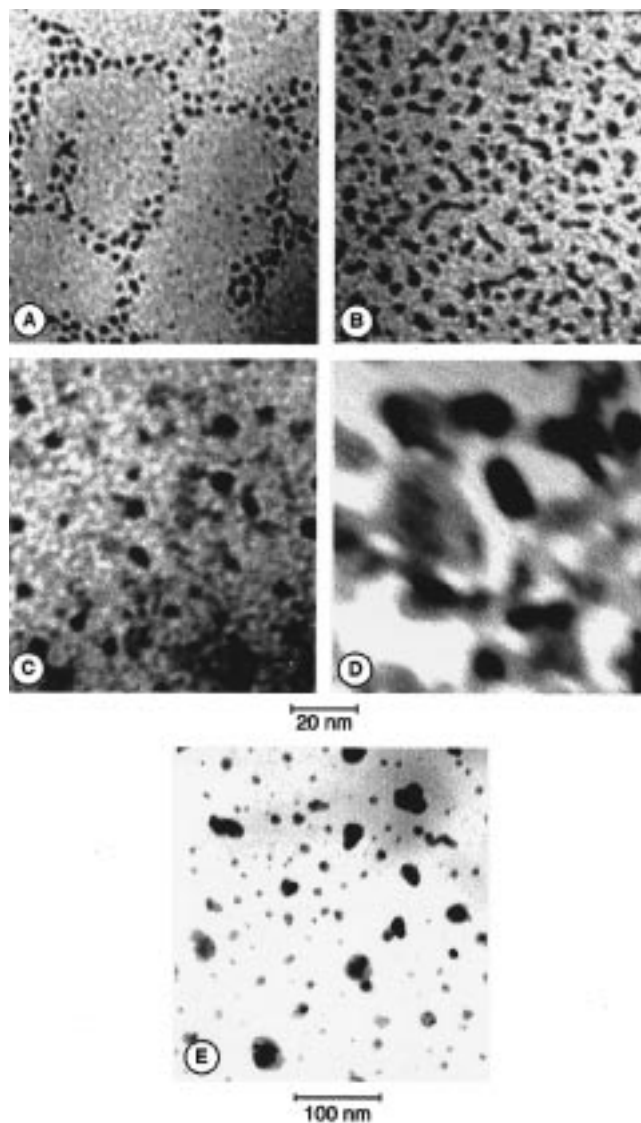


Figure 2. TEM images of sputtered metal particles: Pt/Pd (A), Pt (B), Cu (C), Au (D), and Ag (E).

Table 1. Average Sizes of Metal Particles Determined by TEM Images, and Resulting Thickness of Synthesized PDPHSM Thin Films in Percent of the Initial TPDC Film Thickness^a

sputtered metal	Pt/Pd	Pt	Cu	Au	Ag
average particle size (nm)	2.4	2.6	3.8	>8	18.2
sd	0.4	0.6	0.7	10.3	
PDPHSM/TPDC film thickness (%)	82	82	46	77	5

^a The thickness was measured with a stylus profilometer. sd: standard deviation.

the oxygen content estimated by XPS was small (less than 1.5 atom %) and typical NMR data did not exhibit highly oxidized species. We guess that the absorptions around 1060 cm^{-1} are characteristic of the polymer containing diphenylsilyl units and that at 937 cm^{-1} is due to the cyclic structure of TPDC. Further evidence will be needed to clarify this. The FT-IR spectra of the PDPHSM films were similar to that of chemically prepared PDPHSM (Figure 3c). The ^{29}Si NMR spectra of the films prepared with Cu and Pt/Pd exhibited the same chemical shift as that of the chemically synthesized polymer. However, these spectra were very broad, indicating amorphous structures, and this was consistent with the results of X-ray diffraction. The UV

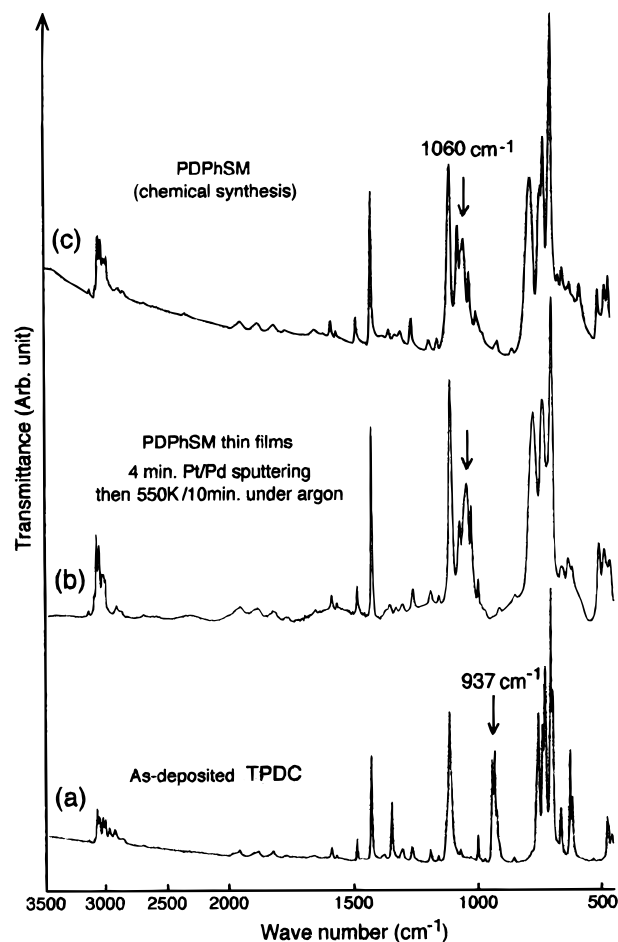


Figure 3. Typical FT-IR spectra of the as-deposited TPDC film (a), PDPHSM thin film (b), and chemically synthesized PDPHSM (c).

spectra of the films exhibited a structure similar to chemically synthesized PDPHSM and TPDC. Thermogravimetric (TG) analysis indicated that the film thermal stability depended on the kind of metal, while this stability was comparable to that of the chemically synthesized PDPHSM. These films showed the same light emission properties upon UV laser (248 nm) irradiation (Figure 4) as that already reported³ for chemically prepared PDPHSM. This suggests that there may be little difference between the polymer produced by this process and the chemically synthesized one, although we have not yet checked the light emission properties (quantum yield, absorption of emitted light by metal particles) in detail.

Fourth Stage: Removal of Unreacted Monomer.

Patterned samples were plunged into an ultrasonic bath of tetrahydrofuran to rinse the remaining TPDC and then dried at 370 K.

Table 1 shows the average diameter of metal particles and the thickness ratio of the polymer film to that of the original TPDC film. The average sizes of the metal particles were in the nanometer range, except for Ag. Under the same sputtering and heat treatment conditions (550 K, 10 min.), the thickness ratio of the polymer films was closely related to the particle size of the deposited metal: the smaller the particle size, the higher the polymerization yield and the resulting PDPHSM film thickness. For instance, the thickness of PDPHSM with Pt decreased to 82% of the original

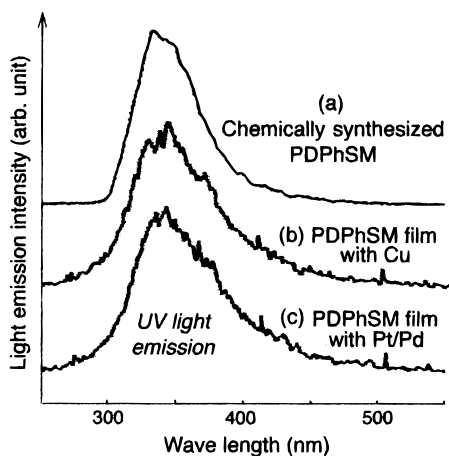


Figure 4. Light emission spectra of PDPHSM during UV laser irradiation: (a) chemically synthesized PDPHSM, (b) film fabricated at 550 K/10 min in air with 4 min of Cu sputtering, and (c) film fabricated at 550 K/10 min in air with 4 min of Pt/Pd sputtering (laser irradiation conditions, 9.9 mJ/(cm² pulse) at 248 nm).

thickness of TPDC, while that in the case of Ag decreased to only 5%. However, it must be mentioned that a simple bulk polymerization at 550 K by a chemical route without catalyst would take several hours.⁶ Actually, TPDC re-evaporation and polymerization occur competitively during the heating process above the TPDC melting temperature since PDPHSM does not sublime or degrade in the tested temperature range (400–550 K).

XPS results showed that the sputtered metal particles were initially located on the film surfaces (Figure 5a). However, during the heat treatment, TPDC melted before polymerization. Metal particles migrated inside the films, and no particles remained on the surface (Figure 5b). Since polymerization was done in air, a small quantity of oxygen and nitrogen (around 1.5 atom %) was incorporated in the films. Moreover, surface roughness, bulk morphologies, and crystallinity of the films changed, depending on the type of metal particles used. For example, Pt/Pd alloy provided transparent and smooth coatings. However, with Cu particles, coatings were opaque and rough.

It seemed that the nanometer-sized metal particles were very effective for polymerization, even for metals such as platinum, which are not known as catalysts for chemically induced polymerization.^{6–8} Another important feature of the polymerization method is that it can be performed both in air or in argon. This fact indicates that the mechanism is different from radical polymerization since it is well-known that oxygen always strongly inhibits this type of polymerization. An ionic mechanism could be proposed as a potential polymerization mechanism by activated species created from the reaction of TPDC with highly reactive ultrafine metal particles, although further study will be needed to clarify the mechanism.

In conclusion, we have developed a new method for fabricating PDPHSM thin films. This polymerization method presents three major advantages:

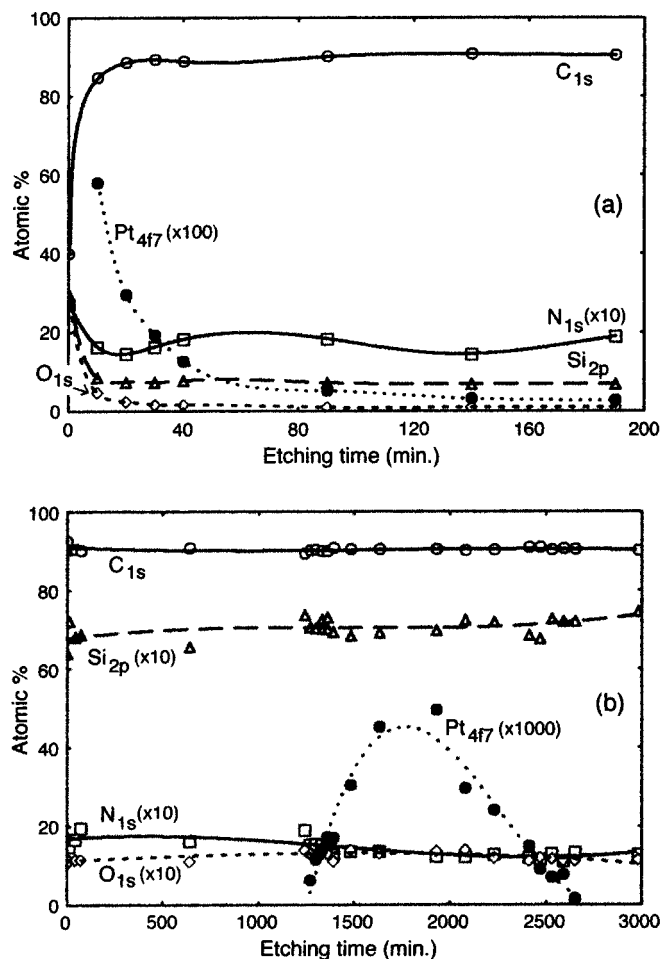


Figure 5. XPS depth profiles of the elements in a film subjected to Pt/Pd sputtering (a) just after sputtering in air and (b) after polymerization at 550 K/10 min in air.

(1) It is possible to make thin films which are difficult to fabricate by conventional method such as spin coating. It is also possible to make small patterns.

(2) This method is based on using conventional devices that are simple and suitable for mass production.⁹ Moreover, the method has also been extended to polydiphenylsiloxane thin film synthesis.¹⁰ This could potentially be applied to ring-opening polymerization of other materials.

(3) It is possible to control the bulk and surface morphologies of coatings by changing the kind of metals used.

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Supporting Information Available: UV-vis, ²⁹Si NMR, and TG analysis of the films produced (3 pages). See any current masthead page for ordering information.

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