Fabrication of Poly(diphenylsilylenemethylene) and Poly(diphenylsiloxane) Thin Films Using Fine Metal Particles

Fabrice Rossignol, Yoshinori Nakata, Hideaki Nagai, Takeshi Okutani, and Masaaki Suzuki*

Hokkaido National Industrial Research Institute, 2-17-2-1,
Tsukisamu-Higashi, Toyohira-ku, Sapporo 062-8517, Japan

Nobuo Kushibiki and Masashi Murakami

Dow Corning Asia Ltd., Research Center, 603 Kishi, Yamakita, Kanagawa 258-0112, Japan

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A new polymerization technique based on the use of sputtered metal particles for the thermal ring-opening polymerization of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (TPDC) was developed. This method facilitates the synthesis of polydiphenylsilylenemethylene (PDPhSM) thin films which are difficult to make by conventional methods because of their insolubility and high melting point. TPDC was first evaporated on silicon substrates and then exposed to metal particle deposition by sputtering prior to heat treatment. The catalytic activities of Pt, Pt/Pd, Au, Cu, and Ag particles were examined. The chemical structure of the film was basically the same, whatever the kind of metal used. However, the polymerization efficiency and film crystallinity depended greatly on the kind of metal under the same sputtering and heating conditions. The parts of the initial TPDC films that were not subjected to metal sputtering were entirely evaporated from the films without any polymerization. This phenomenon allowed us to make small polymer patterns. This method was also applicable to the ring-opening polymerization of hexaphenylcyclotrisiloxane.

1. Introduction

For the past three decades, numerous studies have focused on silicon-based polymers.[1] Their great potential in terms of thermal, mechanical, and optoelectrical properties, as well as their pyrolytic behavior, was recognized early on. Nowadays, this is one of the most active research fields, due to the development of ceramic precursors,[2,3] and research results have already been used for some industrial applications such as Nicalon SiC fibers.[4,5] These fibers are synthesized from polycarbosilanes whose backbones are constituted of Si and C atoms. Poly(diphenylsilylenemethylene) (PDPhSM) and poly(diphenylsiloxane) (PDPhSO) are also of particular interest because their high thermal stability (>673 K), combined with remarkable optical properties. It has been shown recently that, when PDPhSM or PDPhSO are irradiated with UV laser light (248 nm), they exhibit unique light emission properties[6] that show promise for future practical use. However, thin films are difficult to synthesize because PDPhSM and PDPhSO cannot be dissolved in most solvents, even at high temperatures. Consequently, it is impossible to apply the methods currently used for polymer thin film preparation, like spin coating. In addition, melting chemically synthesized powders to further deposit them on a substrate is not recommended, because some degradation related to removal of the phenyl group was reported at temperatures slightly above the polymer melting points.[7]

In this paper, we report a new and simple method for fabricating PDPhSM thin films and patterns, for which the thermal ring-opening polymerization of cyclic compounds is initially activated by sputtered metal particles.[8] We first describe this original method and then investigate the influences of the type of sputtered metal and the heat treatment conditions (temperature, atmosphere, and duration) on the polymerization efficiency. In addition, we will show that the polymerization method can also be successfully employed for fabricating PDPhSO thin films.[9]

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* Corresponding author. Tel: +81-11-857-8953. Fax: +81-11-857-8984. E-mail:masaaki@hniri.go.jp.

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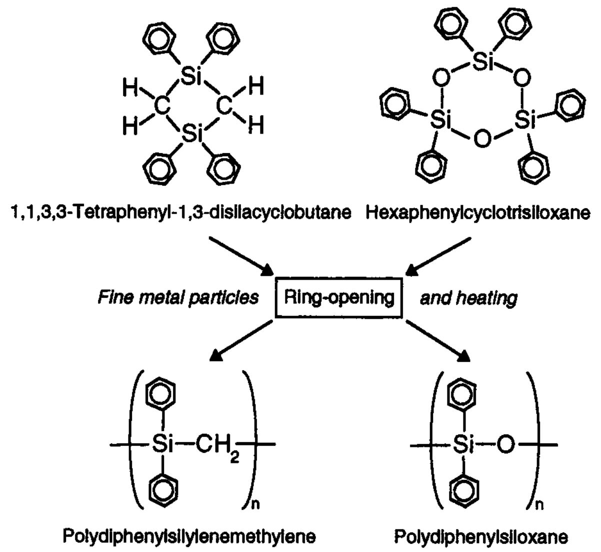

Figure 1. Ring-opening polymerization of TPDC and HPTO cyclic monomers.

2. Experimental Section

2.1. Materials and Polymerization. 1,1,3,3-Tetraphenyl-1,3-disilacyclobutane (TPDC) and hexaphenylcyclotrisiloxane (HPTO) reagents were used as raw materials, respectively, for the PDPhSM and PDPhSO syntheses (Figure 1). TPDC was furnished by Wako Industries and had a melting temperature of 407−408 K. HPTO was supplied by Shinetsu Co. and had a melting temperature of 461−462 K. TPDC was purified by reprecipitation in a chloroform−ethanol mixture before use.

The fabrication method of the polymer films was described briefly in a previous communication.[10] It included four stages:

(1) Monomer Deposition. Cyclic compounds were first evaporated on 4 cm^2 silicon substrates cut from c-Silicon wafers. The monomer films were formed by conventional vacuum evaporation at a residual pressure of 1 Pa. (Strictly speaking, TPDC is a dimer and HPTO is a trimer, but for the sake of simplification, since these two compounds are the molecules from which the polymers are synthesized, we will use the term “monomer” for both of them.) The deposition rate of the monomer was very sensitive to the temperature of molten TPDC. For the present study, a deposition rate of about 1 μm/min was obtained by evaporating at a temperature of 410 K for TPDC and 465 K for HPTO. The evaporation was performed for 10 min to obtain films with a thickness of about 10 μm. Before taking the samples out of the evaporation chamber, the chamber was returned to atmospheric pressure using helium gas to avoid oxidation of the films.

(2) Deposition of Metal Particles. Ultrafine metal particles were deposited on the monomer films by a conventional DC sputtering apparatus (JEOL JFC-1100) in air or argon plasma. Different metallic targets were employed such as Pt/Pd alloy (80/20 wt %), Pt, Cu, Au, and Ag. The applied current and voltage of the plasma discharge were fixed at 8 mA and 500 V, regardless of the metallic target used. The samples were placed perpendicular to the metallic target at the edge of the plasma. The typical sputtering time was 4 min. A mask was occasionaly put onto the monomer films to get a patterned metal deposition.

(3) Thermal Polymerization. The monomer films with metal particles were heated in a conventional electric furnace in an air or argon atmosphere to induce ring-opening polymerization of TPDC. The heating was carried out in the range of 410−550 K for 10 min to 20 h. For the heat treatment in air, the samples were directly inserted in the furnace at the constant temperature. For the heat treatment in argon, the samples were put in the furnace before heating, and a temperature increase of 20 K/min was applied before reaching the constant temperature. In both cases, samples were cooled at 30 K/min and taken out from the furnace after they had cooled to below 370 K.

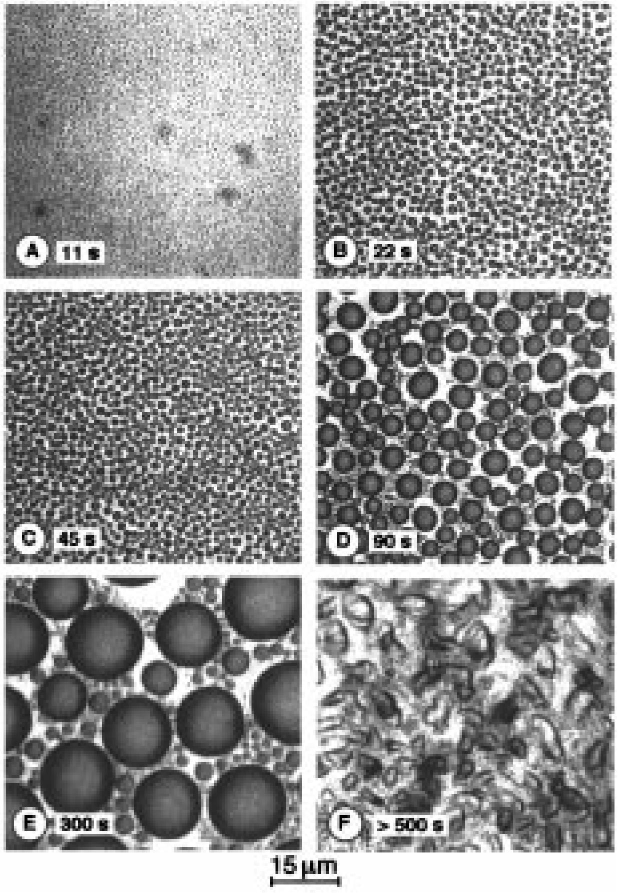

Figure 2. The change of TPDC film morphology on Si wafers with respect to TPDC evaporation time.

(4) Removal of Unreacted Monomer. The samples were plunged into tetrahydrofuran (THF) and subjected to moderate ultrasound. The quality of the pattern was improved by this treatment, possibly due to the removal of the monomers and oligomers.

2.2. Film Characterization. The chemical structure of the film was investigated by both Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer 1600 series) and by ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy (^{29}Si MAS NMR, JEOL GSX). For MAS NMR, many films were scratched and ground to obtain at least the 50 mg of powder necessary to perform an accurate analysis representative of the polymer structure in the form of thin films. NMR spectra were acquired at 53.7 MHz, at a pulse delay of 15 s and with a spinning speed of 4.5 kHz. The crystalline structure was measured by X-ray diffraction with Cu Kα ray (XRD, Rigaku Geigerflex). The film thickness was measured with a stylus profilometer. The metal particles produced by sputtering were observed by a transmission electron microscope (TEM, Hitachi, H-800NA). Since direct TEM observation of the particle deposited on the monomer film surface was difficult, the metal particles were deposited on polymer grids under the same conditions, to allow TEM analysis.

3. Results

3.1. TPDC Deposition. Figure 2 shows the images, taken with an optical microscope, of TPDC films evaporated over different times. In the early stage of vacuum

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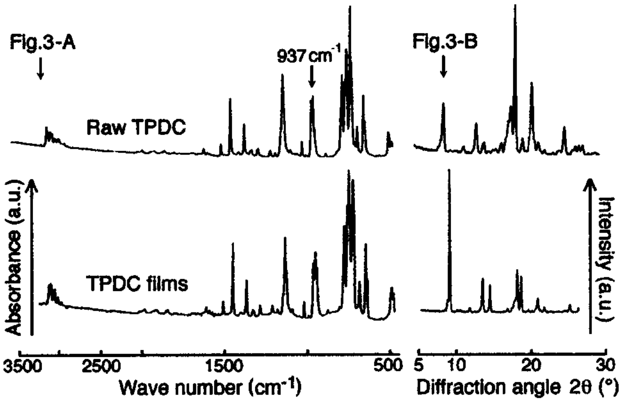

Figure 3. FT-IR spectra and XRD patterns of TPDC raw powders and as-deposited TPDC films by vacuum evaporation. TPDC raw powder was measured by the KBr pellet method.

deposition, TPDC did not form a continuous film but formed small droplets on the silicon surface. The drops were very small (0.1−0.2 μm) and homogeneous at the very early stage (Figure 2A). The droplet diameter homogeneously increased as the evaporation proceeded (Figure 2B). When the spacing between the droplets became too small to allow for an independent expansion of each droplet (Figure 2C), the larger droplets coarsened at the expense of the smaller ones (Figure 2D). When these large droplets reached a critical size (Figure 2E), they spontaneously spread over the substrate surface. Thus, the initial hemispherical droplets tended to be transformed into a continuous coating, although the traces of the droplets could still be observed long after a global continuity had been achieved (Figure 2F).

These droplets exhibited a particular phenomenon. They were in a liquid state just after the evaporation and kept such a liquid state at room temperature, although TPDC should be solid state at room temperature. They were unstable with regard to time, in that they spontaneously spread over the substrate surface after a certain duration, accompanied by a very rapid solidification, which could have resulted in forming continuous films if the initial droplet quantity was large enough. The smaller sized liquid droplets tended to be more stable. For instance, the droplets with an average size of 1 μm kept a liquid state for several hours, while those with an average size of 10 μm were solidified in less than 15 min.

The infrared analysis (Figure 3A) did not show any major differences between the deposited TPDC films and the raw TPDC material. This fact suggested that TPDC did not degrade during the vacuum evaporation process. In both cases, the FT-IR spectra showed an intense absorption peak at 937 cm^{-1}, characteristic of the TPDC cyclic structure.

XRD patterns of raw TPDC and deposited TPDC films revealed more differences compared to their IR spectra (Figure 3B). It is well-known that crystalline materials exhibit orientation when they are in the form of thin films.[11] In such a case, the intensity of diffraction peaks may change, but the peak position should not be changed. In these cases, the position of diffraction peaks was slightly different, indicating a different crystalline structure. Indeed, the condensed TPDC kept its liquid state on the substrates for a while before crystallizing. Contrary to the raw TPDC powder, which was synthesized by reprecipitation from reagents diluted in a solvent,[12] the films crystallized quickly from a concentrated state on the silicon surface. It is likely that there was a difference in the crystalline structure of TPDC between the powder and the evaporated films.

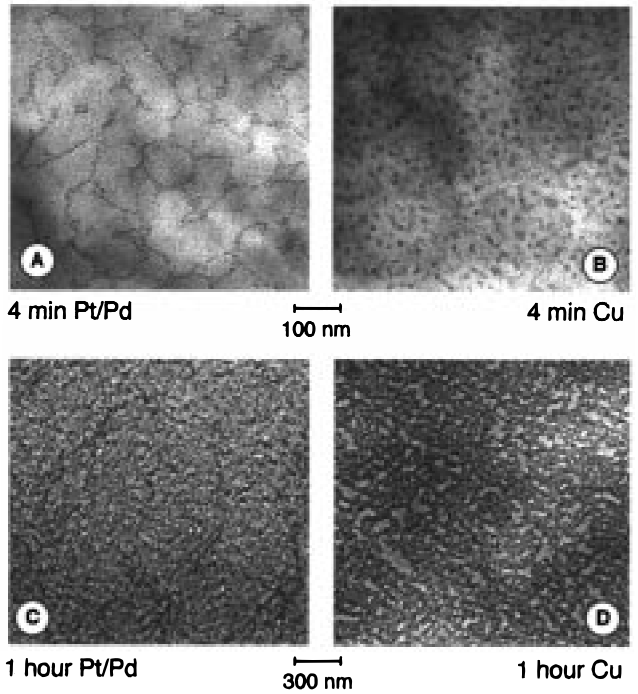

Figure 4. TEM images of the metal particles deposited by sputtering: (A) Pt/Pd, 4 min, in air; (B) Cu, 4 min, in air; (C) Pt/Pd, 1 h, in air; (D) Cu, 1 h, in air.

3.2. Metal Particle Deposition on the TPDC Films by Sputtering. Figure 4 shows the TEM images of the metal particles deposited on a grid for TEM observation. For 4 min sputtering, the metal particles were discontinuously scattered, and the metal particle sizes depended on the metal type, while discharge parameters such as voltage and current were the same. For instance, the average particle sizes were 2.4 nm for Pt/Pd, 2.6 nm for Pt, 3.8 nm for Cu, and 18.2 nm for Ag. The Au particles were strongly agglomerated, and it was rather difficult to measure the size distribution, but the average size of primary Au particles was estimated to be around 8 nm. It is well-known that the sputtering yields differ depending on the kind of metal and the incident ions, if the kinetic energy of the ion is the same.[13] For instance, for Ar ion with a kinetic energy of 400 eV, the sputtering yields of Ag, Au, Cu, and Pt targets were 2.7, 2.0, 1.6, and 1.2, respectively.[14] The differences in the particle sizes probably arose from the different sputtering yields.

On the basis of TEM images, it was possible to roughly estimate the percentage of the surface covered by particles for 4 min sputtering. This percentage was of the same order of magnitude for Pt, Cu, and Ag,

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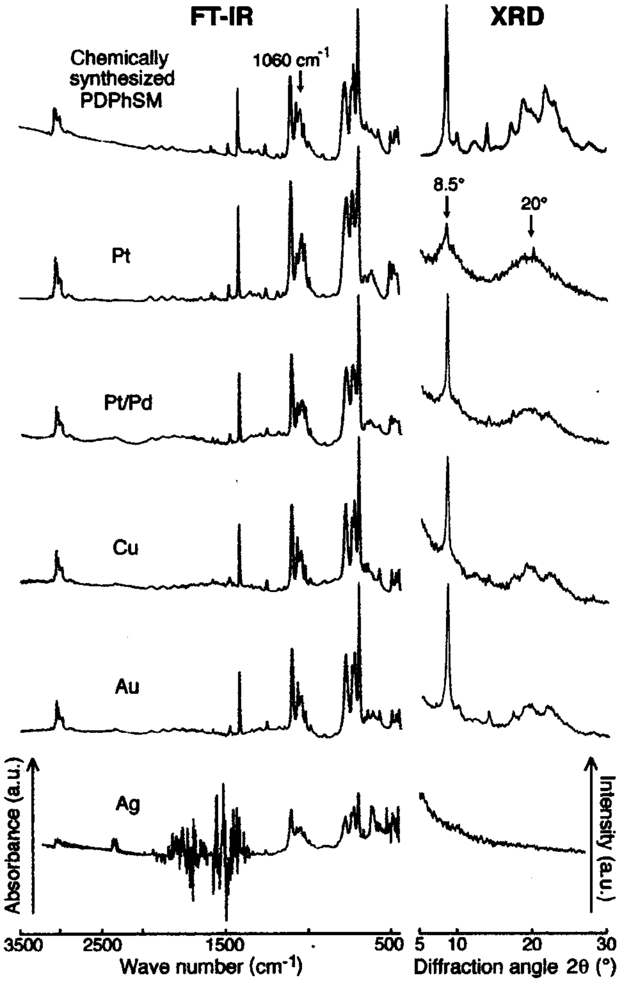

Figure 5. FT-IR spectra and XRD patterns of chemically synthesized PDPhSM and PDPhSM films fabricated by heat treating at 550 K for 10 min in air with different metal particles produced by 4 min sputtering in air.

ranging from 15 to 25%, while the particles were homogeneously distributed and isolated from each other on the surface. In the case of Pt/Pd, the surface distribution was not homogeneous, and particles were aligned according to a characteristic network. Even if the spacing between adjacent particles was very small in the alignments, they were not agglomerated. This network could be explained by the magnetic properties of Pt/Pd particles.

For 1 h sputtering, the particles were strongly agglomerated and covered most parts of the surface. It was also possible to synthesize the PDPhSM films with 1 h sputtering as for 4 min sputtering.

3.3. Thermal Polymerization. *3.3.1. Influence of the Type of Sputtered Metal.* The TPDC films with fine metal particles were heated in an electric furnace to induce thermal polymerization. Figure 5 shows the FT-IR spectra and XRD patterns of the chemically synthesized PDPhSM, together with those of the films subjected to 4 min of various metal sputtering and heat treated at 550 K for 10 min in air. Whatever the kind of metal used, continuous PDPhSM films were obtained with the process conditions mentioned above, although the thickness was very small in the case of Ag. Moreover, no difference could be observed between the FT-IR spectra of PDPhSM films and that of chemically synthesized PDPhSM. The absorption peak at 937 cm^{-1}, characteristic of TPDC, disappeared on the polymerized film spectra, and a new absorption band centered around 1060 cm^{-1} appeared. The absorption band characteristic of the monomer structure is probably due to some vibration mode specific to the cyclic structure with diphenyl units. For PDPhSM, the phenyl groups are more closely packed along the open main chains of the polymer than when they are attached to the ring of the monomer. This should result in an increase of steric effects that may be responsible for the shift toward higher vibrational energies.

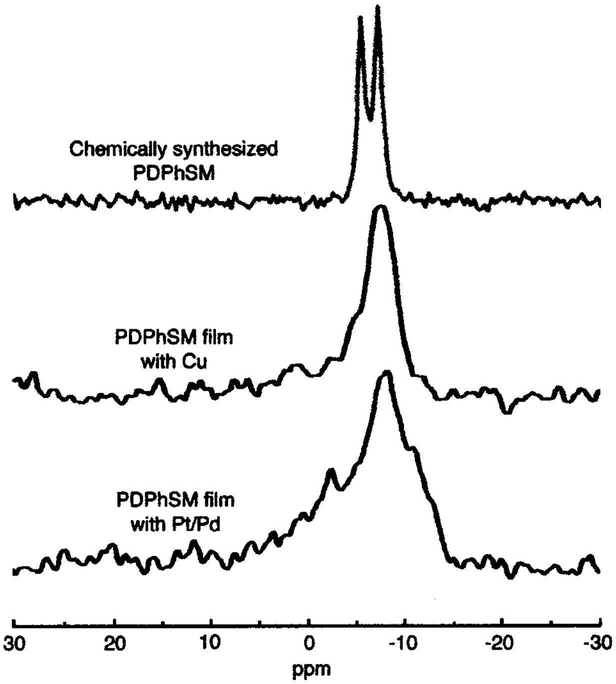

Figure 6. MAS NMR spectra of chemically synthesized PDPhSM and PDPhSM films fabricated by heating at 550 K for 10 min in air with Cu or Pt/Pd metal particles produced by 4 min sputtering in air. Spinning speed, 4.5 kHz; pulse delay, 15 s.

Although the chemical structures of the films seemed to be similar from the FT-IR analysis, XRD patterns exhibited certain differences. While chemically synthesized PDPhSM exhibited sharp diffraction peaks, the films exhibited rather broad diffraction depending on the kind of metal. In particular, the film with Pt exhibited a very broad pattern, indicating an amorphous structure. For the film fabricated with Ag, no peak was observed in the entire angular spectrum, because the residual thickness of the coating after heat treatment was too small to get a significant diffraction signal.

Figure 6 shows the NMR spectra of PDPhSM films synthesized at 550 K for 10 min in air with 4 min of Pt/Pd and Cu sputtering, together with that of chemically synthesized PDPhSM. Each spectrum was characterized by a peak centered around −8 ppm. Since the ^{29}Si MAS NMR technique is very sensitive to the silicon atom environment, and considering that the position of the peak remains identical for all compounds, it clearly indicated similar chemical structures and silicon environments. However, the peak for the films was broader than that of chemically synthesized PDPhSM. The full width at half-maximum (fwhm) of the peaks was 3.7

ppm for Cu and 6.6 ppm for Pt/Pd. This broadening could be attributed to amorphous structures. In addition, there was no signal in the chemical shift range from −30 to −120 ppm, where oxidized silicon species should have shown their NMR absorptions. It was not possible to measure the NMR spectra of the films made with Au or Ag sputtering, since we could not collect sufficient sample amounts for the NMR analysis because of the very low residual thickness of the films after polymerization.

Some experiments have been carried out to evaluate the ability of TPDC to be polymerized without any sputtered metal particles prior to heat treatment, since TPDC can be polymerized without a catalyst by heating in a sealed tube.[15] However, it was not possible to obtain PDPhSM films without metal particles, at least in the tested temperature range. The TPDC films without metal particles were entirely evaporated from the substrate without any polymerization.

When the surface of the silicon substrate was covered by ultrafine sputtered Cu particles (Cu or copper compounds such as copper(II) chloride and copper(II) acetylacetonate are known to be good catalysts for the thermal polymerization of TPDC[16−18]) prior to TPDC evaporation, we could not get continuous PDPhSM films. Therefore, the deposition of metal particles was carried out on the surface of the TPDC films before heat treatment.

3.3.2. Influence of the Heat-Treatment Temperature. Figure 7 shows the FT-IR spectra and XRD patterns of PDPhSM films fabricated with 4 min of Pt/Pd or Cu sputtering then heat treated in the range of 410−550 K for 10 min in air. The polymerization occurred at a lower temperature with the Pt/Pd particles than with the Cu ones. For Pt/Pd, the broad IR absorption peak centered around 1060 cm^{-1}, which was characteristic of the PDPhSM structure, was clearly visible as soon as the temperature reached 450 K, although at this temperature the coating was still constituted of a mixture of monomer and polymer. The peak at 937 cm^{-1}, characteristic of the TPDC structure, entirely disappeared at 500 K. For the coatings made with Cu, it was necessary to heat treat at 550 K to get only a polymer, and there was no sign of polymerization under 550 K. This finding demonstrated that Pt/Pd was more efficient than Cu in activating the TPDC polymerization. Pt/Pd also allowed polymerization at a lower temperature. For instance, it was possible to obtain PDPhSM films at 410 K (just above the TPDC melting temperature) using 4 min of Pt/Pd sputtering and a heat treatment for 20 h in air. It was not possible to get any polymerization with Cu particles under the same conditions.

The XRD patterns depended on the temperature of polymerization for a given metal. The PDPhSM crystallinity increased with the temperature. When the films with Pt/Pd were polymerized at low temperature, they exhibited a low crystallinity. In particular, the diffraction peak located at 8.5° became broad. In contrast, the polymer crystalline structure was a little ordered at elevated temperatures. It resulted in sharp diffraction peaks at 8.5°, as for the ones registered for films synthesized with Cu.

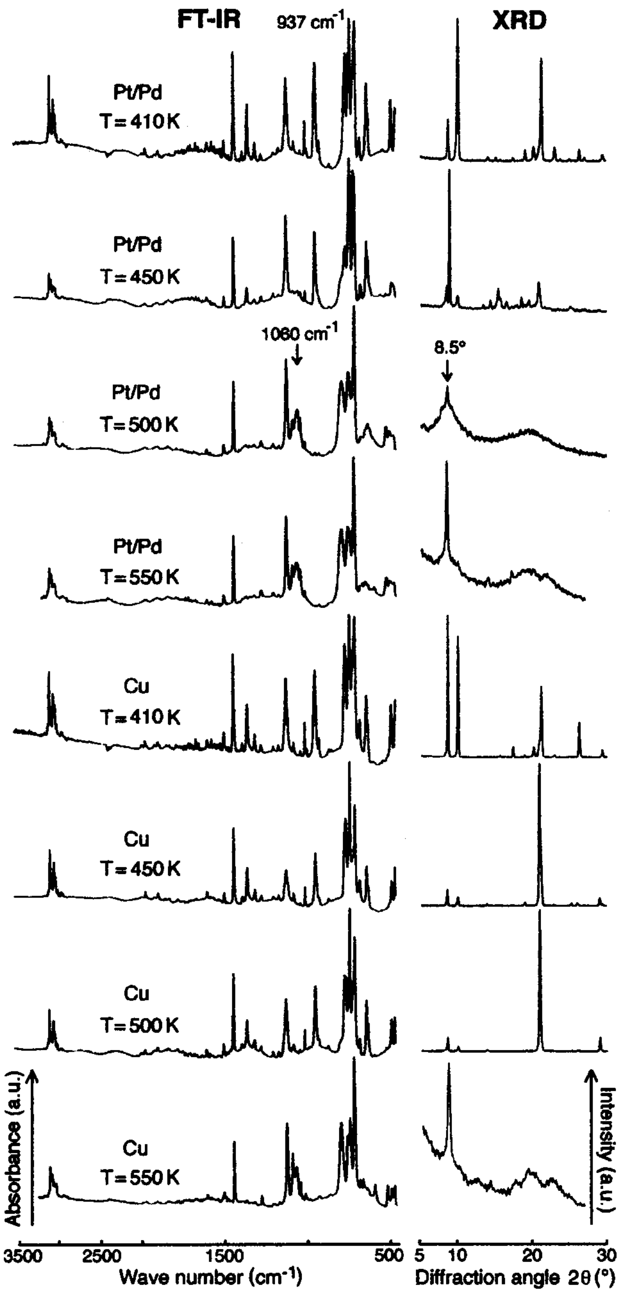

Figure 7. FT-IR spectra and XRD patterns of PDPhSM films fabricated by heating at different temperatures for 10 min in air with Pt/Pd or Cu particles produced by 4 min puttering in air.

3.3.3. Influence of the Heat-Treatment Atmosphere. Figure 8 shows the influence of the heat treatment atmosphere on TPDC polymerization. It was possible to make PDPhSM thin films in argon or vacuum as well as in air. There was no difference between the FT-IR spectra of polymers synthesized in air and those of polymers fabricated in argon or vacuum. This fact suggested that oxygen did not affect this metal accelerated polymerization of TPDC. XRD patterns showed that the films made with Pt/Pd in argon or vacuum exhibited a lower crystallinity than that of the films with Pt/Pd synthesized under the same thermal conditions in air. For the heat treatment in air, the samples were directly introduced into the furnace at a temperature of 550 K. For the heat treatment in argon or vacuum, a temperature increase of 20 K/min was

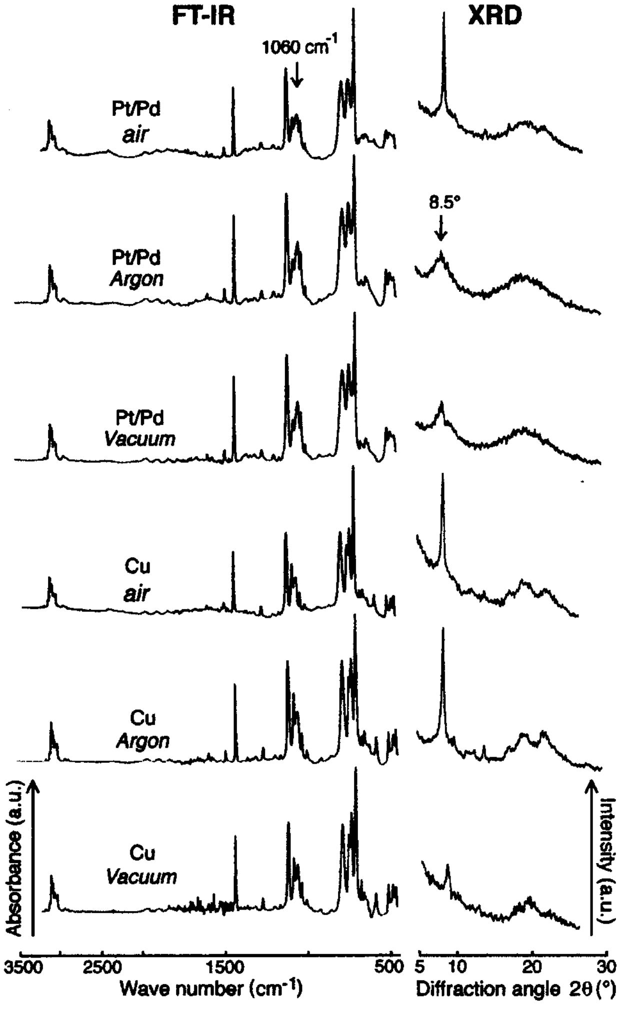

Figure 8. FT-IR spectra and XRD patterns of PDPhSM films fabricated by heating at 550 K for 10 min in different atmospheres with Pt/Pd or Cu produced by 4 min sputtering in air.

applied before reaching 550 K. It was likely that for the films heat treated in the presence of Pt/Pd particles in argon or vacuum, the polymerization had already begun at low temperatures during the temperature increase. This polymerization may even have been finished before the temperature reached 550 K. Moreover, the amorphous structure that was generated at low temperatures partly kept its amorphous state at high temperatures, since the diffraction peak observed at 8.5° remained broad. For the films made with Cu particles in argon or vacuum, the polymerization started at a temperature close to 550 K. The polymerization proceeded at a relatively higher temperature, resulting in the higher crystallinity, as indicated by the sharp peak at 8.5°.

3.4. Patterning Ability. Figure 9 shows the examples of the polymer patterns. As mentioned above, in the early stage of evaporation of the monomer, TPDC formed hemispherical coatings. These hemispherical coatings kept their shape after they were subjected to metal particle deposition by sputtering (Figure 9A). Then, they could form hemispherical polymer coatings by heating (Figure 9(B)). Moreover, some examples of polymer patterns with complex and small shapes are shown in parts C and D in Figure 9.

3.5. Application to Fabricating Polydiphenylsiloxane Thin Films. This method has been successfully employed to fabricate PDPhSO thin films by ring-opening polymerization of HPTO. Figure 10 shows the FT-IR spectrum of HPTO, together with those of the films made under different heat treatment conditions. The absorption peak at 1080 cm^{-1}, characteristic of the PDPhSO structure, clearly appeared only when the heat treatment temperature reached 510 K. Compared to PDPhSM, it was necessary to increase the heat treatment temperature and sputtering times to get a film containing 100% PDPhSO, probably because the HPTO ring structure was more stable than the TPDC one. As a consequence of the low polymerization speed, there was much HPTO re-evaporation, resulting in thinner films.

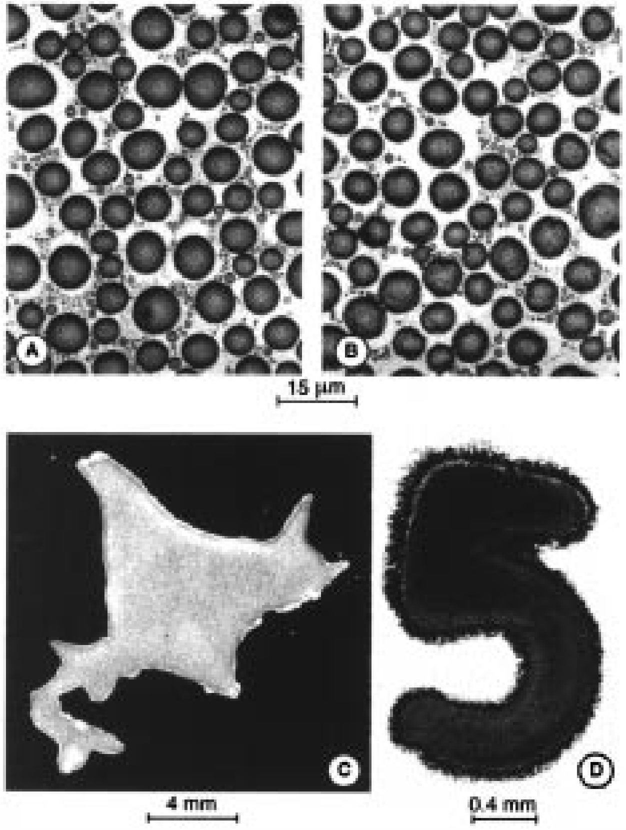

Figure 9. Examples of polymer patterns: (A) hemispherically shaped TPDC coating with Cu particles and (B) of the same material after polymerization of by heating at 550 K for 10 min; (C) PDPhSM pattern with complex shape (Hokkaido island). Polymer patterns were obtained using 4 min of Cu sputtering in air and then by a heat treatment at 550 K for 10 min in air; (D) the small pattern of PDPhSM film.

4. Discussion

4.1. Structure of the Polymer Film. Since IR spectra of the polymer films were almost the same as that of the chemically synthesized one, the chemical structure of the polymer films was basically the same, regardless of the kind of metal particles and heating conditions. However, XRD patterns were different, depending on the kind of metal particles. Each XRD pattern (Figure 5) showed two distinct groups of diffractions with respect to the value of the diffraction angle. The first group was observed for low angles, close to $2\theta = 8.5°$, and generally gave birth to a very narrow and single peak corresponding to high values of diffrac-

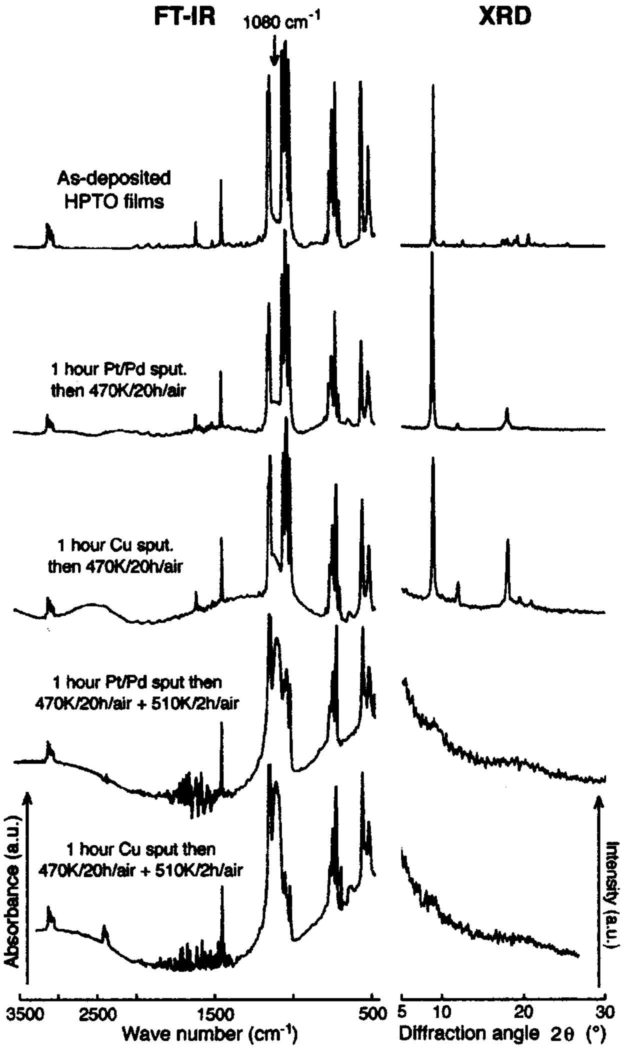

Figure 10. FT-IR spectra and XRD patterns of HPTO and PDPhSO films.

tion plane spacing (d = 1.4 nm). This sharp peak probably corresponds to the regular three-dimensional stacking of polymer chains. The fact that this diffraction peak looked similar for all the polymer films and the chemically synthesized PDPhSM and appeared at exactly the same diffraction angle may be due to a similar three-dimensional stacking structure of the polymer chains.

The second group of diffraction peaks extended from 2θ = 15 to 25° (d = 0.355 to 0.59 nm) mainly in the form of a very broad peak. This broad peak indicates a less ordered structure and may result from the disordered stacking of the atoms along the polymer main chains. It must be noted that the phenyl groups play an important role in the stacking in this direction, because their volume is much larger than the other component, CH2. Hence, the arrangement of phenyl groups probably controls the final crystallinity along the polymer chains. An all-trans PDPhSM molecule has been modeled using CS Chem 3D Pro (Figure 11). It shows that the energy is a minimum when the distance between the phenyl groups lies in the range from 0.35 to 0.38 nm. However, the all-trans structure is the most compact structure possible, that is to say for which the distance between phenyl groups is the shortest. However, it is likely that this distance is larger in the real polymer, since the polymer structure could be a mixture of cis and trans configurations and/or some distortions could occur due to either the irregular stacking of phenyls or the potential insertion of oxygen instead of carbon in the Si−C backbone. Hence, one would expect an increase of the diffraction plane spacing and a peak broadening for which the calculated values of 0.355−0.59 nm from the XRD patterns seem to be consistent. Contrary to the films, the XRD pattern of the chemically synthesized polymer shows many small and sharp peaks above the background amorphous structure in the range of 15−25 degree, indicating a partial order of the atoms along the main chains. Indeed, chemical polymerization is a very slow process (several hours),[16] and during the synthesis, the newly formed PDPhSM chains extend more freely and the phenyl groups are arranged in order

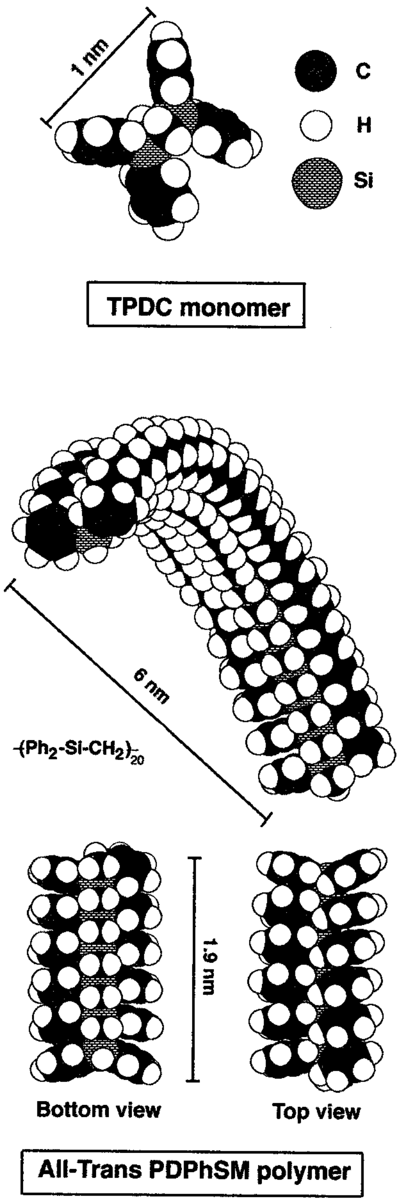

Figure 11. Possible 3D structures of TPDC and PDPhSM molecules calculated with CS Chem3D Pro software.

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to minimize their energy, providing a partial crystallinity. With the method described in this paper, PDPhSM films were synthesized in an extremely short time in comparison with the chemically synthesized polymer. For instance, only 10 min was required to get 100% polymer at 550 K, regardless of the metal used (Figure 5). However, sharp peaks were observed for the films made from Cu and Au, while very broad peaks were observed in this range for the films made with Pt and Pt/Pd. This indicates that Pt or Pt/Pd tended to make films more amorphous than those obtained with Cu or Au, whereas the chemically synthesized PDPhSM polymer was the most crystallized. This fact was very consistent with the results of MAS NMR.

Moreover, the NMR spectra of the films did not show any evidence of highly oxidized species, although the PDPhSM films were synthesized in air. This is an indication that there is no severe oxidation during the polymerization. A detailed study by XPS concerning the oxygen incorporation in the films will be published elsewhere.

4.2. Polymerization Mechanism. In this method, thin polymer films were produced basically through three steps: evaporation of the monomer, the deposition of metal fine particles by sputtering, and heating. It is obvious from the IR spectra (Figure 3) that the evaporation of the monomer does not cause the polymerization.

During the metal particle deposition, monomer films were exposed to the plasma, in addition to the metal particle deposition. The plasma was employed to produce fine metal particles and did not cause direct polymerization like plasma polymerization.[19] It was also reported that some kinds of monomer could be polymerized by plasma exposure.[20] In particular, a cyclic silicon compound, hexamethyltrisiloxane, was shown to be polymerized by plasma exposure.[21] However, in this method, plasma exposure is not the major factor, since polymerization efficiency strongly depended on the kind of metal and the effect of sputtering time on polymerization was very small. As shown in FT-IR spectra, the films exhibited no PDPhSM just after sputtering. However, it must be noted that it does not mean that the plasma has no effect. For instance, the surface reactivity of sputtered metal particles may increase during their short stay in the plasma, or the UV light emitted by the plasma may induce some effects. This will be investigated in detail in future studies.

This thermal polymerization was accelerated by metal particles and exhibited a strong dependency on the metal species. The film thickness did not remain constant during heat treatment, as was reported in a previous communication.[10] The TPDC polymerization and re-evaporation occur competitively during the heating above the TPDC melting temperature. Therefore, the residual thickness of the films as a percentage of the initial TPDC film thickness depended on the polymerization efficiency of the metals: the higher the polymerization efficiency, the higher the residual thickness. However, the particle sizes also strongly depended on the metal species in the case of sputtering under the same plasma conditions. Figure 12 shows the relationship between the particle size and residual thickness. The error bars along the X axis correspond to the standard deviations for the statistical distributions. Moreover, the ratio between the number of atoms present at the particle surface over the total number of atoms (i.e., the ratio of surface area to volume) has been calculated. Such a ratio is often used as an indicator of the size dependence of the ultrafine particle reactivity. The residual thickness exhibited the same tendency as the size dependence of the ultrafine particle reactivity. Moreover, the very high efficiency of particles containing Pt is very surprising because, contrary to Cu, Pt has not been recognized as a good catalyst for chemical polymerization but rather inhibits the reaction.[16] These facts may be one indication that the size effect would be more important than the kind of metal used. At the moment, it is not easy to control the particle size by sputtering. Further investigations are necessary to verify this.

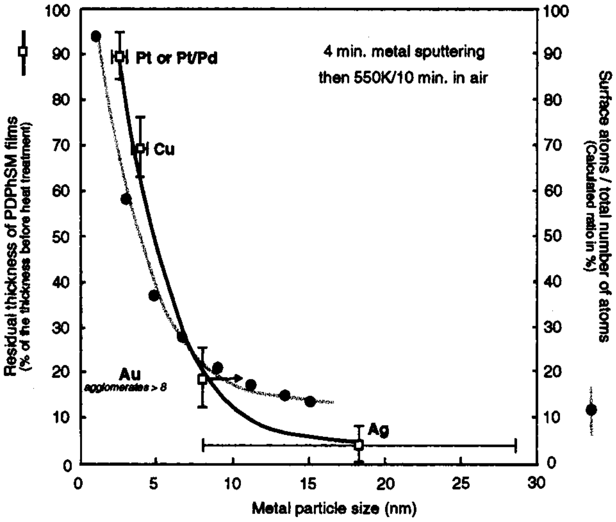

Figure 12. Relationship between the metal particle size and the variation of film thickness during the polymerization.

One important feature of our TPDC ring-opening polymerization method is that it can be performed in air, in argon, or in a vacuum. The fact that the oxygen does not affect the polymerization indicates that the mechanism differs from a 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 the activated species created from the catalytic reaction of highly reactive metal particles with TPDC. Indeed, metallic compounds can be catalysts for many types of polymerization and especially for ionic polymerization.

Ultrafine metal particles or clusters were often used as catalysts for organic reactions.[22−24] However, there are few reports on the polymerization activated by ultrafine metal particles.[25] Recently, El-Shall et al.[26,27]

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reported a new polymerization method for isobutylene using metal ions produced by laser ablation. They ablated the metal target to produce metal ion, then metal ions reacted with isobutylene monomer vapor and generated ionized species. As a result, they could obtain polyisobutylene containing metal particles. In their method, metal ions produced by laser ablation seemed to play an important role, while fine metal particles are a key factor in our method.

In the method reported here, it is possible to form thin films of PDPhSM directly on a substrate and also patterned polymer films. The method uses conventional devices suitable for mass production and a limited number of process stages. Due to the high efficiency of polymerization catalyzed by sputtered metal particles, the polymerization proceeds in an extremely short time compared to the chemically induced one. Moreover, the polymerization method has been extended to polydiphenylsiloxane film synthesis. This could potentially be applied to the ring-opening polymerization of other cyclic materials.

5. Conclusion

We have developed a new polymerization method for TPDC using fine metal particles produced by sputtering. It enabled us to make PDPhSM thin films, which are difficult to make by conventional methods. The chemical structure of the films was basically the same as that of chemically synthesized one, but the crystalline structure of the films differed depending on the kind of metal used. The polymerization efficiency depended strongly on the kind of metal or particle size. An ionic mechanism could be proposed as a potential polymerization mechanism on the basis of the activated species created from the catalytic reaction of highly reactive metal particles.

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