Properties of Poly(diphenylsilylenemethylene) Thin Films Fabricated with Fine Metal Particles

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The properties of poly(diphenylsilylenemethylene) (PDPhSM) thin films were studied. These films were fabricated by a new polymerization technique using ultrafine sputtered metal particles as catalysts. It was shown that the metal particles were spread over the film surface before polymerization, but migrated inside the films during the polymerization to form a three-dimensional distribution. The surface morphology and crystallinity of the films were greatly affected by the metal species used. The surface roughness of the films ranged from 2 to 400 nm, depending on the metal, but could be adjusted within the range by use of a combination of several metals. The thermal stability tended to increase with the crystallinity of the film. The polymer films showed the same long lifetime visible light emission upon UV laser irradiation as those already reported for chemically synthesized polymers.

1. Introduction

Poly(diphenylsilylenemethylene) (PDPhSM) and poly(diphenylsiloxane) (PDPhSO) are very interesting materials because of their high thermal stability and long lifetime visible light emission induced by irradiation with an ultraviolet laser light.[1] However, it is rather difficult to make thin films because they are insoluble in most solvents and exhibit high melting points. In previous papers,[2,3] we reported on a new method for fabricating PDPhSM and PDPhSO thin films using fine metal particles and mainly investigated the polymerization phenomenology. In this method, fine metal particles penetrated into the polymer films during the heating, while a very small amount of metal particles was necessary to activate the polymerization. Therefore, this method could also be interesting for fabricating composite films constituted of fine metal particles and polymer. Moreover, if we control the distribution and concentration of metal particles embedded in the polymer acting as an insulator, some unique properties can be expected like nonlinear optical properties.[4−9]

In this paper, we have studied the polymer film properties, such as surface morphology, thermal stability, and light emission properties. We especially investigated the distribution of fine metal particles in the polymer films after polymerization, since this phenomenon should be closely connected to the polymerization mechanism. In addition, the metal particle distribution is also an important factor for potential optical applications.

2. Experiments

The fabrication method of the polymer films has already been described in a separate paper.[3] The chemical structure of the polymer films and the distribution of metal particles in the films were investigated by X-ray photoelectron spectroscopy (XPS) with monochromated Al Kα X-ray (VG, ESCALAB 220XL). The atomic ratio of each element of the films was calculated using the sensitivity factors provided by VG. The depth profiles of the elements were taken by argon ion etching.

The film morphology was observed by optical microscopy and atomic force microscopy (AFM; Seiko Instruments, SPA-300). The surface roughness, characterized by a standard parameter, Rz, was measured by AFM over a surface area of 10 μm^2. The thermal stability of the synthesized films was evaluated by thermogravimetry (TG; MAC Science Instruments, TG-DTA2000). The experimental parameters were as follows: heating rate, 5 K/min; cooling rate, 20 K/min; maximum temperature, 1073 K; and ambient gas, argon gas flow of 50 cm^3/min. The sample weight was about 10 mg. The TG

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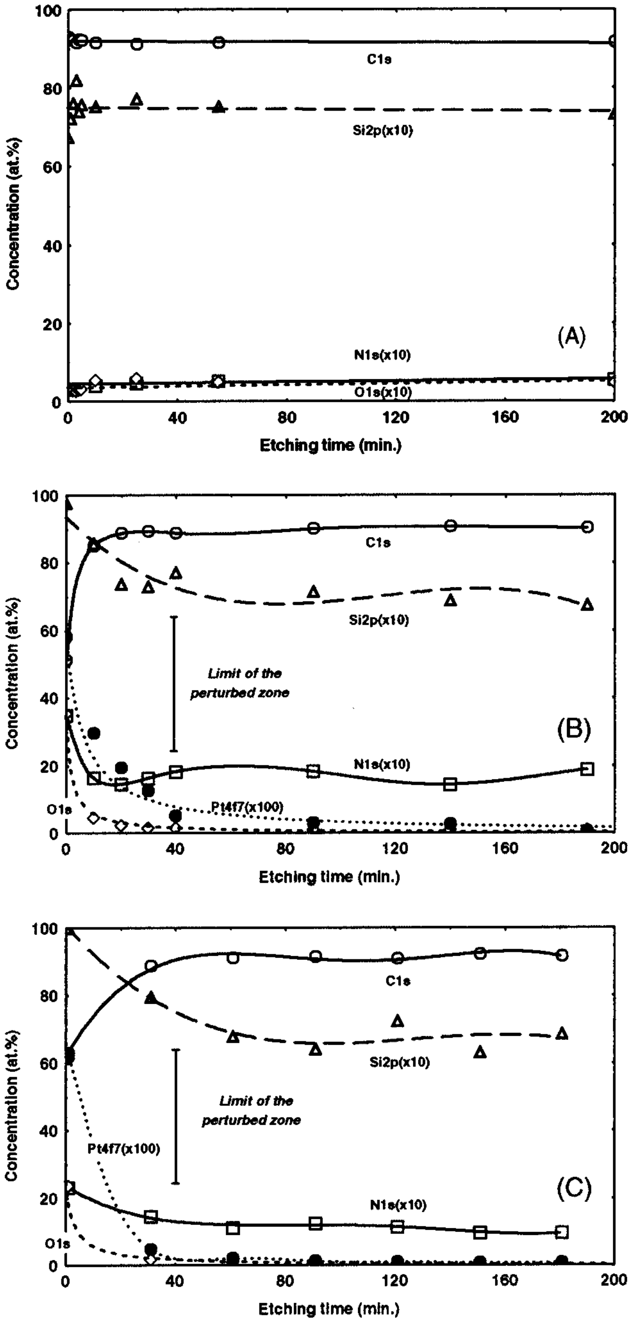

Figure 1. XPS depth profiles of different elements in (A) as-deposited TPDC, (B) TPDC film subjected to 4 min Pt/Pd sputtering in air, (C) TPDC film subjected to 4 min Pt/Pd sputtering in argon.

behavior could not be measured directly on the films. It was necessary to scrape the films with a thin knife to collect some powder, and the powder was put into the TG crucible.

A KrF excimer laser (AQX-150 MPB, $\lambda = 248$ nm, laser fluence = 9.9 mJ/cm^2 pulse) was used as a light source to induce the light emission of the polymer films. The emission spectra were recorded with a monochromator equipped with a CCD detector (TCCD-1024T, Princeton Instruments) at room temperature in air. The detailed experimental apparatus was described elsewhere.[1]

3. Results and Discussion

3.1. XPS Study of the Films. *3.1.1. TPDC Film.* Figure 1 shows the XPS depth profiles of the as-deposited 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (TPDC) film, together with those of TPDC films subjected to 4 min of Pt/Pd sputtering in air or argon. The C/Si atomic ratio in the as-deposited TPDC film was constant, along the film thickness, and equal to 12.4 (Figure 1A). This ratio was very close to the theoretical C/Si ratio[13] of TPDC molecules. This result also supported the fact that TPDC did not degrade during the evaporation process, as we had already confirmed by IR spectroscopy of the films.[3] Moreover, we could observe the presence of a low amounts of oxygen and nitrogen, less than 0.5 atom %. These amounts were constant along the film thickness. The fact that the films did not exhibit a sudden increase, especially of the oxygen content at the surface, showed that they were chemically stable and did not react with the ambient atmosphere. Oxygen and nitrogen were considered to be incorporated during vacuum evaporation, since it was performed under a residual pressure of 1 Pa and the partial pressures of nitrogen and oxygen were not negligible.

The surface of the TPDC film subjected to Pt/Pd particles deposition with an air plasma was affected up to a depth equivalent to 30 to 40 min of ion etching (Figure 1B). The etching rate was estimated using a tantalum oxide film of 100 nm thickness. The etching rate of the tantalum oxide film was estimated to be about 0.2 nm/min. The limit of the perturbed zone created by sputtering therefore corresponded to a thickness of 6−8 nm, that is, no more than 3 times the particle size. Hence, the kinetic energy of the sputtered particles was not enough to allow their deep penetration into the TPDC film, and they just lay on the surface. Moreover, the Pt/Pd content on the surface was low (0.6 atom %) for 4 min of sputtering, and the quantity of deposited metal was too small to form a continuous coating, as we already reported.[3] In addition, it was observed that the oxygen and nitrogen contained in the air plasma reacted with the surface of the TPDC film and formed a thin layer corresponding to 10 min of etching. The atomic percentage of oxygen on the surface reached nearly 35%, while that of nitrogen increased a little in comparison with the inner part of the film up to 3.5%. Oxygen and carbon (52%) were thus the main constituents of the surface after sputtering.

The surface of the TPDC film subjected to Pt/Pd deposition with an argon plasma (Figure 1C) was similar to that subjected to Pt/Pd deposition with an air plasma (Figure 1B). The amount of Pt/Pd particles deposited on this surface (0.6 atom %) and the size of the perturbated zone (6−8 nm) were identical to those measured with the air plasma. The differences were in the amounts of oxygen and nitrogen present in the uppermost layers of the film. The atomic percentage of oxygen reached 23% on the surface, while that of nitrogen increased up to 2.3%. The amounts of oxygen and nitrogen in the surface layers were just a little lower than those resulting from the use of air plasma. This indicated that oxygen and nitrogen were incorporated

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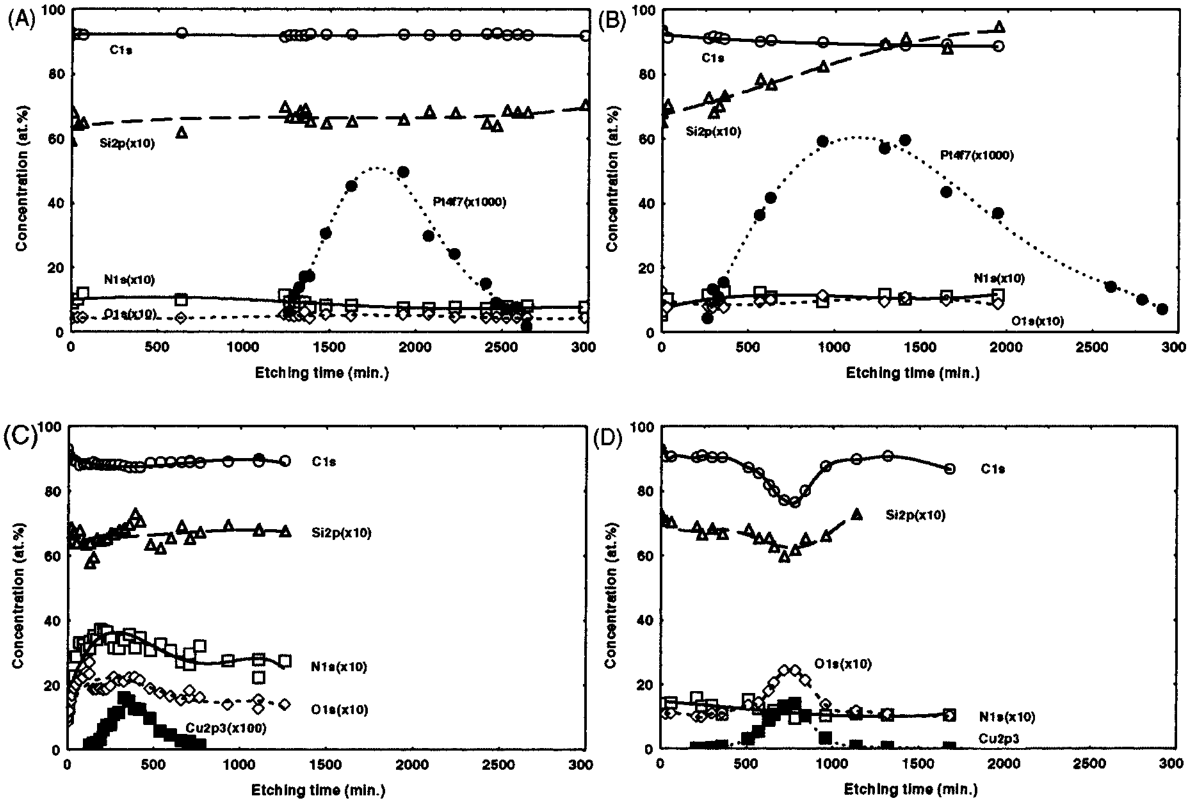

Figure 2. XPS depth profiles of different elements in PDPhSM films fabricated at 550 K/10 min in air and initially subjected to (A) 4 min Pt/Pd sputtering in air, (B) 1 h Pt/Pd sputtering in air, (C) 4 min Cu sputtering in air, (D) 1 h Cu sputtering in air.

not only during the sputtering process but also when the samples were exposed to the ambient atmosphere. Moreover, we would like to mention that the amount of oxygen on the surface was 10 times that of nitrogen, whatever the plasma atmosphere. It was likely that the sputtering generated some activated species on the surface, which were instantaneously oxidized in the air. These species came directly from the plasma or resulted from the interaction between the plasma and the TPDC film, since the samples were located in the plasma active zone. Although it is well-known that a plasma itself can contribute to the polymerization of silicon-based polymers,[10-12] in our case the plasma exhibits a negligible effect compared to the effect of the fine metal particles.

3.1.2. Distribution of Metal Particles in the Polymer Film. (1) Influence of the Type of Metal. Figure 2 shows the XPS depth profiles of different elements in PDPhSM films fabricated with 4 min or 1 h of Pt/Pd or Cu sputtering in air prior to heat treatment at 550 K for 10 min in air. This figure illustrates one of the characteristic points of this process, that is, during the polymerization, the metal particles penetrated deep inside the film and did not remain on the film surface. Since these particles were initially isolated on the surface, it was likely that they were still isolated after they penetrated. The final structure of polymer films then consisted of nanometer-sized metallic entities embedded in PDPhSM, while the amount of metal was very small.

The width of the distributions as well as the average penetration depths depended a lot on the kind of metal and the sputtering conditions. Thus, distributions were broader and penetration depths were much larger for Pt/Pd than for Cu. For 4 min Pt/Pd sputtering (Figure 2A), the distribution width and penetration depth were roughly estimated to be 200 and 350 nm, respectively. In contrast, for 4 min Cu sputtering (Figure 2C), the distribution width and penetration depth were 100 and 80 nm, respectively. Also, different tendencies were observed for Pt/Pd and Cu, when the sputtering time was increased up to 1 h. For Pt/Pd, the average penetration depth was smaller and the distribution width was larger (Figure 2B) than for 4 min of sputtering. For Cu, the average penetration depth was twice that recorded for 4 min of sputtering, whereas the distribution width remained the same (Figure 2D). The primary particle size was the same at 4 min and 1 h sputtering, but the particles were strongly agglomerated for 1 h sputtering. This agglomeration may be responsible for the differences of penetration observed between 4 min and 1 h sputtering. Moreover, if the particle penetration was just a simple sedimentation phenomenon, it would have varied according to the particle weight: the higher the weight, the deeper the penetration for a given time. Considering the average particle diameters determined by TEM[3] (2.4 nm for Pt/Pd and 3.7 nm for Cu) and the theoretical densities of the metal used (21.1 g/cm^3 for Pt, 12.0 for Pd, 19.3 for the Pt/Pd (80/20) alloy, and 8.9 for Cu), we calculated that the average weights of Pt/Pd and Cu particles were respectively 1.4 × 10^{-7} and 2.4 × 10^{-7} mg. Cu entities should thus have penetrated a little deeper than Pt/Pd inside the films. The opposite tendency, which we observed, might have been the result of complex interactions between the penetration speed of the metal particles, the polymerization rate, and the evaporation rate of the monomer. However, it was impossible to precisely determine the nature of these interactions. First, the penetration speed and the polymerization rate were both dynamic phenomena depending on the particle size. Second, the viscosity of the liquid gradually increased as polymerization proceeded, affecting the penetration speed. We could also consider the fact that the polymerization process competed with the evaporation of the monomer. The fact that the evaporation of the monomer was higher with Cu than with Pt/Pd may have contributed to a lower apparent penetration depth of Cu particles.

The C/Si atomic ratio in the films determined by XPS was close to 13, which is the theoretical ratio of the PDPhSM, and the FT-IR analysis did not show the presence of any monomer. This ratio was constant along the thickness, regardless of the kind of metal and the sputtering conditions. It proved that the polymer synthesized by our method had the PDPhSM chemical structure, as we have already pointed out.[3] In addition to the oxygen and nitrogen incorporated during the vacuum evaporation process, we could also observe the insertion of small amounts of oxygen and nitrogen during the polymerization. However, this insertion was surprisingly very low considering that the heat treatment was done in air. It showed that the reaction with oxygen, which is usually a very active process for Si-based compounds, was a minor effect. Such a reaction did not interfere with the polymerization mechanism so as to inhibit it. In most of the polymer films the amounts of oxygen and nitrogen were similar, with a value around 1 atom % (0.5 atom % in the initial TPDC), except for PDPhSM films fabricated with 4 min of Cu sputtering. In that specific case, the contents of oxygen and nitrogen reached 2 and 3 atom %, respectively (Figure 2C). The oxygen and nitrogen contents were generally constant along the thickness and no increase on the surface was observed. However, for Cu sputtering the oxygen content increased, together with that of copper. This was especially obvious for 1 h of sputtering. This oxygen resulted from the oxidation of sputtered particles, either directly in the air plasma or due to the reaction of the fresh surfaces of sputtered copper particles with the ambient atmosphere after particle deposition on TPDC films. Thus, the surfaces of Cu particles embedded in the PDPhSM films after polymerization were probably covered with a thin layer of copper oxide. Such oxidation would not occur with a noble metal like platinum or gold.

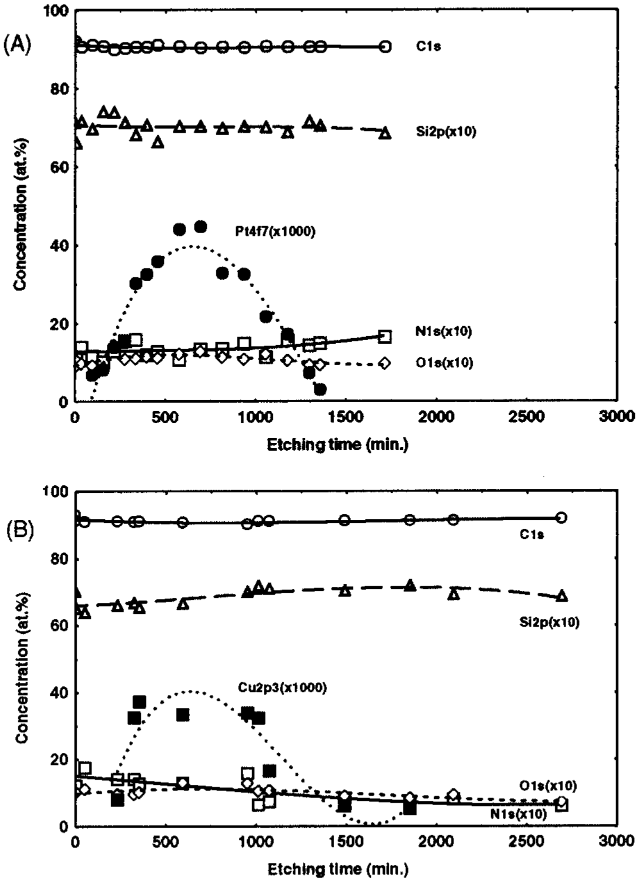

Figure 3. XPS depth profiles of different elements in PDPhSM films fabricated at 550 K/10 min in argon and initially subjected to (A) 4 min Pt/Pd sputtering in air, (B) 4 min Cu sputtering in air.

(2) Influence of the Heating Atmosphere. Figure 3 shows the XPS depth profiles of different elements in PDPhSM films fabricated with 4 min Pt/Pd or Cu sputtering in air, prior to heat treatment at 550 K for 10 min in argon. For the heat treatment in argon, a temperature increase of 20 K/min was applied before reaching the maximum temperature, while for the heat treatment in air, the samples were introduced directly into the furnace at the maximum temperature. The distribution widths of particles were the same for the heat treatment in argon and in air in both cases of Cu and Pt/Pd under the given heat treatment conditions, but the average penetration depths differed. More precisely, Pt/Pd entities did not penetrate as deeply inside the films when thermal polymerization was conducted in argon (Figure 3A). Indeed, we showed that for Pt/Pd the polymerization could occur at a lower temperature than for Cu.[3] So, in argon it was likely that the polymerization had already proceeded during the increase in temperature when the viscosity of the liquid was high. Because of this high viscosity, the Pt/Pd penetration depth was reduced. However, for Cu, the polymerization started to proceed only at a temperature close to the maximum one. Thus, the average penetration depth of Cu particles (Figure 3B) was similar to that observed when the samples were introduced directly at the maximum temperature in air (Figure 2 (C)).

The atomic ratio of C/Si determined by XPS was very close to 13 and constant along the thickness. In addition, the quantities of oxygen and nitrogen inserted in the films (1 atom % each) in argon were the same as if the polymerization had been carried out in air. If a reaction had occurred between the atmosphere and the film during the polymerization, one would have expected a lower oxygen content when the heat treatment was done in argon. Thus, it was likely that the small increase of oxygen and nitrogen contents in comparison with TPDC did not result from a reaction with the heating atmosphere but from the migration of the oxygen and nitrogen present in excess onto the initial TPDC film surface. This hypothesis is in good agreement with the fact that no excess of oxygen or nitrogen was observed on the film surface after polymerization. Finally, we could not see any increase of the oxygen content with the increase of the copper content, because the amount of copper deposited in 4 min of sputtering was too small to generate an oxygen signal by XPS. This indicated that

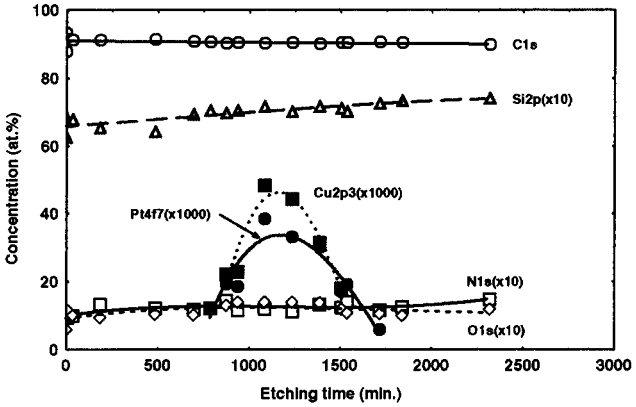

Figure 4. XPS depth profiles of different elements in a PDPhSM film fabricated at 550 K/10 min in air and initially subjected to 2 min Cu then 2 min Pt/Pd sputtering in air.

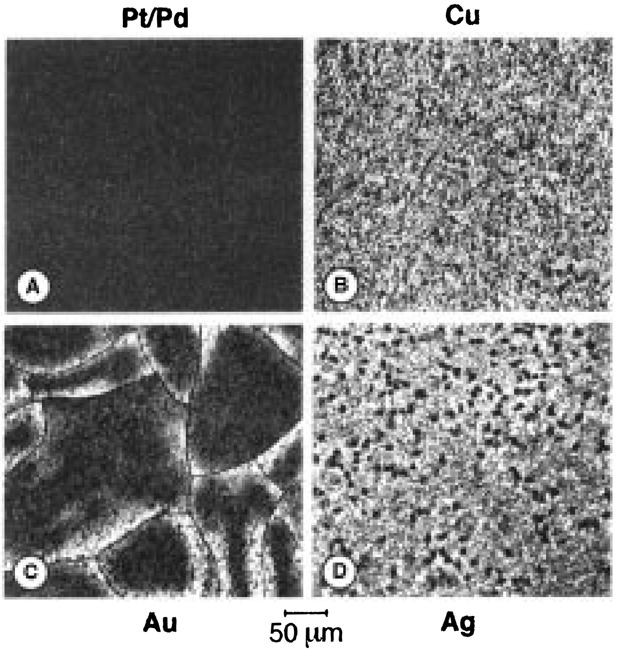

Figure 5. Morphology of PDPhSM films fabricated with 4 min of different metal sputtering [Pt/Pd (A), Cu (B), Au (C), Ag (D)] then heat treated at 550 K for 10 min in air.

Cu particles were not extensively oxidized and that the oxygen amount accompanying Cu was very small compared to that existing in the films.

(3) Combination of Different Metal Sputtering. Figure 4 shows the XPS depth profiles of different elements in PDPhSM films fabricated with 2 min Cu then 2 min Pt/Pd sputtering successively in air, prior to heat treatment at 550 K for 10 min in air. The distribution width of Pt/Pd particles was a little broader than that of Cu particles, but the average penetration depth was the same at about 240 nm (etching time of 1200 min). This depth was higher than when Cu was used alone and smaller than when Pt/Pd was used alone. Pt/Pd and Cu entities interacted with each other during polymerization, so it was possible to change the penetration depth by adding different kinds of metals. This may lead to many interesting developments in the future. In addition, the chemical structure of the synthesized PDPhSM was not affected by the combination of different metal particles, since the C/Si atomic ratio kept a constant value of about 13 along the film thickness. The FT-IR spectrum of this film revealed the same chemical structure as that of chemically synthesized PDPhSM and did not show the presence of any monomer. The amounts of oxygen and nitrogen also remained constant along the thickness, close to 1 atom %, as observed in previous samples (Figures 2 and 3).

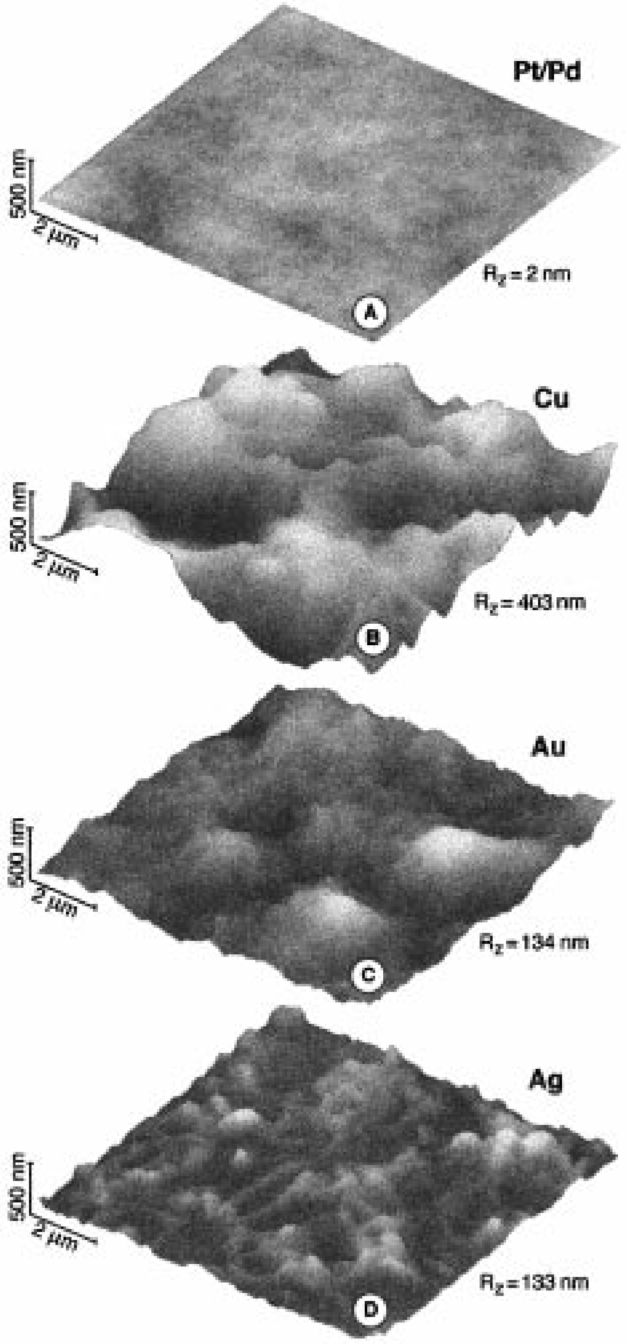

Figure 6. AFM images of the surface morphology of PDPhSM films fabricated at 550 K/10 min in air and initially subjected to (A) 4 min Pt/Pd sputtering in air, (B) 4 min Cu sputtering in air, (C) 4 min Au sputtering in air, (D) 4 min Ag sputtering in air.

3.2. Surface Morphologies of PDPhSM Films. The surface morphologies were first investigated by optical microscopy (Figure 5). The images show that they depended a lot on the kind of metal particles. The films were transparent and smooth, like glass, with Pt or Pt/Pd, but opaque and very rough with Cu and Au. Moreover, the polymerization induced mechanical

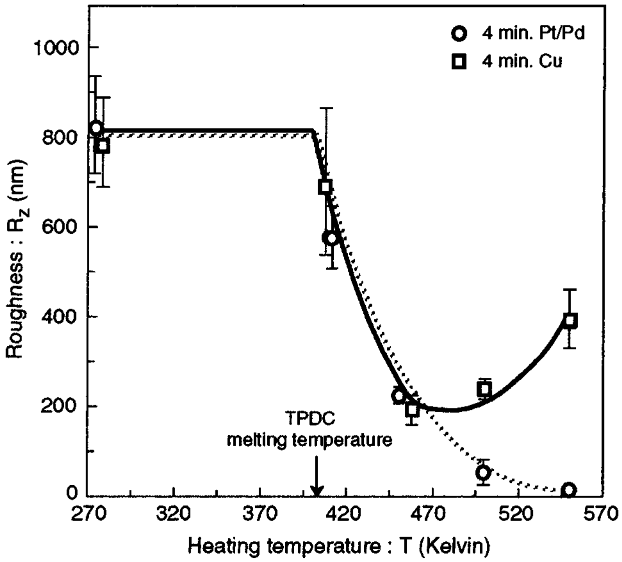

Figure 7. Evolution of the roughness of films subjected to 4 min Pt/Pd or Cu sputtering and then heat treated at different temperatures for 10 min in air.

stresses at the substrate–film interface, probably because of the change of the film thickness during the polymerization. These mechanical stresses could generate the cracking of coatings: the higher the thickness change, the easier the cracking. This cracking was not observed in films made with Pt or Pt/Pd. However, it appeared a little in films made with Cu and more extensively when Au was used to activate the polymerization. It must be mentioned that according to the analyses reported in a separate paper,[3] the appearance of cracks also corresponded to an increase of crystallinity due to the decrease of the polymerization rate. In addition, we verified that, for a given metal such as Cu, the increase of the polymer coating thickness increased the size and the number of cracks induced by mechanical stresses. The films made with Ag were discontinuous because Ag particles were not so effective for polymerization.

Figure 6 shows the AFM images of the surface of PDPhSM films synthesized with 4 min of different metal sputtering and heat treated at 550 K for 10 min in air. This figure points out the range of roughness we could get by changing the type of particles. Actually, the roughness values extended in a domain corresponding to 2 orders of magnitude. For instance, PDPhSM films exhibited an extremely low value of 2 nm when Pt/Pd was used, but the roughness reached 400 nm with Cu, that is, a value 200 times higher. For Au and Ag, roughness values were intermediate between those achieved with Pt/Pd and Cu.

Figure 7 shows the change of the roughness with the heating temperature for the 4 min Pt/Pd or Cu sputtering and then heat treatment at different temperatures for 10 min in air. The roughness did not change below the TPDC melting point and exhibited a similar decrease around the TPDC melting point for both Pt/Pd and Cu. The roughness of the films fabricated with Cu exhibited a minimum value of 200 nm around 500 K and increased up to 400 nm when the temperature reached 550 K. The minimum roughness of 200 nm corresponded to the typical surface roughness of TPDC films entirely melted without any polymerization and then cooled. As confirmed by the FT-IR analysis,[3] with Cu, the polymerization proceeded only above 500 K. The polymerization with Cu was accompanied by a roughness increase. In contrast, with Pt/Pd, no roughness plateau at a value of 200 nm could be observed, indicating that the polymerization occurred as early as 450 K and was accompanied by a decrease of roughness proceeding toward the final value of 2 nm at 550 K.

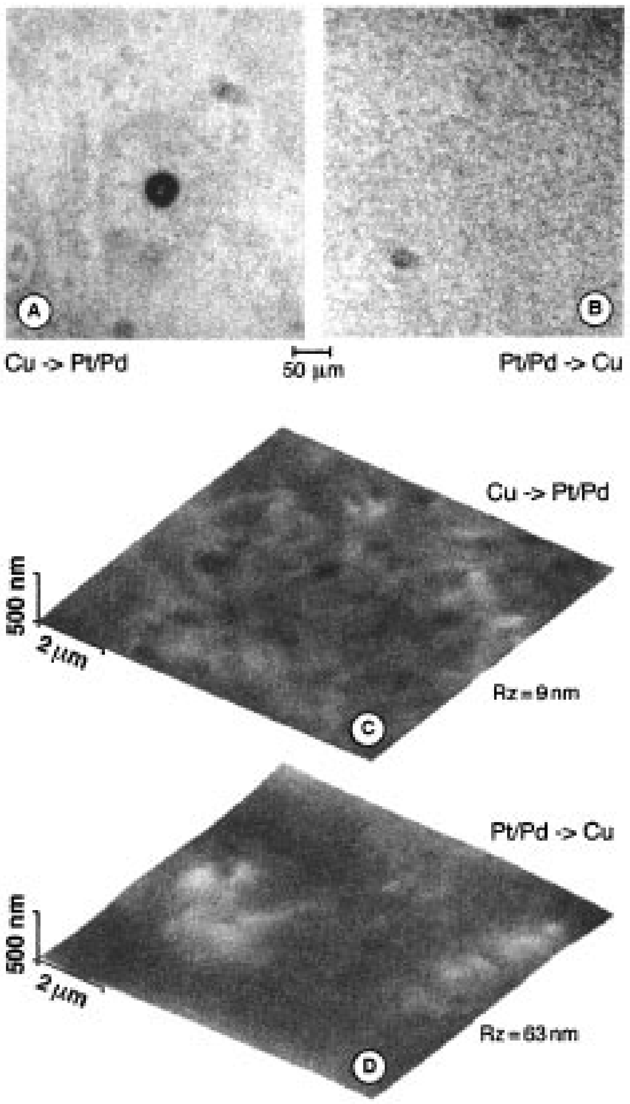

Figure 8. Optical and AFM images of the surface morphology of PDPhSM films fabricated at 550 K/10 min in air and initially subjected to (A and C) 2 min Cu then Pt/Pd sputtering in air, (B and D) 2 min Pt/Pd then Cu sputtering in air.

Figure 8 shows the optical and AFM images of PDPhSM films fabricated by heating at 550 K for 10 min in air and initially subjected to 2 min Cu and then 2 min Pt/Pd sputtering in air, or 2 min Pt/Pd and then 2 min Cu sputtering in air. The combination of metal catalysts made it possible to get an intermediate roughness between those obtained when Pt/Pd and Cu were used alone. However, this roughness varied, depending on the order of the sputtered metal. It was higher when Cu particles were deposited last. This indicated that there was no predominant catalytic process and that Pt/Pd and Cu entities both acted as catalysts for polymerization in the part of the film where they were located. The synthesized PDPhSM film surface effectively ap-

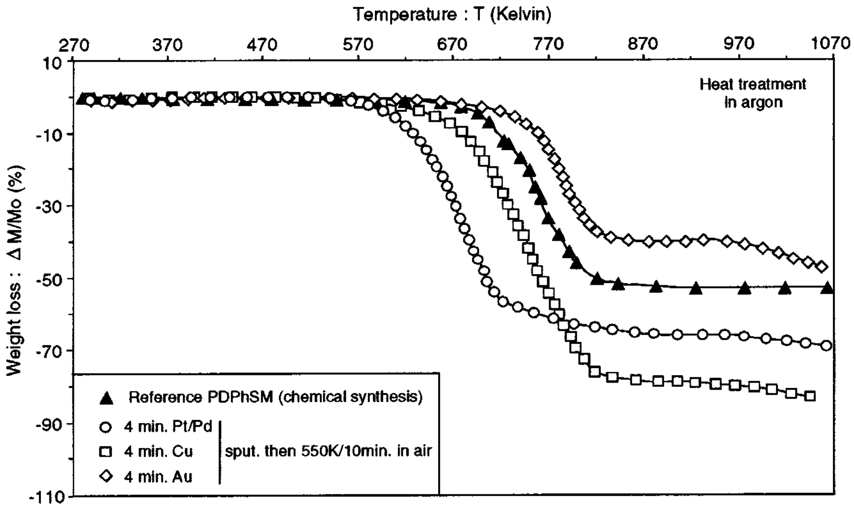

Figure 9. Thermogravimetric measurement of the PDPhSM films together with that of the chemically synthesized PDPhSM.

peared rather heterogeneous in terms of roughness and contained many defects such as pinholes when Pt/Pd was the uppermost sputtered layer (Figure 8 A). It was speculated that the difference of the polymerization rate and penetration depth between Pt/Pd and Cu might cause the pinholes. In contrast, the polymer film surface was homogeneous and defect-free when Cu was the uppermost sputtered layer (Figure 8B).

3.3. Thermal Stability of the Films. Figure 9 illustrates the thermogravimetric behavior of PDPhSM films fabricated at 550 K for 10 min in air and initially subjected to 4 min of different metal sputtering in air, together with that of chemically synthesized PDPhSM. The temperature at which the weight loss reached 5% (Td5) was considered to be one criterion of the thermal stability. The Td5 was 610 K for Pt/Pd, 650 K for Cu, 735 K for Au, and 695 K for chemically synthesized PDPhSM. These films exhibited a thermal stability similar to that of chemically synthesized film, depending on the kind of metal. As previously reported,[3] they exhibited different crystallinities. The film prepared with Pt/Pd appeared to be the most amorphous, while those with Cu, Au, and chemically synthesized PDPhSM were more crystalline. Logically, the thermal stability tended to increase with the crystallinity of PDPhSM.

3.4. Light Emission Properties. The chemically synthesized PDPhSM showed a unique light emission induced by UV laser irradiation.[1] It exhibited a strong UV emission in the 300−400 nm region with a peak located at around 340 nm during the laser irradiation of 248 nm. It then exhibited a long-lifetime visible light emission with a peak at around 500 nm, and the decay time was about 1.2 s. PDPhSM films fabricated by this method were measured for light emission induced by laser irradiation at 248 nm with a CCD detector. The typical examples of the light emission spectra of PDPhSM films were described in a previous communication.[2] The emission spectra of the films during the irradiation were the same as that of the chemically synthesized polymer. This emission could be interpreted as excimer emission from the excited silyl-substituted benzene moiety, contrary to the polysilanes for which a similar emission is currently attributed to transitions in the band created by the σ-bond conjugation in the Si−Si backbone.[13] In addition, the same long-lifetime visible light emission was observed for the films after laser irradiation. While the crystallinity of the films differed, depending on the metal species, the emission spectra of the films were independent of the processing conditions such as metal species, and heat treatment temperature, if the film contained 100% polymer. Further study will be needed to clarify the mechanism of this light emission.

4. Conclusion

The properties of PDPhSM thin films fabricated using ultrafine metal particles were studied. We have found that the metal particles migrated inside the film during the polymerization in this method. This migration might also affect the surface morphology. The change or combination of metals made it possible to adjust the film roughness in a large domain. The films exhibited essentially the same thermal stability and light emission properties as those of chemically synthesized PDPhSM.

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