Fractal Pattern Formation of Metal-Containing Polymeric Thin Films Prepared by Plasma Reaction

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(Received December 7, 1989)

Three kinds of metal-containing polymeric thin films were obtained from copper acetylacetonate (CuAA), titanium tetraisopropoxide (TiTP) and tetramethyltin (TMT) by plasma polymerization. The vaporized metal-organic compounds underwent chemical rearrangement under the action of energetic plasma to give higher ordered thin films consisting of metal and organic polymer layers. Transmission electron microscopy (TEM) photographs of the films consisting of alternative metal and organic regions showed fractal pattern. The fractal dimensions were calculated as 1.87 for CuAA, 1.94 for TiTP and 1.92 for TMT films, respectively. Formation process of fractal pattern was discussed in terms of chemical structure of starting compounds and plasma conditions.

In the recent years there has been an increasing interest in nonequilibrium growth processes accompanying pattern formation phenomena especially the fractal pattern formation phenomena.[1-3]

The formation of fractal pattern is experimentally investigated in such fields as hydrodynamics, deposition process, dielectrical breakdown, tumor growth and others, but much attention has been paid to understand the kinetic of random aggregation or self-assembly process i.e., geometrical cluster formation from large number of subunits or molecules.

The fractal pattern refers to the pattern which has the geometrical property of self-similarity. The fractal geometrical properties with regard to size and shape of the pattern are expressed in terms of the fractal dimension D (Hausdorff dimension). Fractal theory showed that the mass M and the scale such as the radius R of a fractal pattern are related by the fractal dimension D in the power law:

$$M(R) \sim R^D \quad (1)$$

Growth processes of the aggregation, for example, percolation, deflation limited, etc. can be characterized by the own D, therefore, the fractal dimension contains important information about the process and mechanism of the aggregation.

Several models have been proposed to explain different fractal pattern formation processes. The diffusion-limited aggregation (DLA) model developed by Witten and Sander[4,5] for describing the Brownian diffusion is one of them. In this model, particles are added, one at a time, to a growing cluster or aggregate of particles by random walk trajectories. The structures generated by the DLA model exhibit highly ramified clusters and the fractal dimension of these clusters was calculated and found to be less than the Euclidean dimension of the space in which the aggregation process takes place. Computer simulation based on the DLA model showed that the fractals often form in the system with strong randomness, weak anisotropy and low interfacial tension. The percolation model is the other one which can be used to describe metal-containing organic systems where metals distributed in the organic network randomly and percolation phase transition takes place when the fraction of metal contained in the organic compound reaches certain degree.

Plasma polymerization of metal-containing compounds has been attracting considerable attention in recent years since the metals incorporated in organic thin films can dramatically influence the physical, chemical and electrical properties of the resulting films. Plasma contains a series of chemically-active energetic species such as electrons, ions, radicals and photons. Taking insight into the competitive effects of interdiffusion and coagulative energy between metal and organic layers or grain-boundary in the film, we assumed that the plasma may possibly reconstruct the chemical and physical structure of starting compounds to give fractal patterns consisting metal-organic layers.

Kay et al.[6] have reported in detail how plasma processes can control the metal content and metal cluster dispersion in the organic thin film and proposed the principles and methods of metal incorporation into organic thin films. They also observed the abrupt change of electrical conductivity at certain content of metal in the film.

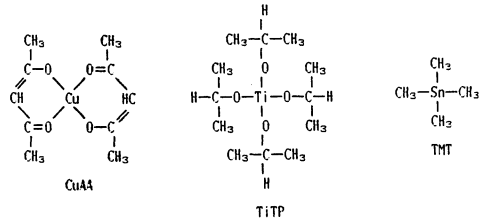
However, the growth process of the crystal fractals, for instance, of metals, should involve the nucleation, which is not considered in the DLA model or the percolation model. In addition, the morphology of fractals may be controlled by the chemical structure of the starting materials (monomer) if any chemical reaction is accompanied. Thus, it seems to be interesting to study whether there should exist the fundamental difference between the DLA fractals and fractal formation of metal-containing polymeric thin films where phase separation takes place at a certain metal content in the polymeric film. So far authors know there has been no experimental results exploring the fractal formation of metal-containing organic film accom-

panied with chemical reaction of metal-organics.

We demonstrated in this paper that the vaporized metal-organic compounds underwent chemical rearrangement under the action of energetic plasma to give thin films with higher ordered structure consisting of metal and organic polymer layers, which according to TEM investigation, showed fractal patterns. An attempt to relate the fractal pattern formation to electrical and other properties of the obtained thin films was made.

Experimental

Sample Preparation. Monomers used are three compounds with different types; copper acetylacetonate (CuAA) where metal atom is coordinated to organic ligand through oxygen atoms (metal complex), titanium tetraisopropoxide (TiTP) where metal is covalently bonded with oxygen atom (metal alkoxide) and tetramethyltin (TMT) where metal is covalently bonded with carbon atom (organometallic).



The apparatus for plasma polymerization used in this experiment consisted of a Pyrex glass bell jar and a pair of parallel electrodes (70 mm in diameter) connected to an RFG-200 radio frequency (Samco International Inc.) operating at 13.56 MHz and a matching network. Detailed schematics, procedure and method of the polymerization were described elsewhere.[7,8] Plasma polymerization was carried out by evaporating liquid TiTP or TMT at ambient temperature. However, solid CuAA was evaporated at about 100 °C.

Measurement. Film thicknesses were determined by multiple-beam interferometry using a Mizojiri-Kogaku type II instrument. The sheet electroconductivity of the films was measured with coplanar electrodes of gold in air at various temperatures. Transmission electron micrographs (TEM) and small angle diffraction (SAD) patterns in the same area was taken from thin film (less than 50 nm) deposited onto a KBr disk which was separated from the film prior to observation by dissolving in a water-ethanol solution. XPS was carried out using a pass energy of 10 keV at 20 mA with an Mg K X-ray source. Sputtering experiments were carried out using argon ions at 5 kV and a current of 2.2×10^{-6} A. The spectrometer was calibrated using gold and silver with the Au $4f_{7/2}$ binding energy at 84 eV and with the Ag $3p_{3/2}$ binding energy at 573 eV. For convenience all spectra were energy referenced to the main photoionization peak in the C 1s region which was assigned a binding energy of 285 ev.

In order to investigate fractal pattern of the texture obtained, their fractal dimensions were measured. There have been many ways to measure the fractal dimension of either numerical and experimental fractal aggregations.

Table 1. XPS Result of Atomic Fractions of Plasma Polymerized Metal-Organic Films[a]

Sample	Element	Atomic fraction in film/%		Atomic fraction in monomer/%	
CuAA	Cu	72.6	$Cu_{1.0}C_{0.34}O_{0.04}$	6.7	$Cu_1C_{10}O_4$
	C	24.7		66.7	
	O	2.8		26.6	
TiTP	Ti	32.2	$Ti_{1.0}C_{0.56}O_{1.55}$	5.9	$Ti_1C_{12}O_4$
	C	18.0		70.6	
	O	50.0		23.5	

a) The fraction of hydrogen atom is excluded.

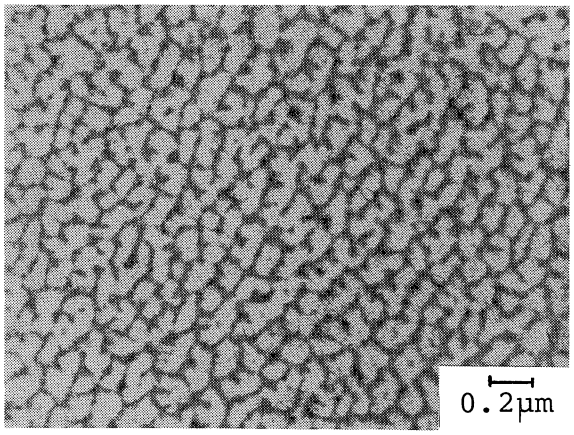
When dealing with the fractal objects on which a measure $M(R)$ is defined, the dimension D is the character which describes the manner of the mass $M(R)$ with the increase of size R. According to the fractal theory,[9] the relation between the Hausdorff dimension D and the fractal size R and mass $M(R)$ is expressed by Eq. 1.

In our case, the fractal pattern on micrographs were sectioned to 120×120 square lattice and $M(R)$ which was the number of lattice consisted by metal which were black in the micrograph was committed by increasing the radius R. The fractal dimension D was obtained by calculating the slope of logarithmic plot of formula given above. A least squares method was used to determine the slope which provide the best estimate.

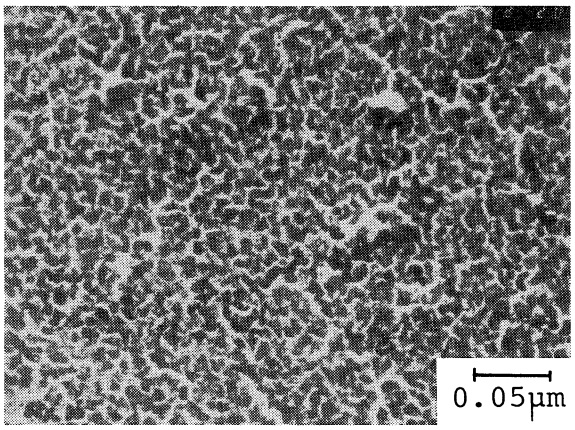
Results and Discussion

Films of polymeric CuAA obtained showed a variety of colors such as colorless transparent, yellow, green, blue and red depending on plasma conditions. It was found that the color and appearance of the films are determined by the total sum of plasma and thermal energies. For example, if keep the plasma duration and monomer temperature constant at 10 min and 130 °C, respectively and increase the plasma power from 10 W to 100 W, the color of the film changed from yellow green to blue or red; if the plasma power and the substrate temperature are kept constant at 100 W and 215 °C, respectively and the plasma duration is changed from 1 min to 20 min, the same color change is observed; this is also in the case where the plasma power and plasma duration are kept constant and the substrate temperature is changed. The conductivity of the film also changed sensitively from 10^{-10} S cm^{-1} to 10^{4} S cm^{-1} by changing the plasma conditions. With increase in the plasma energy, the film become more conductive.[7]

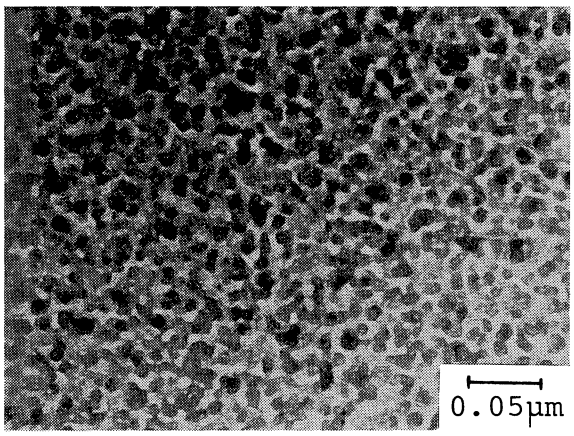
The structure and morphology of the films were investigated by use of electronic, infrared and X-ray photoelectron spectra as well as TEM. The XPS analysis showed that the film is consisted of 72.6 mol% copper, largely of metallic copper and a small amount (a few percent) of Cu_2O at the surface and almost pure copper in the bulk. The peak at 284.5 eV corresponding to primary carbon was observed in the films but the peak corresponding to the bonding of acetylacetone was hardly observed. TEM photograph shown



(a) CuAA

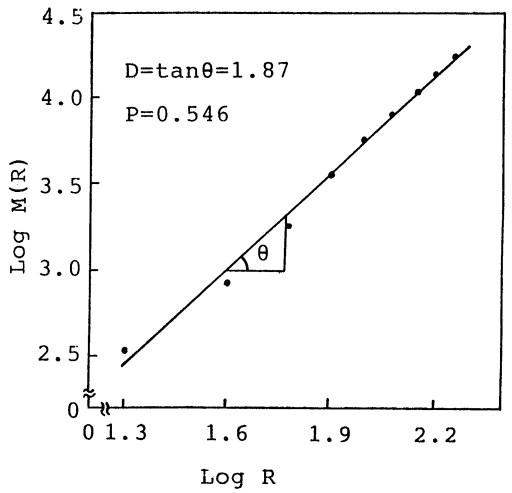


(b) TiTP

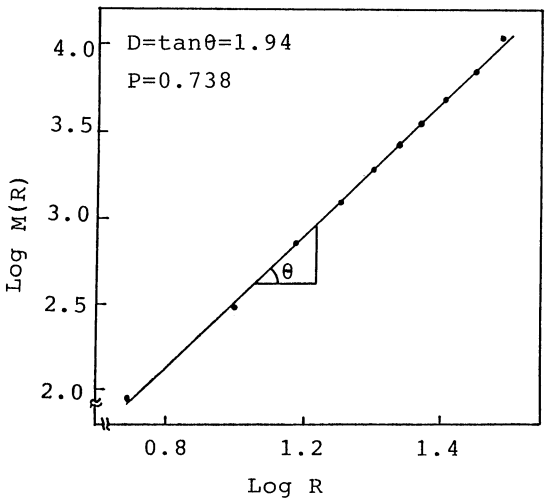


(c) TMT

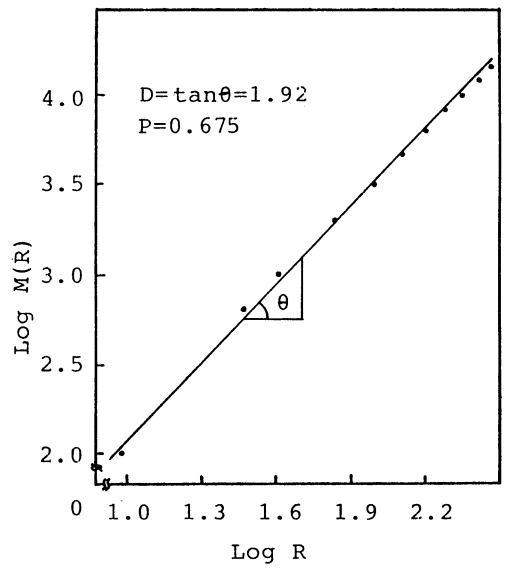
Fig. 1. TEM microphotographs of plasma polymerized metal-organic thin films. a) CuAA: Conditions of sample preparation; plasma power: 100 W, plasma duration: 1.5 min, substrate temperature: 175 °C. Magnification: ×30,000. b) TiTP: Conditions of sample preparation; plasma power: 50 W, plasma duration: 7 min. Magnification: ×200,000. c) TMT: Conditions of sample preparation; plasma power; 100 W, plasma duration: 1.5 min, flow rate of TMT: 4×10^{-2} ml min^{-1} (STP), flow rate of O_2: 30 ml min^{-1} (STP). Magnification: ×200,000.



a) CuAA



b) TiTP



c) TMT

Fig. 2. Logarithmic plot of $M(R)\sim R^D$. a) CuAA, b) TiTP, c) TMT. P is the volume fraction of metal in the film.

in Fig. 1(a) indicated that the film obtained have interesting microscopic features including alternative stripe-like structure consisting of metal and organic layers. The former probably is derived from the agglomeration of the amorphous copper corresponding to the black region in TEM micrograph and the latter by polymerization of corresponding amorphous three-dimensional matrix. This identification was carried out under the assumption that regions exhibiting poor transmission corresponded to the metal species. The SAD patterns of the CuAA sample revealed that the metals in the deposited films are amorphous.

From Fig. 1(a) it is seen that metal and organic layers are of 100 and 200 nm each. In order to investigate fractal patterns quantitatively the fractal dimention D was measured by using described method and was found as 1.87 (Fig. 2(a)).

Since TEM photographs of the CuAA film showed that the morphology in the bulk are almost same regardless of its depth, we concluded that the fractal structure also penetrates the over all sandwich along the direction perpendicular to the substrate and therefore, the fractal is the block structure resulted from the difference of coagulative properties of metals and organics where inter diffusional kinetic energy and activation energy of chemical rearrangement induced by plasma energy plays an essential role. Thus, copper goes away from the polymerized organic region with highly branched network structure to give rise fractal pattern.

In a similar manner plasma-polymerized thin films were prepared from titanium tetraisopropoxide (TiTP) and tetramethyltin (TMT) and their morphological study was also made using TEM (Fig. 1(b) and Fig. 1(c)).

As in the case of CuAA, plasma polymerized TiTP film changed its color with the course of plasma polymerization and the change in plasma power. If the plasma duration was constant at 15 min and plasma power at 30 W, a colorless transparent film was formed. The film obtained under the same duration, but at the plasma power of 20 W showed light blue. The film obtained with plasma power of 35 W, was dark blue. Black film was obtained if the plasma power was 50 W or higher. As well-known, titanium(IV) oxide is colorless transparent and titanium(II) oxide is black. These results show that titanium ions in TiTP are partially reduced in the course of polymerization to give titanium(II) oxide and other suboxide. As in the case of CuAA, alternative 3—6 nm white and 30—60 nm dark regions are seen. XPS and SAD measurements of TiTP indicated that the black portion is largely composed of TiO_x ($0 \leqq x \leqq 2$) and white region is organic matrix with the structure of $-(CH)_n-$.[8] According to SAD investigation, the metal is amorphous which, however, transfer to polycrystalline state by thermal annealing at 500 °C or higher for 15 min in vacuum but no change in chemical composition occurred.

Contrast to the films of CuAA and TiTP, films obtained from TMT were always colorless transparent in the range of experimental conditions (plasma power: 20—100 W, plasma duration: 10—300 min. In this case oxygen was supplied in the course of polymerization with the flow rate of 30 ml min^{-1} to give tin oxide.). However, TEM photograph obtained showed the morphology consisting two phase of oxidized tin and organic region. The size of metal clusters are much smaller than preceding cases: 1—15 nm of tin oxide and 10 nm of organic matrix (Fig. 1(c)).

It was found that the textures of Fig. 1(b) and Fig. 1(c) also took fractal patterns as shown in Fig. 2(b) and Fig. 2(c) and the fractal dimensions were calculated as 1.94 and 1.92, respectively. Thus, it is clear that plasma polymerization of metal-organic compounds under certain conditions can bring about fractal pattern consisting of metal region and organic matrix, the dimension of which is dependent on the chemical structure of starting compound.

At present, it is rather difficult to illustrate the every chemical processes caused by plasma reaction, since the formation process of the film is too complicated. However, using experimental data of the polymerization of metal-containing compounds obtained by E. Kay,[10] H. Biederman,[11,12] and ourselves,[13,14,15] we can roughly illustrate the formation process of metal-organic layers as follows (Fig. 3): Initially, the ionized metal atoms of the metal-organics are reduced to metallic atoms by gaseous plasma which is abundant in energetic electrons:

$$M^{n+} + ne^- \longrightarrow M^0 \qquad (2)$$

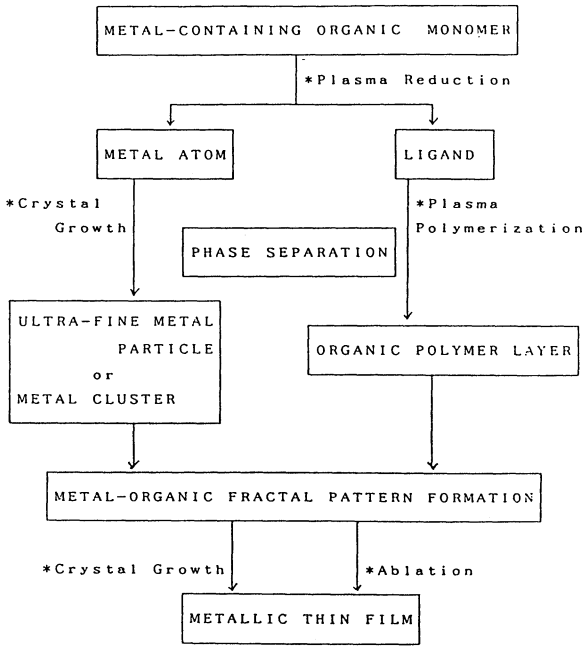
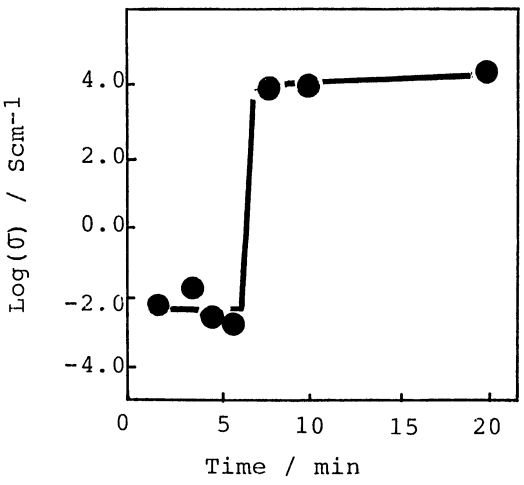


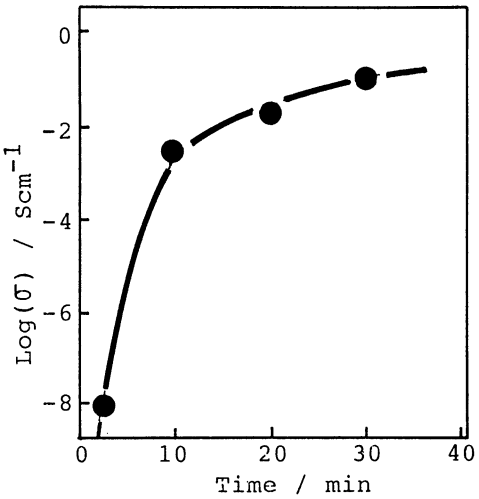
Fig. 3. Process of fractal pattern formation of plasma polymerized metal-containing polymeric films.

then these reduced metal atoms diffuse away and aggregate randomly by thermal fluctuation to give microscopic "nucleases" of metals. Consequently, the "nucleases" agglomerate and form isolated clusters. Here, the interfacial energy of metal and organic layers at the grained boundary may play an essential role. Because this process is similar to the DLA model and it can be imagined from microscopic view that these clusters are isolated dendrform fractal patterns and time changing with the growth of the cluster. However, from a macroscopic view, the clusters have not fractal characteristics and with increase in volume fraction of metals in the film, the size and number of the clusters increase and begin to connect with each other, and eventually, a macroscopic fractal pattern as shown in Fig. 1 is formed. The last process bears some analogy to the metal-insulator percolation transition model. Computer simulation of this percolation transition showed us that the fractal dimension D and P which is the fraction of metal containing in the film are 1.896[16,17] and 0.752[18] respectively. Results obtained in Fig. 2 indicate that the fractal dimension and volume fraction of metal are approximately coincide with those of simulated one. As be presumed from this percolation transition model, the electric conductivity increased abruptly when percolation transition took place in the plasma polymerized metal-organic films and this is clearly shown in the cases of plasma polymerized CuAA, TiTP and TMT films (Fig. 4). In all these cases, abrupt increases of electric conductivity are seen, indicating that the independent clusters formed in the course of polymerization grew large enough to organize contineous morphological structure at this point.

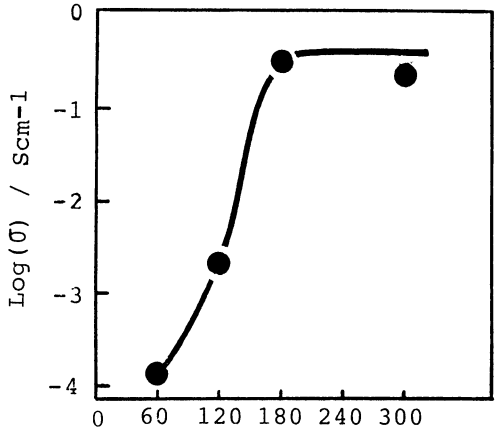
From interdiffusion and agglomeration methods of crystalline Au, Zheng et al. obtained Ge/Au/Ge sandwich films and they observed that the lower the annealing temperature, the less the fractal dimension of the fractal. Therefore, an annealing at higher temperature bring into the formation of island-like structure, and not into the random network.[19] If the actual growth of fractals in our case is largely controlled by diffusion process, it may be correlated, to the bonding energy of starting compounds, and the lower the energy of cleavage of metal-organics, the easier to be activated and to form metal atoms. Because metal atoms can easily diffuse away from the organic matrix and give more number of "nucleases", they give the fractal pattern with higher dimension. CuAA may have the lowest binding energy because it is the coordination bonding between copper and oxygen. The binding energy of tin-carbon covalent bonding is 231 kJ mol^{-1} and that of titanium-oxygen is 606 kJ mol^{-1}. This seems to be in conflict with our experimental results because TiTP has the highest bonding energy and has the highest fractal dimension. Although, we have not any information to explain this result at present, these experimental results



a) CuAA



b) TiTP



c) TMT

Fig. 4. Dependence of conductivity of plasma polymerized metal-containing polymeric films on plasma duration. a) CuAA, plasma power: 100 W, substrate temperature: 215 °C. b) TiTP, plasma power: 50 W, Substrate temperature: ambience. c) TMT, plasma power: 20 W, flow rate of TMT: 1.5×10^{-3} ml min^{-1} (STP), flow rate of O_2: 30 ml min^{-1} (STP).

allowed us to conclude that the formation process of metallic layers is not predominant for determining the fractal pattern, but the formation of organic layer plays more important role for it. The formation of organic layer is essentially a chemical process and its chemical structure is determined as a result of vigorous chemical rearrangement (cleavage and recombination of chemical bondings, elimination of atoms, etc.) of constituent atoms which is solely associated with the chemical structure of ligand molecules. In any cases, detailed kinetic and morphological study in correlation with plasma energy should be made.

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas. New Functionality Material-Design, Preparation and Control, the Ministry of Education, Science and Culture (63604510).

The authors are indebted to Dr. M. Nozaki (Mitsubishi Paper Mills Limited) for the courtesy of XPS measurements. The authors also express their sincere gratitude to Prof. T. Tsuruta (Tokyo Science University) for the encouragement and useful discussions.

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