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Preparation of inorganic-organic hybrid films containing particles using electrophoretic deposition method

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The composite films of methylsiloxane inorganic-organic hybrid and MoS_2 particles have successfully been fabricated by electrophoretic deposition of MoS_2 particles in a mixed solution of methyl ethyl ketone (MEK) and inorganic-organic hybrid sol. The addition of 20 vol% hybrid sol into a MEK suspension increased the amount of MoS_2 deposition twice as much as that of MoS_2 deposition in MEK alone. The fraction of particles deposited on a substrate in MEK-20 vol% sol was estimated to be much larger than that in MEK. The hydrolyzed methyltriethoxysilane in a hybrid sol modified MoS_2 particles, resulting in lower negative zeta potential, which reduces the repulsion force among particles and makes the incorporation of particles into a deposition film easier. The surface modification also enables the incorporation of particles into a deposit by the interaction of surface modifiers. These factors enhance the incorporation of MoS_2 particles in electrophoretic deposition in MEK-sol.

1. Introduction

Inorganic-organic hybrid materials via a sol-gel process have been investigated for their unique features [1–3]. The hybrid materials not only provide the sum of the individual contributions from inorganic and organic components but also have the possibility of providing remarkable properties that have been unknown in conventional materials. Interesting applications of inorganic-organic hybrid materials have been reported for water-repellent coatings, optical waveguides, dielectric films and others [4–6]. Most of the hybrid materials are based on organofunctional silanes, which contribute to the siloxane backbone and at the same time play the role as a carrier of organic functions. The incorporation of various metallic elements other than Si has been investigated in anticipation of altering properties of the hybrid materials reflecting the nature of the elements [7–9].

Numerous functional particles are known such as zeolite with selectivity, MoS_2 with lubricant property and AlN with high thermal conductivity. The introduction of functional particles into inorganic-organic hybrid materials is expected as one of the means to enlarge the possibility of the hybrid materials furthermore owing to the synergistic effect of hybrid materials and particles [10, 11]. To make full use of the properties derived from particles, it is important to control the arrangement of particles in hybrid materials. Electrophoretic deposition process is desirable for arranging particles with high packing density because a dense and uniform ceramic powder deposit can be made rapidly on a conductive substrate with various shapes [12]. Recently, sol-gel and electrophoretic deposition methods have been combined to obtain thick films of silica-based materials [13, 14]. However, there are few papers on the preparation of composite films of inorganic-organic hybrid and particles. The method to prepare composite films so far reported is to carry out electrophoretic deposition of organically modified ceramic particles, followed by photopolymerization [15].

In this paper, electrophoretic deposition of particles has been attempted in a solution containing inorganic-organic hybrid sol to prepare a composite film of inorganic-organic hybrid and particles. This technique consists of electrophoretic deposition of particles and dip-coating of inorganic-organic hybrid material that fills the space among the particles when a substrate is withdrawn from the suspension. Methylsiloxane hybrid and MoS_2 were chosen as a representative hybrid material and functional particle, respectively, to prepare a composite film of inorganic-organic hybrid and particles. The effect of hybrid sol on electrophoretic deposition of MoS_2 particles has also been investigated.

2. Experimental

2.1. Preliminary experiment—choice of organic solvent

In order to find the appropriate organic solvent to deposit MoS_2 particles, electrophoretic deposition of MoS_2 particles was carried out in organic solvents of acetone, methyl isobutyl ketone, methyl ethyl ketone (MEK), ethyl acetoacetate, acetylacetone,

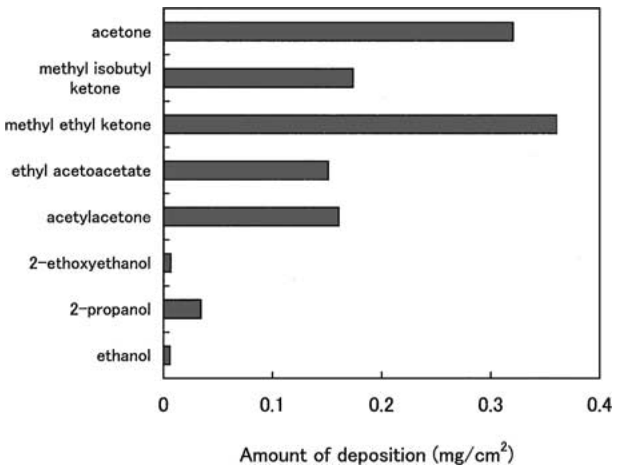

Figure 1 Amount of MoS_2 deposition in various organic solvents.

2-ethoxyethanol, 2-propanol and ethanol, which were commercially available. MoS_2 powder with an average diameter of 0.4 μm was obtained from Soekawa Chemical Co., Ltd. The electrophoretic deposition was performed on stainless steel substrates (SUS304) of $32 \times 50 \times 0.45$ mm using a 80 mesh platinum sheet of 100×100 mm as an electrode in a 300 cm^3 beaker. The distance between the substrate and platinum electrode was 10 mm. A constant DC voltage was applied with a PAD500-1.2A regulated power supply (Kikusui Electronics Corp.). The MoS_2 particle concentration, applied voltage and deposition time were 2 mg/cm^3, 100 V and 60 sec, respectively.

The MoS_2 particles were deposited on a stainless steel substrate when the substrate was used as an anode regardless of the organic solvents. The films on substrates were dried at 70°C for 30 min in air before weighing. The comparison of the amounts of deposition in various organic solvents is shown in Fig. 1. The amount of deposition of MoS_2 particles in ketones was larger than that in alcohols. MEK gave the largest amount of deposition and a deposition film with a smooth surface. Thus, MEK was chosen as an organic solvent to deposit MoS_2 particles electrophoretically.

2.2. Preparation of inorganic-organic hybrid film containing particles

For the preparation of inorganic-organic hybrid sol, alcohol is usually used as a mutual solvent to hydrolyze alkoxysilanes because alkoxysilanes and water are immisible [16]. Alcohols, however, were not effective to electrophoretic deposition of MoS_2. On the other hand, MEK, which is found to be appropriate to the electrophoretic deposition, is difficult to be used to prepare an inorganic-organic hybrid sol because of the immisibility of MEK and water.

The procedure for the preparation of inorganic-organic hybrid film containing particles is shown in Fig. 2. First, MoS_2 particles were dispersed in MEK. Then, the inorganic-organic hybrid sol prepared in ethanol was added to the MEK suspension. The hybrid sol is miscible with MEK. The molar ratio of methyltriethoxysilane, acetic acid, water and ethanol was $1:0.5:3:2$. The fraction of hybrid sol to MEK was 20 vol%. MoS_2 particle concentration of the MEK-sol suspension was 2 mg/cm^3. Applied voltage and deposition time were 0–400 V and 15–60 sec, respectively. Substrates were withdrawn from the MEK-sol suspension with a speed of 5 mm/sec after electrophoretic deposition. Other experimental conditions for electrophoretic deposition were the same as those in the deposition of MoS_2 particles in MEK without hybrid sol. The amount of deposition was measured after drying the film at 70°C for 30 min in air. Heat-treatment was carried out at 450°C in nitrogen for 30 min to develop network structure of the methylsiloxane hybrid film. Both heating and cooling were carried out at a rate of 10°C/min.

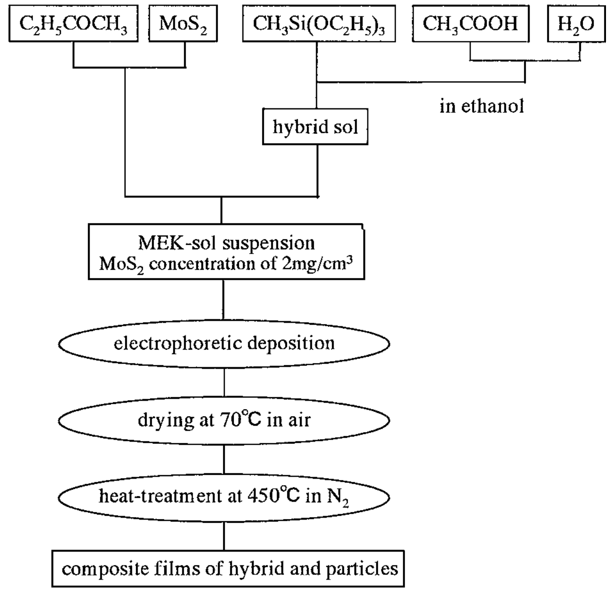

Figure 2 Procedure for the synthesis of a composite film of inorganic-organic hybrid and particles.

2.3. Characterization methods

The structure of the hybrid film was characterized with a Perkin-Elmer System 2000 Fourier transform infrared (FT-IR) spectrometer. Electric conductivity of the solvents containing MoS_2 particles were measured with a Model SC82 conductivity meter (Yokogawa Electric Co.).

For the purpose of investigating the elution of molybdenum and sulfur ions, MoS_2 particles were dispersed in MEK and MEK-sol solutions. The particle concentrations of the suspensions were 2 mg/cm^3. The supernatant solutions of the suspensions were filtered using a PTFE syringe filter with a pore diameter of 0.2 μm. The concentrations of molybdenum and sulfur ions in the filtered supernatant solutions were measured by inductive coupled plasma (ICP) spectroscopy using an SPQ9000 (Seiko Instruments Inc.) and an ICAP757 (Nippon Jarrell-ash), respectively.

Zeta potential of MoS_2 particles was measured with an ELS-8000 electrophoretic light scattering spectrophotometer (Otsuka Electronics Co., Ltd). To estimate the effect of hybrid sol on zeta potential, MoS_2 particles were dispersed into a pure MEK and a MEK-20 vol% sol to give particle concentrations of 2 mg/cm^3. The concentrations of these suspensions were too high to observe particles by laser scattering.

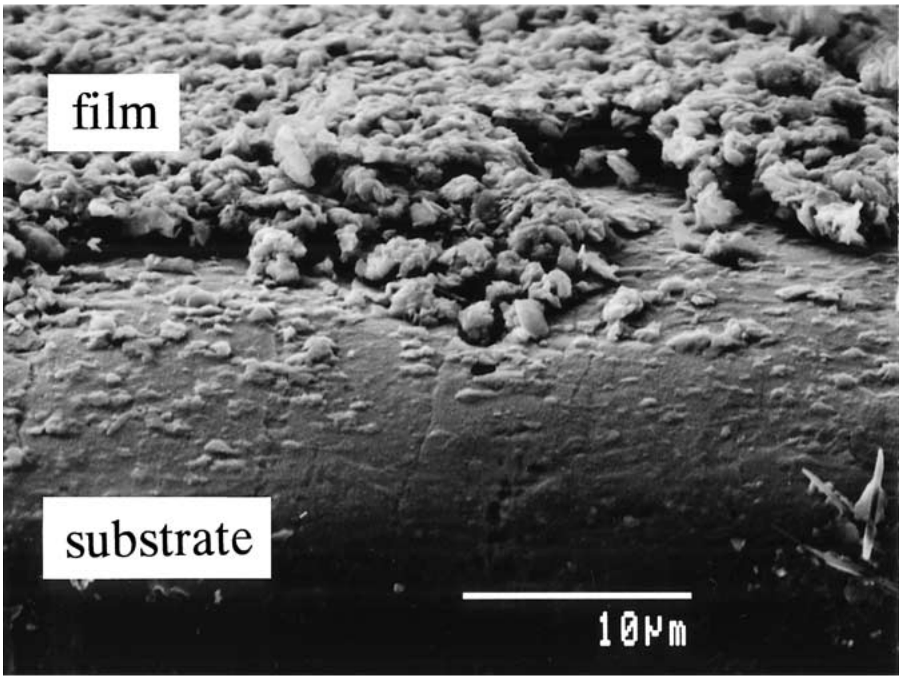

Figure 3 SEM micrograph of inorganic-organic hybrid film containing MoS_2 particles.

Thus, each suspension was diluted with MEK to about 0.04 mg/cm^3 before measurement.

3. Results and discussion

3.1. Composite film of inorganic-organic hybrid and particles

The composite film of inorganic-organic hybrid and MoS_2 particles has successfully been synthesized on an anode substrate by using an electrophoretic process. The SEM micrograph of the composite film after heat-treatment at 450°C is shown in Fig. 3. The thickness of the obtained composite film was uniform. The MoS_2 particles in the composite film were glued to the substrate by inorganic-organic hybrid materials while MoS_2 particles deposited without hybrid sol peeled off easily by scrubbing.

Fig. 4 shows an FT-IR spectrum of inorganic-organic hybrid film without particles which was dip-coated on a silicon wafer and heat-treated at 450°C in N_2. The absorption peaks around 1000–1100 cm^{-1} come from Si—O—Si bonds. The absorption peaks around 1270 cm^{-1} and around 2970 cm^{-1} are ascribed to the Si—CH_3 stretching vibration and the C—H stretching vibration of a methyl group, respectively. The film contains methyl groups in a siloxane network through Si—CH_3 bonds even after the heat-treatment.

To estimate the contribution of electrophoretic deposition of hydrolyzed alkoxysilanes themselves, electrophoretic deposition was carried out using a mixed solution of MEK-20 vol% hybrid sol without MoS_2 particles. The deposition was performed on a substrate in two cases, where a substrate was used as a cathode and as an anode. The applied voltage was 500 V and deposition time was 30 sec. As a result, the amount of deposition was approximately 0.04 mg/cm^2 in both cases, which was at the same level as that obtained by only dip-coating. In a composite film, the mass fraction of hybrid material deposited by electrophoresis is considered to be negligibly small as compared to that of MoS_2 particles.

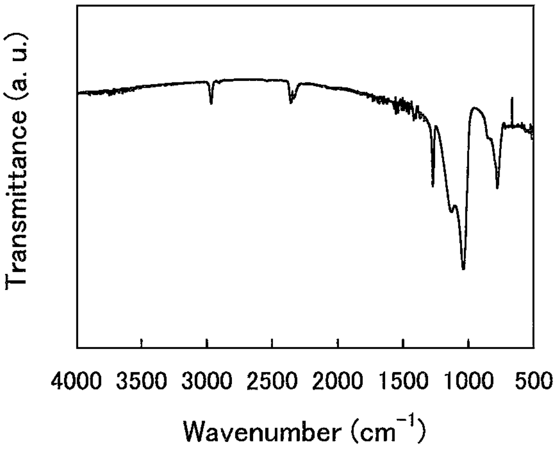

Figure 4 FT-IR spectrum of inorganic-organic hybrid film after heat-treatment at 450°C in N_2.

3.2. Amount of deposition of MoS_2 in MEK and in MEK-sol

The amount of deposition (m) can be expressed as

$$m = \alpha CvSt \quad (1)$$

where α is a fraction of particles deposited on a substrate, C is a concentration of particles in the suspension, v is the velocity of the particle under the influence of the electric field, S is the deposition area and t is the deposition time [17]. In the organic solvent, the thickness of the electrical double layer can be assumed to be so thick as compared to the radius of the particle that Huckel's equation can be used to obtain v:

$$v = 2E\varepsilon_r\varepsilon_0\zeta/3\eta \quad (2)$$

where E is the average electric field, ε_r is the dielectric constant of dispersion medium, ε_0 is the permitivity of

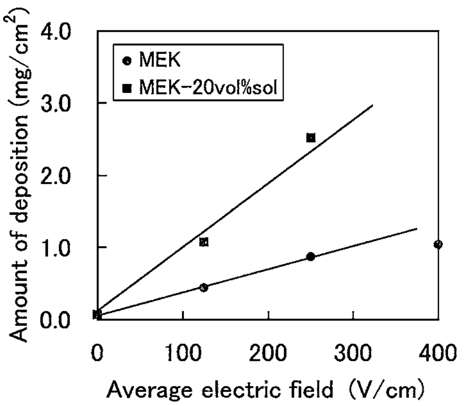

Figure 5 Relationships between amount of deposition and average electric field in electrophoretic deposition of MoS_2 particles in MEK and MEK-sol. The deposition time was 60 sec. The average electric field was obtained by dividing the applied voltage by the distance between electrodes (10 mm).

vacuum, ζ is the zeta potential of particles in the dispersion medium and η is the viscosity of the dispersion medium [18]. By combining Equations 1 and 2, the amount of deposition is expressed as

$$m = (2/3)\alpha CE\varepsilon_r\varepsilon_0\zeta St/\eta \qquad (3)$$

Fig. 5 shows the relationship between the amount of deposition and average electric field in the electrophoretic deposition of MoS_2 in MEK and MEK-20 vol% hybrid sol. The average electric field is given by dividing an applied voltage by the distance between electrodes. The deposition time was 60 sec. The amount of deposition was nearly proportional to the average electric field in both cases. When no voltage was applied, only an inorganic-organic hybrid film was dip-coated on a substrate in the case of MEK-sol whereas nothing was deposited in the case of MEK. When average electric field was the same, the amount of deposition in MEK-sol was more than twice as much as that in MEK. Although the amount of deposition in MEK-sol includes the weight of hybrid material, the contribution is only 0.04 mg/cm^2 from the results of electrophoretic deposition of hybrid sol. Thus, it can be said that the addition of hybrid sol increases the efficiency of the electrophoretic deposition of MoS_2 particles.

Fig. 6 shows the relationship between the amount of deposition and the deposition time in the electrophoretic deposition of MoS_2 in MEK and MEK-20 vol% hybrid sol. The amount of deposition was also proportional to the deposition time in both cases. The linear relationships shown in Figs 5 and 6 suggests that our experimental data can be understood based on Equation 3.

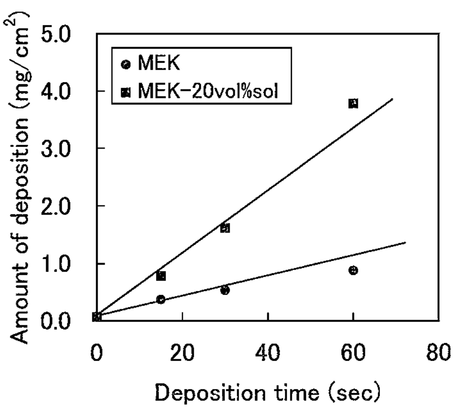

Figure 6 Relationships between amount of deposition and deposition time in electrophoretic deposition of MoS_2 particles in MEK and MEK-sol. The applied voltage was 125 V.

TABLE I Concentration of molybdenum and sulfur ions in supernatant solutions of suspensions

	Concentration (ppm)	
Suspension	Mo	S
MEK	2.3	2.5
MEK-20 vol%sol	6.5	2.9

3.3. Electrification mechanism of MoS_2 particles

Table I summarizes the concentration of molybdenum and sulfur ions in supernatant solutions of MEK and MEK-20 vol% sol with particle concentration of 2 mg/cm^3. The elution of molybdenum and sulfur ions in MEK-sol is higher than that in MEK. Hybrid sol seems to promote the elution of molybdenum and sulfur ions from MoS_2 particles.

Fig. 7 shows the changes of the electric conductivity of MEK and MEK-20 vol% sol by increasing MoS_2 particle concentration. When no particles are contained, the electric conductivity of MEK-sol is higher than that of MEK. The inorganic-organic hybrid sol contains ions derived from ascetic acid and water. Such ions may contribute to the conduction of electricity, leading to the higher conductivity in MEK-sol. The increase in conductivity in MEK-sol by increasing particle concentration is higher than the one in MEK. The steeper inclination of the line in MEK-sol results from the higher elution of molybdenum and sulfur ions in MEK-sol as shown in Table I.

The zeta potential of the MoS_2 particles in MEK was −52 mV and that of the MoS_2 particles in MEK-20 vol% sol was −14 mV. MoS_2 particles are negatively charged in both MEK and MEK-sol, which is consistent with the deposition on an anode substrate. The relatively high negative zeta potential of −52 mV in MEK is thought to result mainly from absorption of eluted sulfur anions. In the case of MEK-hybrid sol, MoS_2 particles are involved in complicated adsorption accompanying various species derived from hybrid sol

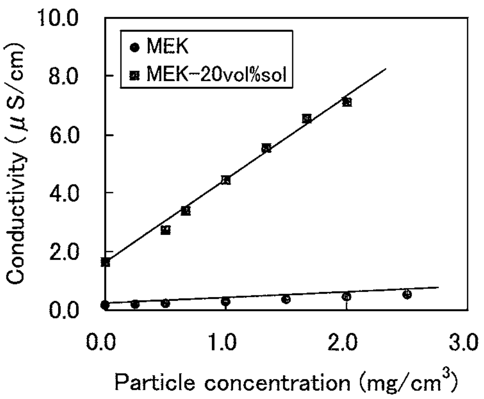

Figure 7 Relationship between MoS_2 concentration and conductivity.

as well as elution of molybdenum and sulfur. It is speculated that the adsorption of hydrolyzed methyltriethoxysilane on the surface of MoS_2 particles by hydrogen bonding such as Mo-S$\cdots$HO-Si reduces the number of anions, decreasing the zeta potential to approximately one fourth of that in MEK.

3.4. Effect of hybrid sol on electrophoretic deposition

Electrophoretic deposition includes two major processes, e.g., electrophoresis and deposition of particles on a substrate, which are expressed by v and α in Equation 1, respectively. The electrophoresis of particles depends on the electric field and the nature of the suspensions as shown in Equation 2. The fraction of particles deposited on a substrate, α, can be calculated using Equation 3. In the cases of the electrophoretic deposition in MEK, α is calculated to be 0.2 and v to be 1.8×10^{-4} [m/s] using the following experimental data together with dielectric constant and viscosity of pure MEK:

$$m = 0.44\ [\text{mg}],\ E = 125\ [\text{V/cm}],$$
$$C = 2\ [\text{mg/cm}^3],\ \varepsilon_r = 18.5,\ S = 1\ [\text{cm}^2],$$
$$t = 60\ [\text{s}],\ \zeta = 52\ [\text{mV}] \text{ and } \eta = 0.378\ [\text{mPa}\cdot\text{s}].$$

On the other hand, α and v in MEK-20 vol% sol are calculated to be 1.8 and 5.0×10^{-5} [m/s] using the following parameters:

$$m = 1.07\ [\text{mg}],\ E = 125\ [\text{V/cm}],$$
$$C = 2\ [\text{mg/cm}^3],\ \varepsilon_r = 18.5,\ S = 1\ [\text{cm}^2],$$
$$t = 60\ [\text{s}],\ \zeta = 14\ [\text{mV}] \text{ and } \eta = 0.378\ [\text{mPa}\cdot\text{s}].$$

The dielectric constant and viscosity of MEK-20 vol% sol are assumed to be the same as those of pure MEK, because the fraction of hybrid sol is only one-fifth. Although there is a large difference in dielectric constant among water ($\varepsilon_r = 80.1$), acetic acid ($\varepsilon_r = 6.2$) and MEK ($\varepsilon_r = 18.5$), the concentrations of water and acetic acid in MEK-20 vol% sol are about 3 and 1.6 wt%, respectively. Thus, the effects of them on the dielectric constant are considered to be small. Since it cannot be true that the parameter α exceeds one, the calculated value of α for MEK-20 vol% sol seems to be overestimated. The errors of E, ε_r, η and ζ whose exact values are difficult to obtain as well as the assumption of Huckel's equation may result in the overestimation of α for MEK-20 vol% sol. Although the estimated value of α includes some errors, we can say at least that α in MEK-20 vol% sol is much larger than that in MEK. The difference in α is considered to be responsible for the larger amount of deposition in MEK-sol because electrophoresis of particles expressed by v cannot explain the difference in the amount of deposition.

Two reasons are considered for the larger value of α in MEK-sol than in MEK. One is zeta potential of MoS_2 particles. As the zeta potential of particles becomes higher, the particles move faster toward a substrate but the deposition of particles on a substrate is more suppressed owing to the repulsive force between particles. Hayashi *et al.* have reported that the amount of deposition of $CaSiO_3$ powder with zeta potential of approximately 15 mV is larger than that of the powder with zeta potential of more than 30 mV [19]. Thus, the parameter α in MEK-sol where the zeta potential of the particles is -14 mV is considered to be higher than that in MEK in which particles bear high zeta potential of -52 mV because of the easy agglomeration of particles on a substrate due to the moderate zeta potential.

Another reason for the larger value of α in MEK-sol is the effect of surface modifiers of particles. When sol is included in the suspension, particles are considered to be partly modified with hydrolyzed methyltriethoxysilane having silanol groups like MoS$\cdots$HO—Si$\equiv$. The deposition of particles modified with hydrolyzed methyltriethoxysilane results in the deposition film with many silanol groups. When a particle moving toward a substrate under a given electric field comes in the vicinity of the uppermost layer of the deposit, the silanol groups on the surface of the particle can make hydrogen bonds among silanol groups on the deposition film. As a result, the particle can be incorporated into the deposition film by a hydrogen bond. The particles may also be incorporated into a deposit by the entanglement of surface modifiers derived from methyltriethoxysilane. The deposition processes by using the interaction of surface modifiers, which are not included in the electrophoretic deposition in MEK, are considered to increase the fraction of particles that can be deposited on a substrate.

The amount of deposition is proportional to E and t in a MEK-sol as shown in Figs 5 and 6, suggesting that the amount of deposition by the interaction of surface modifiers is also proportional to E and t. The number of particles suspending near a substrate increases proportionally with the electric field. This may enhance the chance of interaction among surface modifiers to incorporate particles into the film, resulting in a relationship shown in Fig. 5. The linear relationship in Fig. 6 suggests that the ratio of particles incorporated into a film by the interaction of surface modifiers is almost constant during the electrophoretic deposition.

The addition of 20 vol% hybrid sol is found to double the amount of deposition of MoS_2 particles owing to the much higher α as compared to the one in MEK. The difference in zeta potential of MoS_2 particles and the interaction of surface modifiers increase the fraction of particles deposited on a substrate in a MEK-sol suspension.

4. Conclusions

A new technique to fabricate a composite film of inorganic-organic hybrid and particles by electrophoretic deposition has been demonstrated. Electrophoretic deposition of MoS_2 particles were carried out in both MEK and MEK-20 vol% hybrid sol suspensions. Electrophoretic deposition in MEK-20 vol% hybrid sol yields a composite film in which particles are fixed by inorganic-organic hybrid material.

The amount of deposition was proportional to the average electric filed and deposition time in both MEK and MEK-sol. The amount of deposition of MoS_2 in

MEK-sol was more than twice as much as that in MEK. The fraction of particles deposited on a substrate in MEK-20 vol% sol was found to be much larger than that in MEK. The hydrolyzed methyltriethoxysilane in hybrid sol modified MoS_2 particles. As a result of surface modification, the particles in MEK-sol have smaller negative zeta potential than that in MEK, which makes agglomeration of particles on a substrate easier. The surface modification also enables the incorporation of particles into a deposition film by hydrogen bonding and entanglement of surface modifiers. The lower zeta potential and the interaction of surface modifiers enhance the incorporation of particles into a deposit.

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