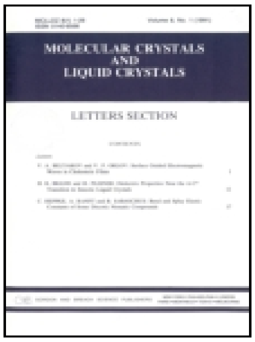

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Fabrication of Al_2O_3 Coatings on Metal Substrates by Electrophoretic Deposition by the Addition of Polydimethylsiloxane-Based Organic-Inorganic Hybrid Materials as Binders

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Polydimethylsiloxane (PDMS)-based organic-inorganic hybrids have been studied because of their high dielectric strength, heat resistivity, and flexibility. In this study, we fabricated Al_2O_3 coatings on metal substrates with sufficient electrical insulation, heat conductivity, and thermal stability by electrophoretic deposition (EPD) using PDMS-based hybrid binders. The scratch hardness, thermal conductivity, and electrical breakdown strength of the Al_2O_3 coating before and after heat treatment at 300 °C for 500 h were 2.0 N, 3.1 W/mK, and 60 kV/mm, respectively. These results demonstrate the usefulness of EPD using PDMS-based hybrid binders for fabricating flexible heat dissipative substrates used in high-temperature environments.

Keywords organic–inorganic hybrid; polydimethylsiloxane; electrophoretic deposition; Al_2O_3 coating; long-term thermal stability

Introduction

The increase in heat generated in semiconductor devices with higher levels of miniaturization and integration and the increase in the operation temperature of power semiconductor modules require countermeasures against heat radiation. One such countermeasure involves the development of metal-core substrates. The metal-core substrate usually consists of a metal plate, an insulating layer, and a metal foil as a conductive layer. The insulating layer, in addition to providing electrical insulation, is also required to exhibit high thermal conductivity to increase the heat dissipation performance of the metal-core substrate.

To enhance the thermal conductivity of the insulation layer, various techniques have been proposed for processing ceramic coatings on metal substrates. For aluminum and aluminum alloy substrates, anodic oxidation can be used. Anodic oxidation offers advantages in terms of mass production capability, lowered manufacture cost, and the ability to use large substrates. Anodic oxidation leads to a porous structure and hence, a sealing treatment is required for obtaining high levels of electrical insulation [1]. In addition, the thermal conductivity of an anodically oxidized aluminum layer is less than 2.0 W/mK [2].

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Plasma sprayed alumina layer shows a high degree of electrical insulation; however, the thermal conductivity of the layer was reported to be less than 3.0 W/mK [3]. Alumina films obtained by aerosol deposition technique show a higher thermal conductivity of 4–5 W/mK and higher electrical insulation properties of 1.2 kV per 10 μm [4]. However, aerosol deposition is not suitable for mass production and for using large substrates. Electrophoretic deposition (EPD), which allows for better control of film thickness and affords relatively uniform coatings on large and complex shaped substrates at low costs, is a more attractive technique for processing ceramic coatings in comparison to other methods such as plasma spraying and aerosol deposition [5]. Alumina coatings obtained by EPD using polyimide binders are well-known for their good insulating properties; however, increasing their thermal conductivity is a challenge. To increase the thermal conductivity of EPD alumina films, a high volume ratio of alumina is required in the in alumina-polyimide composite layers. However, with increase in the ratio of alumina in the EPD layer, defects, such as cracks or internal voids, are easily generated on the EPD layer during curing. This phenomenon occurs because of the thermal stress due to large elastic modulus of the EPD layer and a difference in the thermal expansion coefficient between the EPD layer and the metal substrate. To reduce the thermal stress, fabrication of an EPD layer dispersed in polyimide on a carbonaceous substrate with a lower thermal expansion coefficient than metals was reported [6], although such a substrate may be inferior to the metal-core substrate in terms of the total thermal conductivity.

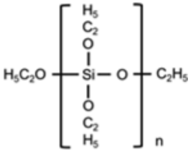
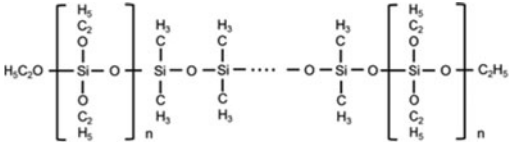
In this paper, to achieve high thermal conductivity and electrical insulation, we used a flexible organic-inorganic hybrid obtained from polydimethylsiloxane (PDMS) as a binder resin for the EPD to fabricate an Al_2O_3 coating on an aluminum substrate. The PDMS-based hybrid exhibits a high degree of flexibility [7–9], excellent electrical insulating properties [10–14], and an excellent heat resistance against temperatures exceeding 250°C [10, 13, 15]. The composition of the suspension made from the PDMS-based hybrid sol used for the EPD was appropriately adjusted to relax the thermal stress by lowering of the elasticity modulus of the EPD layer and reducing the mismatch of the thermal expansion coefficients of the EPD film and the aluminum substrate, while maintaining the mechanical strength of the EPD film. The EPD films were characterized for their electrical insulation properties, thermal conductivity, and long-term thermal stability.

Experimental

Sample Preparation

The composition of the suspension used for the EPD is summarized in Table 1. A powder of α-Al_2O_3 (AA-05, Sumitomo Chemical Co.) with a mean particle size of 0.5 μm and Brunauer-Emmett-Teller (BET) surface area of about 3.0 m^2/g was used for the EPD. Super dehydrated 2-Propanol (Wako Pure Chemical Industries Ltd.) was used as the dispersion medium for the preparation of the Al_2O_3 powder suspensions. Monochloroacetic acid (MCAA, Wako Pure Chemical Industries Ltd.) was used as the stabilizing and dispersing agent [16]. Ethylsilicate $Si_7O_6(OC_2H_5)_{16}$ (ES45, also referred to as E_S, Tama Chemicals Co. Ltd.) and ethylsilicate-terminated PDMS (E_S-PDMS) with an average molecular weight of 27,000, synthesized according to the procedure provided in the literature [10] were used as raw materials for the binders. The chemical structures of ES and E_S-PDMS are shown in the Table 1. The electrophoretic suspensions were prepared by adding 5–20 g of the hybrid sol composed of 5 g of E_S and 0–15 g of E_S-PDMS to 100 g of the suspension containing

Table 1. Composition of the EPD suspension

	Materials	Weight [g]	Sol concentration in suspended materials[wt%]
Dispersion media	IPA (2-propanol)	72.25	—
	monochloroacetic acid (stabilizing and dispersing aid)	12.75	—
Suspended materials	α-alumina (a mean particle size of 0.5 μm)	15	—
	sol : Es , Es-PDMS, or Es+ESPDMS  Ethylsilicate (Es) (Mw=1,000)  n=7 Ethylsilicate-terminated PDMS (Es-PDMS) (Mw = 27,000)	0–20	0–57

15 g of Al_2O_3 powder, 12.75 g of MCAA, and 72.25 g of 2-propanol. The concentration of the abovementioned hybrid sol in the suspended material corresponds to 25–57 wt%. The suspension made from the sol composed of solely E_S or E_S-PDMS alone were also used for EPD for comparison. Aluminum plates (99.9%) (25 mm × 20 mm × 0.2 mm or 25 mm × 20 mm × 2.0 mm) were used as the substrates for the EPD. A stainless steel plate of identical dimensions was used as the counter electrode. The EPD cell was a two-electrode system, consisting of a Teflon beaker and the electrodes. The distance between the electrodes was set as 60 mm. A constant current was applied between the substrate and the counter electrode using a DC power supply (Anatech Ltd., Pro3900). Deposition occurred at the anode. After deposition, the sample obtained was kept at 250°C for 2 h to eliminate the solvent and cure the PDMS-based hybrid materials used as the binder. The heating rate was 10°C /min.

Characterization

The surface morphologies of the prepared EPD films were observed using atomic force microscopy (AFM). The scratch hardness of the EPD films was measured by a hardness test pencil (Model 318-S, Erichsen). The extent of warping in the substrate after curing, originating from the mismatch in the thermal expansion coefficients of the coating and the metal substrate, was measured by a gap measuring gauge (100MZ, Riken Sokuhan Co. Ltd). Thermal conductivities of the EPD Al_2O_3 films were measured by a steady-state method using the measurement system described in reference [17].

The alternating current (AC) breakdown strength E_B was measured using a plane-to-plane electrode system. The diameter of the plane was 10 mm with a 5.0 mm curvature. The AC voltage (with a frequency of 60 Hz) was applied to the sample in a fluorinated inert liquid (Fluorinert^{TM}). The values of E_B and thermal conductivity of the samples were also evaluated after heat treatment at 300°C for 500 h. All the measurements were carried out at room temperature.

Results and Discussion

The alumina coating (50 μm in thickness) was deposited by supplying a current density of 1.5 mA/ cm^2. In the case of the EPD coating obtained on a thin aluminum substrate (0.2 mm in thickness), the substrate could undergo warping after curing at 250°C because of the suspension type. This is attributed to the thermal stress between the cured coating and the metal substrate. Figure 1 shows (a) the scratch hardness and (b) amount of warping of the EPD substrates versus the sol concentration in the suspended materials. In EPD films obtained from suspensions containing only E_S, with increase in the amount of E_S, the scratch hardness and substrate warping increased. In EPD films obtained from suspensions containing only E_S-PDMS, despite an increase in the amount of E_S-PDMS of up to 50wt%, substrate warping did not occur, although the scratch hardness remained below 0.7 N. These results indicate that the addition of a hybrid sol composed of E_S-PDMS could improve the flexibility of the EPD film, but the effect of the binders, which increase adhesion between the alumina particles, is insufficient. In EPD films obtained from a suspension of a hybrid sol composed of E_S and E_S-PDMS, the scratch hardness increased with increase in the amounts of the hybrid sol, and reached 2.0 N if the deposition was carried out from a suspension containing 57 wt% of the hybrid sol , although substrate warping did not occur. These results indicate that the addition of an appropriate amount of the PDMS-based hybrid sol composed of E_S and E_S-PDMS would improve the flexibility of the EPD film,

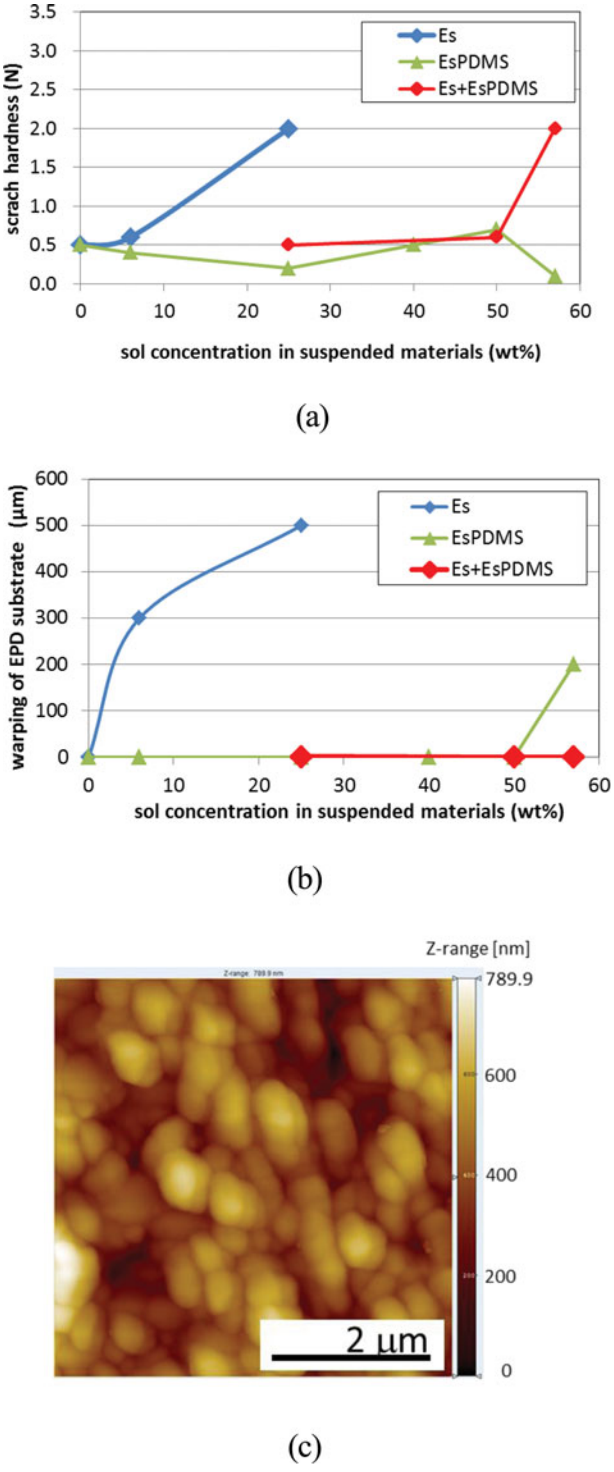


Figure 1. (a) Scratch hardness and (b) warping of the EPD substrates as a function of the versus sol concentration in suspended materials. (c) AFM image of the deposited film. Scanning area = 5 μm × 5 μm.

increase adhesion strength between the binders and the alumina particles, and enhance the mechanical strength of EPD film. When the optimized suspension mentioned above was used for the EPD process, the deposited film obtained on a 2.0 mm thick substrate did not exfoliate or crack. The surface and morphology of the films were observed after the EPD and curing. The AFM image of the EPD coatings is shown in Fig. 1(c). A dense oxide layer without pores is desirable to achieve a high thermal conductivity. The deposited film appeared sufficiently compact and regular. The thermal conductivity and E_B of the Al_2O_3 coating prepared using a suspension with 57 wt% of the hybrid sol composed from E_S and E_S-PDMS was 3.1 W/mK and 62.7 ± 3.8 kV/mm, respectively. These values are greater than those reported in the literature for EPD films [2]. After heat treatment at 300°C for 500 h, the EPD films did not crack or peel. The thermal conductivity and E_B of the EPD layer after heat treatment at 300°C for 500 h was 3.1 W/mK and 63.9 ± 2.0 kV/mm, respectively; hence, the values did not change after the heat treatment. These results suggest the usefulness of EPD using PDMS-based hybrid materials for the fabrication of flexible heat dissipative substrates that can be used in high-temperature environments.

Conclusions

Al_2O_3 coatings on metal substrates with good electrical insulation properties, heat conductivity, and thermal stability were fabricated by EPD using PDMS-based organic-inorganic hybrids as binders. The amount of the PDMS-based hybrids was optimized to obtain stronger EPD films that did not undergo substrate warping. The EPD film prepared using PDMS-based hybrids as binders exhibited a scratch hardness, thermal conductivity, and E_B of 2.0 N, 3.1 W/mK, and 60 kV/mm, respectively, which remained unaffected after heat treatment at 300°C for 500 h. These results suggest the usefulness of the EPD process using PDMS-based hybrid materials for the fabrication of flexible heat dissipative substrates that can be used in high-temperature environments.

Acknowledgments

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