Effect of Processing Parameters and Powder Size on Microstructures and Mechanical Properties of Y_2O_3 Coatings Fabricated by Suspension Plasma Spray

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ABSTRACT

The suspension plasma spray (SPS) technique has been used to obtain dense Y_2O_3 coatings and to overcome the drawbacks of the conventional air plasma spray (APS). SPS uses suspensions containing micrometer or sub-micrometer sized powders dispersed in liquid media. In this study, microstructure developments and mechanical properties have been investigated as functions of particle size of source material and plasma processing parameters such as plasma power and stand-off distance. The microstructure of the coating was found to be highly related to the particle size and the plasma processing parameters, and it was directly reflected in the hardness and the adhesion strength. When fine powder (BET 16.4 m²/g) was used as a raw material in the suspension, there was, with increasing stand-off distance, a change from a dense structure with a slightly bumpy surface to a porous structure with a cauliflower-like surface. On the other hand, when a coarse powder (BET 2.8 m²/g) was used, the coating density was lower, with microscopic splats on the surface. Using fine Y_2O_3 powders, the coating layer with an optimum short stand-off distance showed a high hardness of approximately 90% of that of sintered Y_2O_3 and an adhesion strength several times higher than that of the coating by conventional APS.

Key words : Suspension plasma spray, Y_2O_3 , Particle size, Processing parameter

1. Introduction

The plasma processing apparatus for the semiconductor industry uses many ceramics as plasma-facing materials.¹⁻⁸⁾ The plasma consists of reactive radicals and ions from fluorocarbon gases, which react with the ceramics and cause erosion.⁶⁻⁹⁾ Al_2O_3 is a typical plasma resistant material and Y_2O_3 is increasingly being used because of its superior plasma etching resistance.^{7,8)} Even though Y_2O_3 is very effective as a plasma resistant material, if it is made of sintered parts, it is too expensive because of the very high cost due to the tremendous raw material consumption. To tackle this cost issue, plasma spray coatings, typically atmospheric plasma sprays (APS), have been widely used to obtain thick Y_2O_3 coatings on various substrates.¹⁰⁾ Recently, however, coating using APS is being investigated as a source of particulate contamination as critical dimensions in semiconductor devices are scaled down to 20 nm. Generally, APS coating uses granules with sizes of tens of micrometers. Thus, impacts and solidification of melted granules on the substrate can result in lamellar structures and various defects such as pores and surface cracks. The low adhesion

strength of Y_2O_3 coating using APS has been attributed to this lamellar structure; it is also thought that this material can cause particulate contamination due to preferential erosion on structural defects.³⁾

The suspension plasma spray (SPS) process is a new technique using submicrometer-sized raw materials instead of the tens of micrometer sized granules used in APS. The fine raw material is dispersed in liquid media such as alcohol or water. The suspension is then injected into a plasma jet stream, which is directed to the substrate. Since fine powders are used, the formation of large lamellar structures can be prevented, possibly producing diverse microstructures of the coating. Using this new technique, many studies have been performed on thermal barrier coatings; however, studies on Y_2O_3 coatings have so far been rare.¹¹⁻¹³⁾ While, for thermal barrier coating, coatings with higher porosity or vertical cracks are preferred because they increase the thermal durability of the coatings, Y_2O_3 coating, as a plasma-facing material, needs a highly dense structure.^{3,8,14)}

In this study, Y_2O_3 raw materials with different particle sizes were used for a suspension plasma spray. In addition, the effects of the plasma processing parameters, such as the plasma power and the stand-off distance were examined in terms of the microstructural development of the coatings. Then, hardness and adhesion strength were measured to indirectly evaluate the density and the mechanical reliability when these materials are applied to semiconductor pro-

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cessing equipment. In addition, the crystalline structure and non-stoichiometry of the coating were analyzed. Finally, the mechanism of the microstructure development is discussed in terms of the Knudsen and Stokes effects.

2. Experimental Procedure

Two types of Y_2O_3 powders were used: fine Y_2O_3 powder (99.99%, D_{50} : 1.04 μm , High Purity Chemicals, Japan) and coarse Y_2O_3 powder (99.99%, D_{50} : 5.03 μm , High Purity Chemicals, Japan). BET surface area was estimated using a surface area analyzer (Tristar II 3020, Micromeritics, USA); the values determined were 16.4 m^2/g for fine powder and 2.8 m^2/g for coarse powder. All powders were dispersed in ethanol and the solid content was 10 wt%. The suspension was ball-milled for 24 h. As milling media, zirconia balls with a diameter of 15 mm were used. The suspensions were stabilized by the addition of a dispersant of 0.1wt% (Darvan C, RT Vanderbilt Co., USA).

A Mettech Axial III (Northwest Mettech, Canada) was used for the high power plasma spray coatings. Alumina substrate was ground to an average surface roughness of R_a , 0.6 μm . Stand-off distance was 50 to 150 mm, plasma power values were 80, 65, and 40 kW, total gas flow rate was 245 L/min, and suspension feeding rate was 45 ml/min. Gas composition was 7.5 Ar, 1.5 N_2 , and 1.0 H_2 . The substrate holder, with an overall diameter of 40 cm, was rotated at the speed of 3.5 rev/s and gun speed was 35 mm/s in vertical motion.

Microstructure and morphologies of the SPS coatings were analyzed using a scanning electron microscope (SEM, JSM-6390, JEOL, Japan). Coating surface was analyzed directly after coating, and cross-section was polished to a 1 μm finish. High magnification microstructures were obtained through transmission electron microscopy (TEM, Tecnai F20, FEO, USA). TEM samples were prepared by the focused ion beam method (FIB, NOVA 200, FEI COMPANY, USA).

XPS analysis of the SPS coatings was performed using an XPS (PHI 5000, Ulvac-phi Co., Chigasaki, Japan) at a pass energy of 23.5 eV (Table 1). The measurement was conducted using an electron flooding gun to prevent peak position shift induced by charging of the specimen surface, because these specimens are normally insulators. The surface spectrum was analyzed using curve fitting software (Avantage, Thermo Fisher Scientific, East-Grinstead, U.K.). As a reference, a Y_2O_3 sample sintered under air atmosphere was used. O/Y ratios of the coatings were normalized

using the O/Y ratio of 1.5 of the sintered Y_2O_3 .

Hardness was measured by Vickers indentation (HV-114, Mitutoyo Corporation, Japan). The coating surfaces were polished to 1 μm using a diamond paste. Procedure was done with a load of 2 kg and loading time of 10 s. An average of 5 indentations was considered as the hardness. The adhesion bond strength of the coating was measured using the pullout method. Coated surface was bonded to a metal coupon with a diameter of 8 mm using epoxy adhesive (ENSURE CP-7406, Foto polymer, Singapore). Then, the pull-out was carried out using a universal testing machine (UTM, R&B Inc., Korea) at a crosshead speed of 0.5 mm/min.

3. Results

3.1. Microstructures of coatings from fine powders

Figure 1 shows the surface microstructures of the Y_2O_3 coatings, which were plasma sprayed using fine Y_2O_3 powders (16.4 m^2/g) at a power of 80 kW with respect to the

Fig. 1. Surface microstructures of coatings produced using fine Y_2O_3 powder at plasma power of 80 kW with respect to the stand-off distance: (a) 50 mm, (b) 75 mm and (c) 100 mm.

Table 1. Details of XPS Conditions

Parameter	Condition
Pass energy (eV)	23.5
Step (eV)	0.05
Times per step (ms)	60
Repeat (#)	10

stand-off distance. At the short distance of 50 mm, the surface showed a slightly rough morphology, the so-called bumpy structure whose size is around 100 μm . With increasing stand-off distance, the irregularity intensified, producing a more pronounced bumpy structure. At 100 mm of stand-off distance, the surface exhibited a cauliflower-like structure with the development of empty spaces between the cauliflower columns.¹³⁾ The transition from slightly bumpy to cauliflower-like structure seems to occur at the stand-off distance of around 75 mm. The transition distance depended on the power of the plasma spray (Fig. 2). At the lower power of 65 kW, cauliflower structures appeared at the stand-off distance of 50 mm. At the power of 40 kW, the width of the columns became narrower.

To directly check the density and microstructure of the coatings, the cross-sections were observed after polishing. Fig. 3 (a) shows that the coating produced at a plasma power of 80 kW and stand-off distance of 50 mm contains a very small fraction of pores. At lower magnification, it appears fully dense, which is in sharp contrast to the usual porous microstructure of the conventional plasma-sprayed coating. At 100 mm of stand-off distance under the same plasma power, the coating showed irregularly-shaped interconnected pores (Fig. 3 (b)).

At lower plasma power, this kind of behavior became more pronounced. Figures 3 (c) and (d) show a cross-section of the coating produced at the plasma power of 40 kW with respect to the stand-off distance. At 50 mm, it is more porous than the coating from 80 kW. Furthermore, at the longer distance of 100 mm, the coating showed a very porous columnar structure, with connected voids between

the columns.

From the microstructure of the surface and cross-section, it can be inferred that the lower power of the plasma and the longer distance promote the development of a porous columnar structure that might be induced by non-directional impinging of molten droplets.¹²⁾ Generally, if particles incident on the surface only have a velocity component normal to the substructure, it is easier to fill the whole surface, resulting in a dense microstructure. But, when the particles have various directional components, some area of the substrate can be partially shadowed, producing voids in the coating. This shadow effect can be the cause of the cauliflower-like top surface.^{13,15)}

Figure 4 shows the TEM microstructures of the coating deposited at a plasma power of 80 kW and stand-off distance of 50 mm. This coating consisted of small Y_2O_3 particles with sizes in the hundreds of nm. Between the particles, very small pores of around 100 nm were observed, though the coating looked very dense at lower magnification, as can be seen in Fig. 3(a).

Fig. 2. Surface microstructures of coatings produced using fine Y_2O_3 powder at plasma stand-off distance of 50 mm with respect to the plasma power: (a) 65 kW and (b) 40 kW.

Fig. 3. Cross-sectional microstructures of coatings produced using fine Y_2O_3 powder at plasma power of 80 kW: plasma stand-off distance (a) 50 mm, (b) 100 mm and 40 kW: plasma stand-off distance (c) 50 mm, (d) 100 mm.

Fig. 4. TEM microstructure of coatings produced using fine Y_2O_3 powder at plasma power of 80 kW and plasma stand-off distance of 50 mm.

3.2. Microstructures of coatings from coarse powder

The particle size of Y_2O_3 powders was found to have very strong effects on the microstructure development. Fig. 5 shows the surface microstructures of coatings using coarse Y_2O_3 powder ($2.8 \text{ m}^2/\text{g}$) at two different plasma powers and two stand-off distances. There were no columnar structures in any of the samples. The surfaces were roughly flat, without any particular structures, showing simple particle deposition. The magnified microstructures (Fig. 6) show small microscopic splats with abundant small particles. The splat size was on the order of micrometers, which is much smaller than the size of splats obtained when using the conventional plasma spray. In addition, small voids between splats were observed, and these were more pronounced for coatings produced at longer stand-off distances.

Cross-sections of coatings produced using coarse powers showed some porosity; this porosity was apparently higher

than that in the coatings produced using smaller powders (Fig. 7). Pores were distributed throughout the coating and are easily distinguishable in the microstructure; these samples showed quite similar porosity except for the coating produced at lower plasma power of 65 kW and longer distance of 100 mm. For this condition, the microstructure was so loose that it was difficult to obtain a polished microstructure (Fig. 7 (d)). The TEM microstructure shows that there were some large pores between the Y_2O_3 particles (Fig. 8).

The absence of a columnar structure or cauliflower-like surface structure in the coating produced using coarse Y_2O_3 powder seems to be closely related to the strong directional impacts of large Y_2O_3 particles. The directions of the large molten particles appear to be less affected by the gas flow on the substrate surface; as a result, the particles seem to be deposited at an angle normal to the substrate. Thus, the shadow effect is weak, and does not result in columnar microstructures.

3.3. Crystalline structures and O/Y ratio of Y_2O_3 coating

The crystalline structures of the Y_2O_3 coating were investigated by X-ray diffraction, as shown in Fig. 9. In both

Fig. 5. Surface microstructures of coatings produced using coarse Y_2O_3 powder at two plasma powers and two stand-off distances: (a) 80 kW-50 mm, (b) 80 kW-100 mm, (c) 65 kW-50 mm, and (d) 65 kW-100 mm.

Fig. 6. Surface microstructures of coatings produced using coarse Y_2O_3 powder at two plasma powers and two stand-off distances: (a) 80 kW-50 mm, (b) 80 kW-100 mm, (c) 65 kW-50 mm, and (d) 65 kW-100 mm.

Fig. 7. Cross-sectional microstructures of coatings produced using coarse Y_2O_3 powder at two plasma powers and two stand-off distances: (a) 80 kW-50 mm, (b) 80 kW-100 mm, (c) 65 kW-50 mm, and (d) 65 kW-100 mm.

Fig. 8. TEM cross-sectional microstructures of coatings produced using coarse Y_2O_3 powder at plasma power of 80 kW with respect to the plasma stand-off distance: (a) 50 mm and (b) 100 mm.

cases of using fine and coarse powders, coatings produced at the stand-off distance of 50 mm exhibited cubic structures with very minor amounts of monoclinic phase. On the other hand, for the longer stand-off distance, mixed phases of cubic and monoclinic structures were observed regardless of the particle sizes. In conventional plasma spraying of Y_2O_3 , only the cubic phase was reported.^{17,18)} However, in SPS, because of differences in the masses of the molten droplets, the shorter solidification time of the molten droplet compared to that of the molten droplet in the conventional plasma spray may be the cause of the monoclinic phase development. In previous the investigation of the electron beam PVD of Y_2O_3 ,^{19,20)} monoclinic phase formation of the Y_2O_3 coating was believed to be due to the effect of the quenching of the deposited Y_2O_3 atoms.

In order to investigate the other cause of monoclinic Y_2O_3 crystallization, the oxygen to yttrium ratios were measured using X-ray photoelectron spectroscopy. To quantify the ratio, bulk Y_2O_3 sintered under atmospheric condition was used as a reference and its O/Y ratio was normalized to 1.5. The O/Y ratio of the coatings obtained at 80 kW plasma power was 1.21 at a stand-off distance of 50 mm and 1.36 at

a stand-off distance of 100 mm. These values indicate that oxygen preferentially evaporated during the particle melting and deposition throughout the spray process. An interesting point is that the coating deposited at a 50 mm distance has a much lower O/Y ratio than the coating deposited at a 100 mm distance, though both have O/Y ratios lower than the stoichiometric value of 1.5. The lower O/Y ratio from the coating at the 50 mm distance matches with the color of the coating, which is slightly dark gray. Thus, the lower O/Y ratio is not the main cause of the formation of the monoclinic Y_2O_3 crystalline phase, because it rather supports the slower cooling of molten particles and hence allows more evaporation until complete solidification at a shorter stand-off distance is achieved.

3.4. Mechanical properties of Y_2O_3 coatings

Mechanical properties such as hardness and adhesion strength are practically important for the application of coatings in the semiconductor industry. Hardness represents the erosion resistance caused by foreign objects. In addition, coatings with higher hardness are believed to have denser structures with fewer defects like pores and cracks; these materials possibly produce less particulate contamination when they are exposed to fluorocarbon-based plasma in semiconductor processing equipment.

Figure 10 (a) shows the hardness variation of the coatings with respect to the powder size and stand-off distance. The hardness of the coating produced using fine Y_2O_3 powder decreased considerably with increasing distance, while the hardness of the coatings produced using coarse powder decreased slowly with the distance. This behavior seems to be related to the microstructure development. The fact that the coatings made using the fine powder exhibited a cauliflower-like and porous structure with increasing distance resulted in a significantly reduced hardness with distance. On the other hand, the coarse powder showed a relatively unchanged microstructure with distance, which was reflected in the moderately reduced hardness with the stand-off distance.

The hardness was also a function of the plasma power at any given stand-off distance (Fig. 10 (b)). At higher power, the higher velocity and temperature of the molten particles may be causes of the higher hardness of the coating. Quantitatively, hardness values at optimum conditions approached ~90% of the hardness of sintered Y_2O_3 ; this is indicated as a dashed line in the figure, showing that this coating can be a good candidate material for use as a dense plasma-facing material.

Adhesion strength of a coating is also an important factor for applications because premature delamination can be prevented during coating application.^{21,22)} The measured adhesion strength decreased with the distance, showing a maximum value of around 35 MPa at the shortest stand-off distance; this adhesion strength value is a few times higher than that of the conventionally plasma-sprayed coating (Fig. 11). All of the failures occurred due to crack propaga-

Fig. 9. X-ray diffraction patterns of coatings produced at plasma power of 80 kW: (a) fine and (b) coarse powders.

tion through the interface between and substrate and coatings.

4. Discussion

Compared to the conventional plasma spray method using

Fig. 10. Vickers hardness of coatings with respect to the (a) stand-off distances and (b) plasma power.

Fig. 11. Adhesion Strength of coatings produced at plasma power of 80 kW with respect to the stand-off distance.

granules of a few tens of micrometers, suspension plasma spraying uses a suspension containing micrometer- or sub-micrometer-sized particles as a source material. This size difference can affect the interaction between particles and plasma, resulting in considerable effects on the microstructure development. First of all, the particle size in SPS is smaller than the mean free path of the plasma gases, a few micrometers at a plasma temperature of around 10000 K.²³⁾ So, the interaction between particles and gases is reduced, and is less likely to transfer momentum to the particles; this is known as the Knudsen effect.^{24,25)} Therefore, not only is the particle velocity in SPS usually lower than that in conventional APS, but also the velocity decreases easily with increasing stand-off distance due to the particles' lower inertia. Then, velocity and the related kinetic energy of the molten particles in SPS are not as high as those in conventional APS, resulting in less densification driving force coming from the impact of the molten particles on the substrate.

Second, the smaller particle size and lower velocity result in lower values of the Stokes number S_t ,^{24,25)}

$$S_t = \frac{\rho_p \cdot d_p^2 \cdot v_p^2}{\mu_g \cdot l_{BL}},$$

where ρ_p , d_p , and v_p are the density, diameter, and velocity of the molten particles, and μ_g and l_{BL} are the viscosity of the gas and the thickness of the boundary flow layer along the substrate surface, respectively. If S_t is lower than 1, this means that the particles cannot easily penetrate the boundary flow layer, which is the compressed zone with high pressure just over the substrate surface. When SPS and conventional APS are compared, the relative ratio of the Stokes numbers in SPS and APS can be expressed as follows:

$$\frac{(S_t)_{SPS}}{(S_t)_{APS}} = \left(\frac{d_p^{SPS}}{d_p^{APS}} \right)^2 \cdot \left(\frac{V_p^{SPS}}{V_p^{APS}} \right)^2.$$

As mentioned earlier, the particles in SPS are around 100 times smaller than the particles in APS. Also, V_p^{SPS} is lower than V_p^{APS} . Thus the ratio $(S_t)_{SPS} / (S_t)_{APS}$ is less than 0.0001, implying that molten particles in SPS cannot easily penetrate the boundary flow layer. Instead, the molten particles likely follow the gas flow along the substrate surface. This means that the velocity of molten particles has significant velocity components parallel to the substrate surface. This phenomenon would become more severe as particle speed decreases at longer stand-off distance or lower plasma power. That directional diversity of the particle impacts, similar to random ballistic collisions, may produce the columnar or cauliflower-like microstructures of the coating due to the increased shadow effects.

When the stand-off distance is sufficiently long, the particles can be partially solidified during their flight to the substrate. Then, adhesion and densification of particles after impact must be greatly impaired, resulting in a much lower

Fig. 12. Surface microstructures of coatings produced using fine Y_2O_3 powder at plasma power of 80 kW and stand-off distance of 150 mm: (a) surface and (b) cross-section.

deposition rate and a very porous microstructure. Indeed, the microstructure of the coating produced at a plasma power of 80 kW and distance of 150 mm (Fig. 12) was found to be much thinner and to have a very porous coating.

Figure 13 shows the microstructure development map of coatings produced using fine powder as a function of stand-off distance. When fine Y_2O_3 was used in SPS at shorter distances, we were able to obtain a dense microstructure with a slightly bumpy surface. With increasing distance, porous and cauliflower-like structures start to appear due to increased non-directional particle impacts. Finally, at a sufficiently long distance, particles started to solidify during flight, resulting in a thin and porous coating.

5. Conclusions

The microstructure and mechanical properties of Y_2O_3 coatings prepared using suspension plasma spray have been investigated as functions of particle size of the raw material and plasma processing parameters. With increasing stand-off distance, coating changed from one with a dense structure with a slightly bumpy surface to a porous one with a cauliflower-like top surface when fine Y_2O_3 powder was used. On the other hand, when coarse Y_2O_3 was

used, there were microscopic splats on the surface with abundant small particles, showing lower density. The plasma power also affected the microstructures of the coatings. The hardness and adhesion strength of the coating were also found to depend on the particle size of the raw material and on the plasma processing parameters. At the optimum coating condition, using fine Y_2O_3 powder, hardness reached approximately 90% of the hardness of Y_2O_3 bulk sintered in an air atmosphere. The adhesion strength of the coating produced by SPS was several times higher than that of the conventional coating. The high hardness, combined with the high adhesion strength, of the coating developed in this study shows that the suspension plasma spray Y_2O_3 coating is a new candidate material that can replace currently available sintered or APS Y_2O_3 ceramics in the semiconductor industry.

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Fig. 13. Schematic of microstructure development map of coatings as a function of stand-off distance when fine powders were used in SPS.

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