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Preparation of Transparent Yttrium Oxide Film by Aerosol Deposition Method

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Transparent yttrium oxide (Y_2O_3) film was prepared by aerosol deposition method (AD film). The AD film (10 μm thickness) had a 50 –70 % transmittance in the 400-800-nm-wavelength region. By transmission electron microscopy of this AD film, a highly dense Y_2O_3 layer without voids and a clear interface between the layer and the quartz substrate used were observed. The layer was composed of nonoriented Y_2O_3 crystallites of size less than 100 nm. Some mechanical and electrical properties of AD film were investigated. The adhesion force of the interface between the Y_2O_3 layer and the substrate and the volume resistance of the film were estimated as 80 MPa and 10^{14} Ω・cm, respectively. The influence of plasma treatment (in CF_4/O_2 atmosphere) on the surface of the AD film, namely, eroded depth, surface roughness and nanostructure were also evaluated. Furthermore, the structural comparison of the AD film to some films prepared by other methods was discussed.
Key words: aerosol deposition method, yttrium oxide film, transparency, plasma treatment, eroded depth

1. INTRODUCTION

In semiconductor manufacture, the components that constitute the chamber used in plasma chemical vapor deposition (CVD) and dry etching systems should be resistant to halogen plasma. Although aluminum alloy [1], high-purity Al_2O_3, AlN, and quartz are used as chamber components, their plasma resistance is not sufficiently high. As the corrosion proceeds, the formation of contaminant particles, namely harogenide, occurs [2]. The contaminant particles have an effect on a proportional defective in semiconductor manufacture because they are suspended in the chamber. Therefore, materials that have excellent plasma resistance are demanded to improve the structure of semiconductor devices [2]. In recent years, the application of Y_2O_3 film prepared by CVD and thermal spraying to a coating with plasma resistance has been studied. However, the deposition rate of CVD is too low to fabricate the Y_2O_3 thick film, and the microstructure of the Y_2O_3 film prepared by thermal spraying is not sufficiently dense.

The aerosol deposition method (ADM) is expected to achieve a high deposition rate and a high film density. ADM is attractive for the deposition of ceramic film with a thickness of 1-100 μm at room temperature [3-7]. In ADM, submicron particles are accelerated by gas in a nozzle up to a velocity of 100-300 m/s [8] and impinged on a substrate. As a result of the impact, dense ceramic layers are formed. For ADM, there have been some reports on deposition results, the mechanical and electrical properties of the Al_2O_3 thick film formed [9], the microstructure and electric properties of the Pb(Zr, Ti)O_3 (PZT) thick film [3,5-7] and NiZnCu ferrite thick film obtained [4, 10]. The principle of ADM is based on shock loading solidification due to the impact of fine ceramics particles, which are accelerated by carrier gas [4, 5, 7]. It is considered that particles are fractured to smaller sizes and rebound on each other during impact of the particles with the substrate. It appears that the deposition mechanism is related to the fracture and plastic deformation of the primary particles [6].

Judging from the characteristic of ADM, this process is a candidate for the fabrication of plasma-resistant materials. Therefore, the purpose of this study is to apply ADM to the fabrication of Y_2O_3 film and its plasma resistance.

2. EXPERIMENTAL

A commercially available Y_2O_3 powder (purity 99.9%) was used for ADM. The average particle size of the powder was 0.5 μm. Figure 1 shows a schematic illustration of the ADM used in this investigation. The fine powder formed an aerosol flow by mixing with a carrier gas in the aerosol chamber. The aerosol flow was transported through a tube to a nozzle with an orifice size of 20 × 0.4 mm^2. This flow was accelerated and ejected from the nozzle into a deposition chamber. The deposition chamber was evacuated with a rotary pump and a mechanical booster pump. Nitrogen gas was used as a carrier gas and the flow rate was 5 L/min. The pressures in the deposition chamber and in the aerosol chamber were 90-150 Pa and 45-60 kPa, respectively. The substrate was placed at a distance of 10 mm from the nozzle and was maintained at room temperature. The scanning speed of the nozzle motion along the substrate was 5 mm/s. Y_2O_3 powders bombarded the substrate and formed the films. The substrate mounted on an X-Y drive stage was reciprocated.

The microstructures of the AD films were observed by optical microscopy, scanning electron microscopy (SEM) (S-4100, Hitachi, Ltd.), and transmission electron microscopy (TEM) (H-9000UHR, Hitachi, Ltd.). A thin foil for TEM observation was prepared by focused ion beam method. The transparency of the AD film at a 200-800 nm wavelength was measured using a spectrophotometer (UV-3150, Shimadzu Co.).

The electrical properties such as withstand voltage and volume resistance were measured essentially following the testing methods of JIS C 2110 and JIS C2141, respectively. The adhesion force of the interface between the Y_2O_3 layer and the substrate was estimated

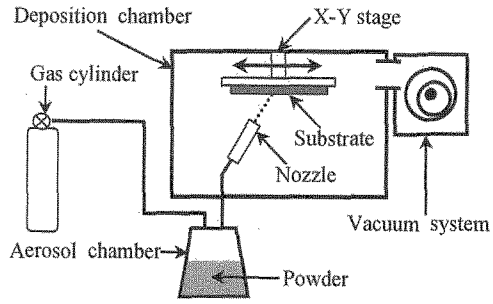

Fig. 1 Schematic illustration of aerosol deposition method (ADM).

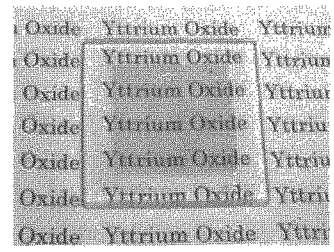

Fig. 2 Optical photograph of transparent Y_2O_3 film on quartz substrate prepared by ADM at room temperature. The thickness of the film was 10 μm .

using a material force tester (EZ Graph, Simadzu Co.). A rod was epoxied onto the surface of the film. The rod was clamped in the tester and was pulled at 90° in a tensile test [11, 12]. The hardness of the film was measured using a dynamic ultra-microhardness tester (DUH-W201, Shimadzu Co.) by the indentation method applying 0.29-0.49 N for 5 s.

The influence of plasma treatment on the surface of the samples was evaluated using a plasma reactor (DEA-506, ANELVA Co.). The plasma reactor consists of two parallel electrodes powered by a radio-frequency generator (13.56 MHz). The samples were placed on the lowest electrode. Part of the surface of the samples was covered with a silicon wafer. CF_4 (flow rate: 40 sccm) and O_2 (flow rate: 10 sccm) were introduced into the reactor. The fluorination treatment duration was 180 min with an incident plasma power of 1 kW. After plasma treatment, eroded depth and surface roughness were measured by employing a stylus-type, surface profile measuring system (Dektak3030, Veeco Instruments Inc.) and a surface roughness profile measuring system (SURFCOM 130A, Tokyoseimitsu Co., Ltd.). Ten measurements of the roughness were performed per sample. Roughness parameters like Ra (arithmetic deviation from the mean line through the complete profile) and Rz (maximum profile depth) as well as corresponding surface profiles were recorded. The eroded depth was estimated by the difference in level between the area covered and that not covered with the silicon wafer. Nanostructure of the samples was observed with SEM.

3. RESULTS AND DISCUSSION

3.1 Optical property and microstructure

Figure 2 shows an optical photograph of the transparent Y_2O_3 film on the quartz substrate prepared by ADM. A square pattern was observed and the area of the film was 20 × 20 mm^2. The thickness of the film was 10 μm and the deposition rate was estimated as 1 μm/min. The deposition rate of ADM was higher than that of other deposition methods such as sputtering, CVD, plasma laser deposition, and plating [4, 6]. This high deposition rate is one of the most notable features of ADM.

Figure 3 shows the transmittance spectra of the Y_2O_3

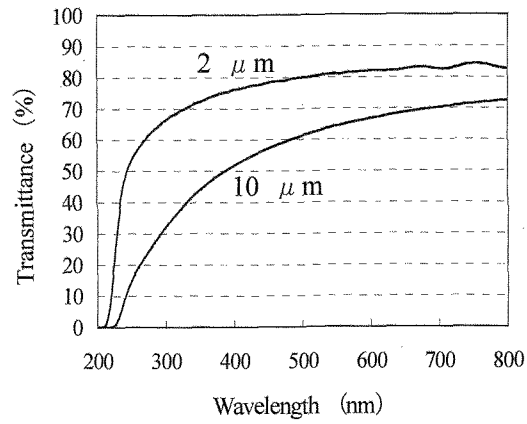

Fig. 3 Transmittance spectra of the Y_2O_3 film of 2 μm and 10 μm thickness on quartz substrate prepared by ADM.

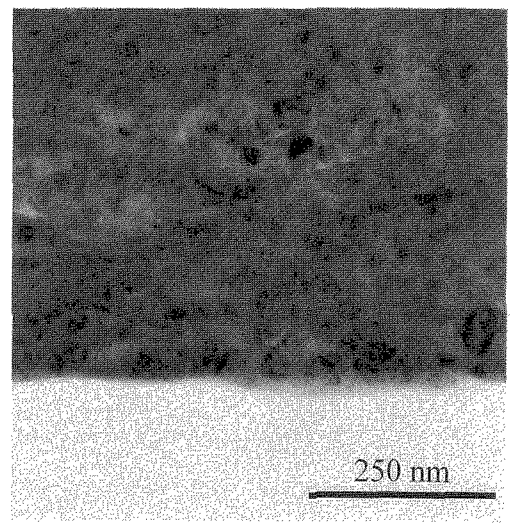

Fig. 4 Cross-sectional TEM image of Y_2O_3 film on quartz substrate prepared by ADM.

Table I Electrical and mechanical properties of Y_2O_3 film on Al alloy substrate prepared by ADM.

Electrical property		Mechanical property	
Volume resistance (Ω · cm)	Withstand voltage (V/μm)	Adhesion force (MPa)	Vickers hardness (GPa)
$>10^{14}$	300	80	9.2

films of 2 μm and 10 μm thickness on the quartz substrate prepared by ADM. Transmittance increased in the 200-800-nm-wavelength region as film thickness decreased. The films of 2 μm and 10 μm thicknesses had 78-85 % and 52-70 % transmittances in the 400-800-nm-wavelength region, respectively. The transmittance curve of the film of 2 μm thickness exhibited a sharp edge at 250-300 nm. It is suggested that the film is homogeneous and free from pores and inclusions.

Figure 4 shows a cross-sectional TEM image of the Y_2O_3 film on the quartz substrate prepared by ADM. A highly dense Y_2O_3 layer without voids and a clear interface between the layer and the quartz substrate were observed. The Y_2O_3 layer was composed of nonoriented Y_2O_3 crystallites of size less than 100 nm. It was found that the decrease in crystallite size is related to the fracture of Y_2O_3 particles during the deposition. According to the TEM observation, the film has a high transparency as seen in Fig. 3 because the Y_2O_3 layer consists of very small crystallites and is highly dense with no pores so that light scattering is kept to a minimum. This type of nanostructured Y_2O_3 layer cannot be prepared by conventional ceramics processing based on the sintering of powders and thermal spraying. It can be said that ADM is a useful method of fabricating thick nanocrystalline Y_2O_3 film with a high deposition rate.

3.2 Electrical and mechanical properties

Table I shows the electrical and mechanical properties of the Y_2O_3 film on an aluminum alloy substrate prepared by ADM. The volume resistance and withstand voltage of the film were $>10^{14}$ Ω · cm and 300 V/μm, respectively. The volume resistance of the film was in good agreement with that of sintered Y_2O_3. The adhesion force of the interface between the Y_2O_3 layer and the aluminum alloy substrate was 80 MPa, which was much higher than that of films prepared by other deposition processes. It is thought that this high adhesion force is based on the dense structure of the interface between the Y_2O_3 layer and the substrate as shown in Fig. 4. The Vickers hardness of the film reached 9.2 GPa. The fine

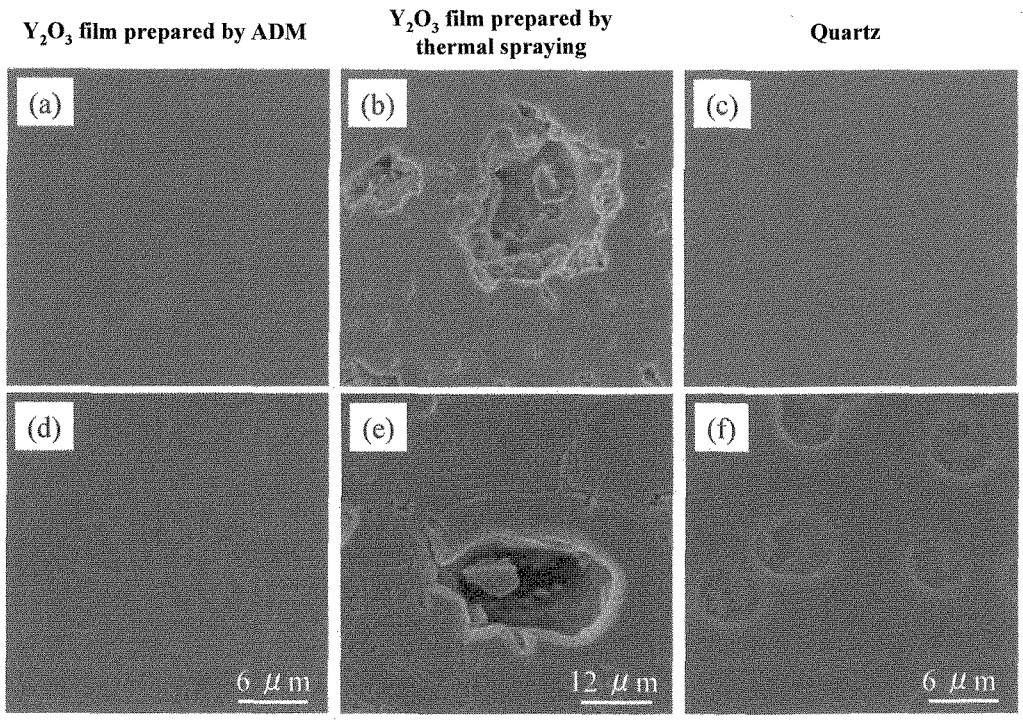

Fig. 5 SEM images of surfaces of samples. Y_2O_3 film prepared by ADM before plasma treatment (a), Y_2O_3 film prepared by thermal spraying before plasma treatment (b), quartz before plasma treatment (c), Y_2O_3 film prepared by ADM after plasma treatment (d), Y_2O_3 film prepared by thermal spraying after plasma treatment (e), and quartz after plasma treatment (f). Plasma conditions are as follows: process gas, CF_4 (40 sccm)/O_2 (10 sccm); exposure time, 180 min; radio-frequency power, 1 kW (0.55 W/cm^2, 13.56 MHz).

Table II Eroded depth of the samples after plasma treatment in CF_4/O_2 atmosphere for 180min.

Samples	Eroded depth (nm)
Y_2O_3 film prepared by ADM	260
Y_2O_3 film prepared by thermal spraying	443
Sintered Al_2O_3 (99.99%)	954
Sapphire bulk	1381
Quartz	14000

particles constituting the film were strongly bonded. The hardness of the film was higher than that of sintered Y_2O_3 (6.7 GPa) and Y_2O_3 film prepared by thermal spraying (5.4 GPa). It is suggested that these excellent electrical and mechanical properties were caused by the highly dense layer as shown in Fig. 4.

3.3 Plasma resistance

Table II shows the eroded depth of the samples after plasma treatment (in CF_4/O_2 atmosphere) for 180 min. The eroded depth of the Y_2O_3 film prepared by ADM was one order of magnitude lower than that of sapphire bulk. Namely, in plasma treatment, the lifetime of the film is much longer than that of conventional materials. Although the eroded depth of the Y_2O_3 film prepared by ADM and that of the Y_2O_3 film prepared by thermal spraying were similar, the differences in the surface roughness of them by plasma treatment were observed. The surface roughness of the film prepared by ADM slightly changed from 0.02 μm to 0.03 μm (Ra), and from 0.14 μm to 0.17 μm (Rz). On the other hand, that of the film prepared by thermal spraying significantly changed from 0.10 μm to 0.17 μm (Ra), and from 2.17 μm to 3.20 μm (Rz).

Figure 5 shows SEM images of the surfaces of the samples before and after plasma treatment. The microstructure of the Y_2O_3 film prepared by ADM was hardly changed, some pores and cracks were not observed (Fig. 5 (a), (d)). On the other hand, there were some pores with a size of approximately 20 μm on the surface of the Y_2O_3 film prepared by thermal spraying even before plasma treatment (Fig. 5 (b)) . After plasma treatment, the edges of the pores were gradually eroded, and many cracks appeared on the surface (Fig. 5 (e)). Similarly, after plasma treatment, some pores with a size of approximately 10 μm on the surface of quartz were observed (Fig. 5 (f)). It is suggested that the contaminant particles with the above micrometer size were generated when conventional materials were eroded by plasma treatment. In contrast, in the Y_2O_3 film prepared by ADM, it is suggested that the size of the contaminant particles was on the nanometer order because the film was composed of crystallites of size less than 100 nm as shown in Fig. 4.

4. Conclusion

A transparent Y_2O_3 film was prepared by ADM at room temperature. The deposition rate was 1 μm/min. The 10-μm-thick film had a 50-70 % transmittance in the 400-800-nm-wavelength region. According to TEM observation, the Y_2O_3 layer consisted of nonoriented crystallites without voids and inclusions. This nanostructured Y_2O_3 layer cannot be prepared by conventional ceramics processing based on the sintering of powders and thermal spraying. The electrical and mechanical properties of the film were excellent because of the highly dense Y_2O_3 layer. Moreover, the eroded depth of the film after plasma treatment was much smaller than that of conventional materials. It is possible that the Y_2O_3 film prepared by ADM will become a candidate plasma-resistant material because of its highly dense structure.

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