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Effect of the pressure of sputtering atmosphere on the physical properties of amorphous aluminum oxide films

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Amorphous aluminum oxide films were prepared by rf-sputtering at various values of the pressure of sputtering atmosphere, and their density, refractive index, Young's modulus and internal stress were measured. The physical properties of the present films depended on the pressure of sputtering atmosphere. The density, refractive index, and Young's modulus decreased with the pressure below about 6.5 Pa, beyond which they increased. The compressive stress and tensile stress were induced in the films depending upon the pressure of sputtering atmosphere, and the tensile stress reached a maximum at the pressure of 6.5 Pa and then decreased as the pressure increased. From the results of the energy-dispersive X-ray analysis (EDX), it was found that the pressure of sputtering atmosphere gave a large influence to the chemical composition (the atomic ratio, O/Al) of the film. The pressure dependence of the physical properties was successful to be explained by the change of chemical compositions of the films. The presence of OH group in the films was verified by using FT-IR, and their microstructure was investigated by SEM study. © *2000 Kluwer Academic Publishers*

1. Introduction

Although alumina is classified in the category of so-called intermediates which contribute in part to the glass network structure, it is obtained as amorphous materials by unconventional glass-making methods such as reactive or nonreactive vapor deposition, sol-gel formation, and anodization. Sputtering is one of the most effective techniques to make amorphous materials which could not be vitrified by an ordinary melting method. Sputtered amorphous alumina is promising for ceramic coatings on the substrates such as steels, or inorganic or organic materials. Zhu *et al.* deposited alumina films on superalloys by reactive sputtering and examined their high-temperature corrosion resistance [1]. Cueff *et al.* made studies of thin alumina coatings sputtered on polyethylene terephthalate [2–4]. The physical properties and structure of amorphous alumina prepared by rf-sputtering method were reported in our previous studies [5–7]. Zhao *et al.* investigated the dependence of the roughness of amorphous alumina films deposited on silicon substrates by reactive rf sputtering upon the rf power and gas pressure [8]. Stadler *et al.* examined the microstructure and optical properties of amorphous Al_2O_3 fabricated by rf magnetron sputtering as a function of deposition (substrate temperature, O_2 flow rate) and annealing conditions [9]. However, there are few reports about how the various physical properties of sputtered amorphous alumina change depending upon the sputtering condition such as pressure of the sputtering atmosphere, sputtering power, or substrate temperature. Thus, in this study, the amorphous aluminum oxide films were prepared by rf-sputtering at various values of the pressure of the sputtering atmosphere, and the physical properties of the films such as density, refractive index, Young's modulus, and internal stress were measured. The relation between the working pressure of sputtering atmosphere and the physical properties of the present films was discussed.

2. Experimental procedure

2.1. Sample preparation

The rf-sputtering apparatus used was the same reported previously [5]. Alumina plate with 3 mm thickness was used as a target. The target area was 65 mm in diameter. A fused silica or copper plate was used as the substrate depending upon the physical property to be measured. The substrate temperature was measured by a Chromel-Alumel thermocouple contacted directly with the substrate. The chamber was evacuated first to about 6×10^{-4} Pa to remove any residual gases that might have been present in it. Then the argon-oxygen sputtering gas (main impurity; $N_2 < 100$ ppm, $H_2O < 10$ ppm) was introduced up to a fixed pressure, and rf input power of 100 W was applied between the target and substrate. Presputtering was performed for 30 minutes. The sputtering conditions used are listed in Table I. The films prepared were identified as amorphous solids by XRD.

TABLE I Sputtering conditions

Sputtering gas	Ar(75%)-O_2(25%)
Sputtering gas pressure	2.66 ∼ 20 Pa
Sputtering power	100 W
Target-Substrate distance	38 mm
Substrate	Fused silica, Copper

2.2. Physical property measurements
2.2.1. Density and refractive index
A sink-float method was used to determine the density of the prepared films [10, 11]. The film was stripped from the copper substrate, and floated in a mixture of heavy and light liquids with the ratio of the liquids being adjusted until the mixture matched the density of the film. The density of the liquid was then was determined by the Archimedes' principle using a platinum standard. As a mixture of heavy and light liquids, methylene iodide and acetone were used for samples with the density below 3.3 g/cm^3, while clericis's solution and water for all samples.

The refractive index was determined by the spectrophotometric method [12, 13] for the amorphous film deposited on the fused silica substrate. The reflectance at the normal incidence was measured by using Hitachi-330 spectrophotometer.

2.2.2. Young's modulus
Young's modulus of the films was determined by using the suspending flexural vibration method. A film was deposited on the fused silica substrate and the resonance frequencies of both the film-free substrate and the film-substrate composite were measured. To achieve a constant measuring temperature, the measuring sample was set in an air bath unit. The system and the details of the measurement were previously described [14].

2.2.3. Internal stress
When the film-substrate composite is deformed by the moment of the bending induced by the internal stress of a film, the equation which relates the internal stress of a film, σ and the radius of curvature of the composite, R is

$$\sigma = \left[\frac{E_s t_s^2}{6t_f(1-\nu_s)}\right]\left(\frac{1}{R}\right) \quad (\text{at } t_f \ll t_s) \qquad (1)$$

where E_s, ν_s, and t_s are Young's modulus, Poisson's ratio, and thickness of a substrate, respectively [15]. The t_f represents film thickness. From Equation 1, the internal stress of a film, σ can be obtained by measuring a radius of curvature of a film-substrate composite, R. The measurement and analysis of curvature of the composite were performed using FUJINON Laser Interferometer F601 and FUJINON Fringe Analyzer FX-03. To achieve a constant measuring temperature, the measuring sample was set in LINKAM Heating Freezing stage(LK-600PH). In order to decide the radius of curvature of the composite, R, the data from the Fringe Analyzer were fed into the computer and analyzed by the least square approximation to a circle.

The fused silica with optical flatness (thickness 1.0 mm) was used as a substrate. The back side of the substrate was polished with abrasive paper in order to prevent an interference fringe produced by the reflection of laser light at the surface and the back sides of the substrate. After the substrate was cleaned ultrasonically, it was heat-treated in order to remove the strain occurred by polishing. It is known from the preliminary experiment that the strain can be removed by heat-treatment at 600°C for two hours. The film was deposited on the substrate having about 1 μm thickness. The film thickness was measured precisely by using the surface texture measuring instrument, SURFCOM 110B (Tokyo Seimitsu, Japan).

2.3. FT-IR measurement
Infrared absorption spectra of the film-substrate composite samples, which are prepared by depositing the films on the fused silica substrate, and fused silica substrate were measured in the region between 4000 and 400 cm^{-1} using an FT-IR apparatus (Model FTIR-8300, Shimadzu, Japan). These spectra were recorded at a resolution of 4 cm^{-1}. The thickness of the films was about 1 μm, and that of the substrate was 1.0 mm.

2.4. SEM and EDX measurements
The morphological and chemical characterization of the present amorphous films on the fused silica substrates were conducted using a field-emission scanning electron microscopy (SEM; Model JSM-890, JEOL, Japan) equipped with an energy-dispersive X-ray analysis (EDX; Model PV9900, Philips, The Netherlands). SEM was operated at 15 kV of the accelerating voltage. For the chemical characterization of the films by EDX, α-alumina and fused silica were used as a reference material.

3. Results
3.1. Physical properties
3.1.1. Density and refractive index
The values of density of the samples determined using clericis's solution and water were similar to those using methylene iodide and acetone. The results of the density measurements for the present amorphous samples are shown in Fig. 1 as a function of the working pressure of sputtering atmosphere. It can be seen that the density decreased, reached a minimum at about 6.5 Pa, and then increased with increasing the working pressure.

The refractive indices of the present amorphous samples are plotted in Fig. 2 as a function of the pressure of sputtering atmosphere. The result of the refractive index is very similar to that of the density.

3.1.2. Young's modulus
The results of Young's modulus measurements are shown in Fig. 3 as a function of the pressure of sputtering atmosphere. Young's modulus decreased abruptly with the pressure below about 6.5 Pa, beyond which it increased.

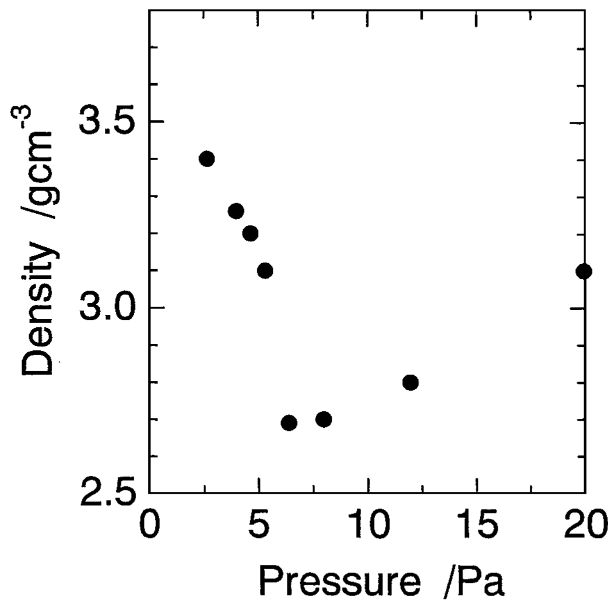


Figure 1 Density of amorphous aluminum oxide films as a function of the pressure of sputtering atmosphere.

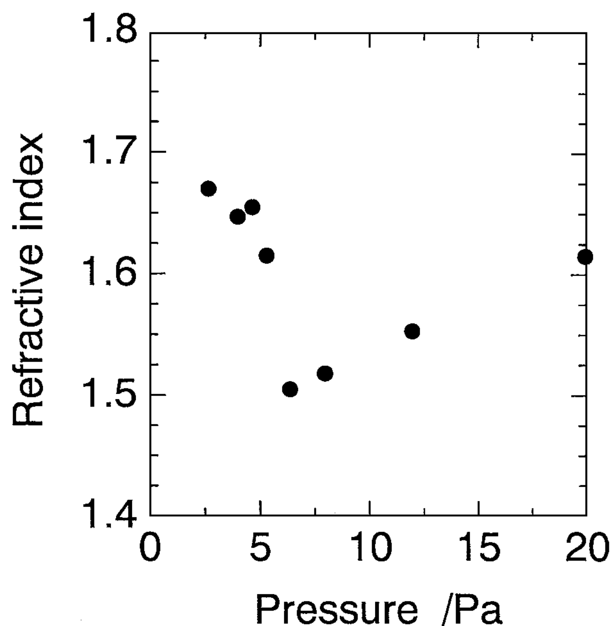


Figure 2 Refractive index of amorphous aluminum oxide films as a function of the pressure of sputtering atmosphere.

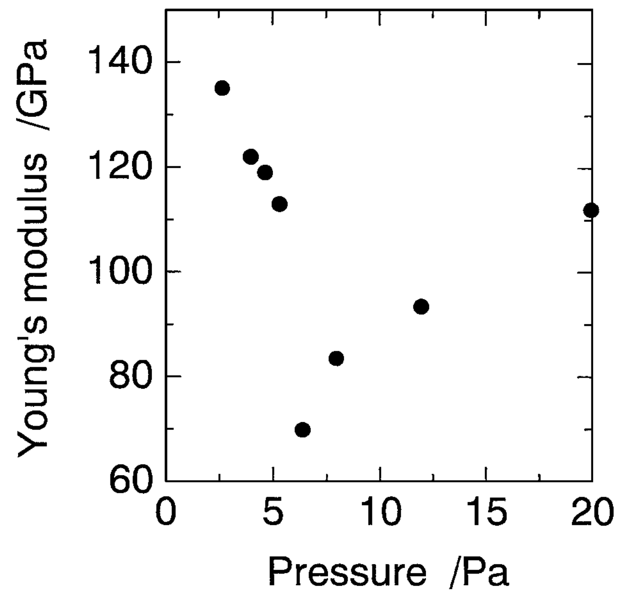


Figure 3 Young's modulus of amorphous aluminum oxide films as a function of the pressure of sputtering atmosphere.

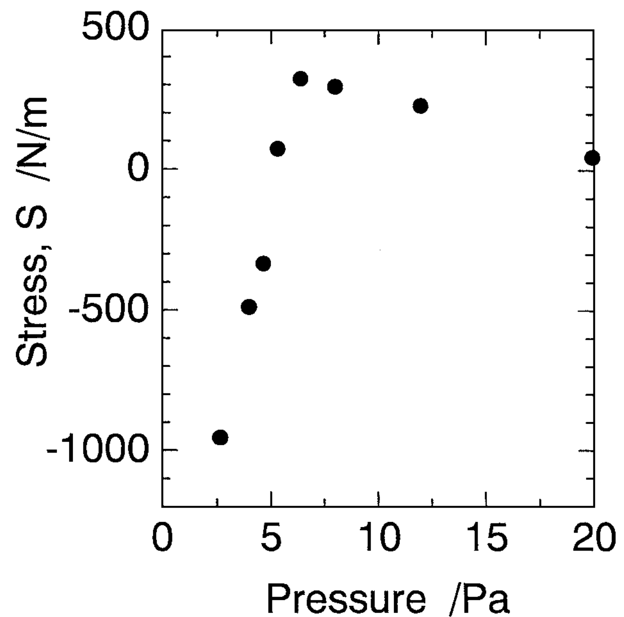


Figure 4 Stress, *S* of amorphous aluminum oxide films as a function of the pressure of sputtering atmosphere.

3.1.3. Internal stress

A radius of curvature of each composite was determined at 30°C, and the stress, σ of a film was calculated according to Equation 1. The values of 73.2 GPa and 0.169 were used for E_s and ν_s, respectively [16]. Generally, the stress, $S = \sigma \times t_f$ is used to evaluate the stress of a film because the stress value σ changes depending upon the thickness of a film. The relation between the stress, S and the working pressure of sputtering atmosphere is shown in Fig. 4, in which the compressive stress is represented with minus number, and the tensile stress is with positive number. The accuracy for the stress was ±10%. It was seen that the compressive and the tensile stress were induced in the present films depending upon the working pressure. The compressive stress was induced in the films prepared under the lower pressure, and decreased abruptly with increasing the pressure. The pressure at which the stress changed from the compressive to the tensile was about 5.3 Pa. The tensile stress reached a maximum at the pressure of 6.5 Pa, and then decreased as the pressure increased.

3.2. Characterization of films

3.2.1. Infrared spectra

In Fig. 5, the difference spectra between the infrared spectra for the film-substrate composite samples and that of substrate are shown in the region from 3700 to 3000 cm^{-1}. The broad bands around 3450 and 3200 cm^{-1} can be seen in three difference spectra. The intensity of the band at around 3450 cm^{-1} showed a maximum for the film prepared at the sputtering gas pressure of 8.0 Pa, while that at around 3200 cm^{-1} didn't depend on the pressure.

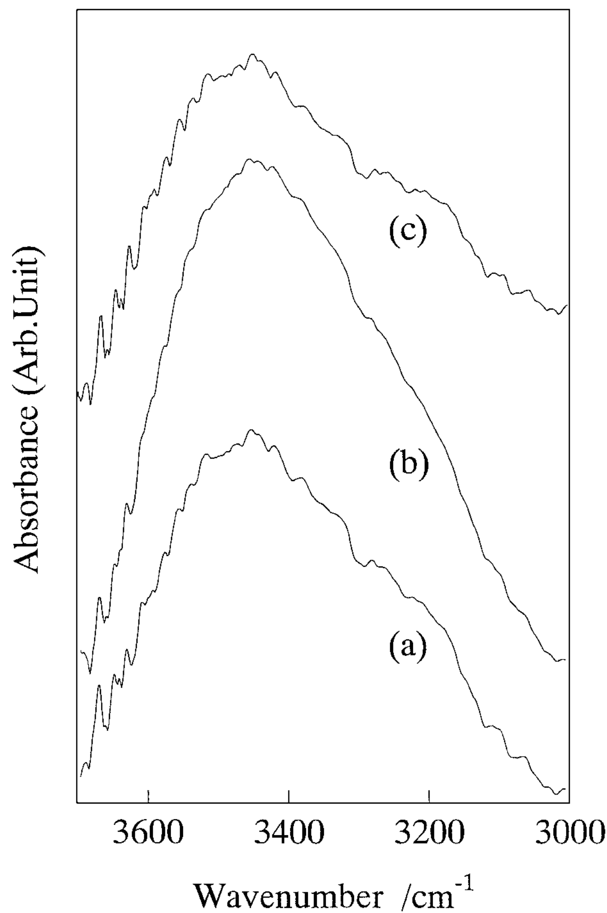


Figure 5 Difference spectra between the FT-IR spectra of the film-substrate composite samples prepared at the pressure of (a) 4.0, (b) 8.0, and (c) 20 Pa and that of substrate.

3.2.2. Chemical compositions of films

In order to confirm whether EDX could be used to determine the chemical compositions (the atomic ratio, O/Al) of the present films, the intensity of O K_α and Al K_α or Si K_α lines was measured by using EDX for α-alumina and fused silica of reference material. The results of the measured intensity showed that the atomic ratio, O/Al was 1.50 for a-alumina, and that the ratio, O/Si was 2.00 for fused silica. The accuracy was below $\pm 0.5\%$. Generally, it is said that EDX analysis is not well appropriate for light elements, such as oxygen. These results indicate, however, that it is possible to determine the atomic ratio, O/Al of the present samples from the intensity of O and Al obtained by using EDX. The atomic ratio, O/Al of the present films determined by EDX is shown in Fig. 6 as a function of the pressure of sputtering atmosphere. The chemical composition (the atomic ratio, O/Al) depends largely upon the working pressure. As the pressure increased, the ratio increased abruptly, reached a maximum at about 6.5 Pa, beyond which it decreased.

3.2.3. Microstructure of films

Fig. 7a–c show the SEM micrographs of the films coated on the fused silica substrate by sputtering at the sputtering gas pressures of 2.7, 6.4, and 20 Pa, respectively. From these micrographs, a large difference was not recognized between three films. As the sputtering gas pressure increased up to 6.4 Pa, however, the structure of the films became looser, and the channel was formed. For the sample prepared at the pressure above 6.4 Pa, the width of the channel got narrow, and the structure became dense again.

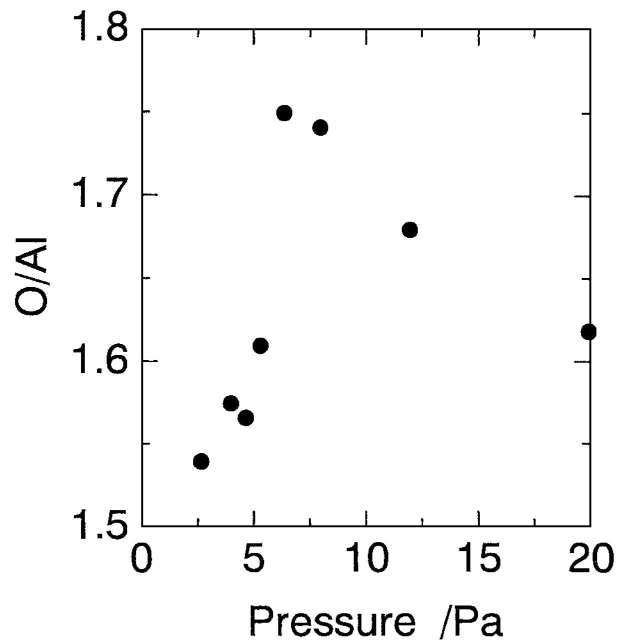


Figure 6 The atomic ratio, O/Al of amorphous aluminum oxide films as a function of the pressure of sputtering atmosphere.

4. Discussion

4.1. Physical properties

4.1.1. Density, refractive index, and Young's modulus

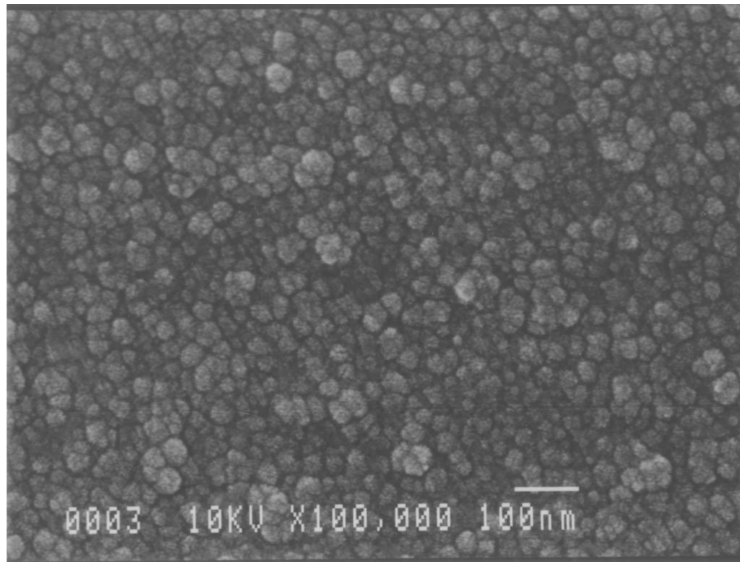
The results of density, refractive index, and Young's modulus of the present amorphous films were re-plotted as a function of the chemical composition (the atomic ratio, O/Al), which are shown in Figs 8–10, respectively. The density, refractive index, and Young's modulus decrease linearly with increasing the atomic ratio, O/Al. This means that these physical properties of the present amorphous films are governed largely by their chemical compositions.

4.1.2. Internal stress

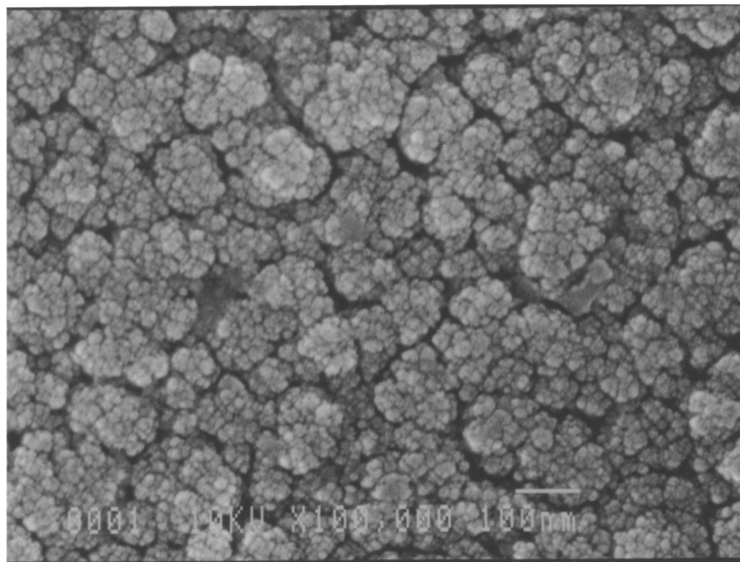
The internal stress of a film is composed of the thermal stress, σ_{th} and the intrinsic stress, σ_{I}. The former comes from the difference between the thermal expansion coefficient of the substrate and that of the film, and the latter is related to the preparation process of the film. Thermal stress, σ_{th} is given by [17]

$$\sigma_{\text{th}} = \frac{E_{\text{f}}(\alpha_{\text{f}} - \alpha_{\text{s}})(T_{\text{d}} - T)}{(1 - \nu_{\text{f}})} \tag{2}$$

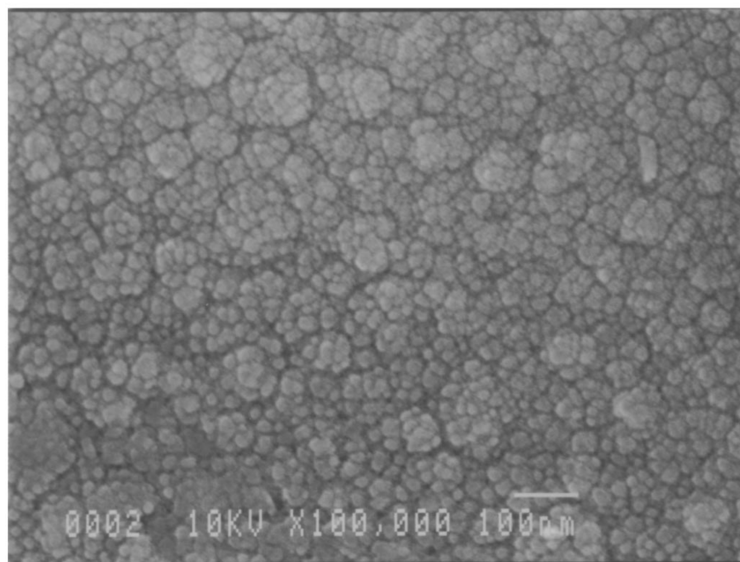
where E, α, and ν are Young's modulus, thermal expansion coefficient, and Poisson's ratio, respectively. The subscript s and f correspond to the substrate and the film. T_{d} is the film forming temperature. When the value of $5.0 \times 10^{-7}/°\text{C}$ is used as the thermal expansion



(a)



(b)



(c)

Figure 7 SEM micrographs of the films on the substrate prepared at the pressure of (a) 2.7, (b) 6.4, and (c) 20 Pa.

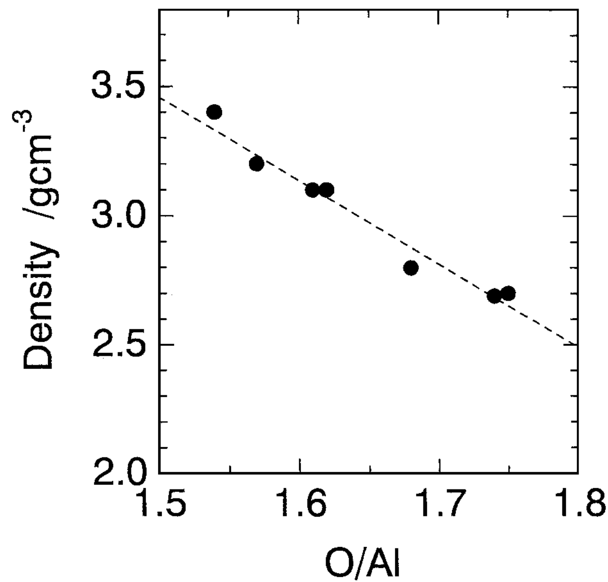


Figure 8 Density of amorphous aluminum oxide films as a function of the atomic ratio, O/Al.

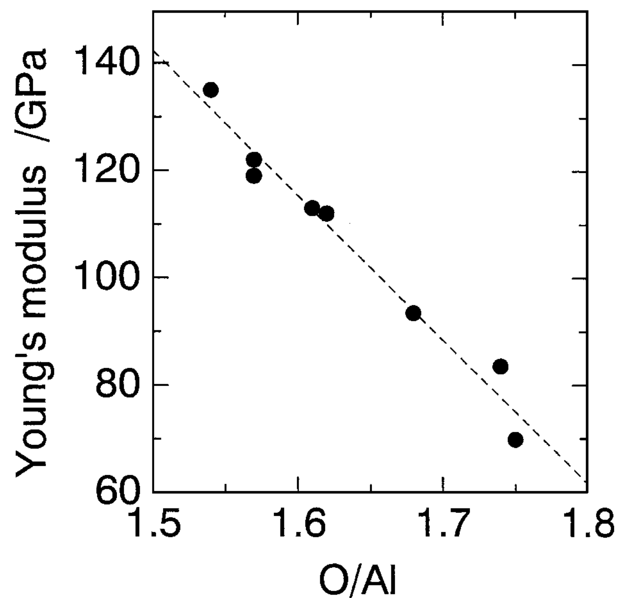


Figure 10 Young's modulus of amorphous aluminum oxide films as a function of the atomic ratio, O/Al.

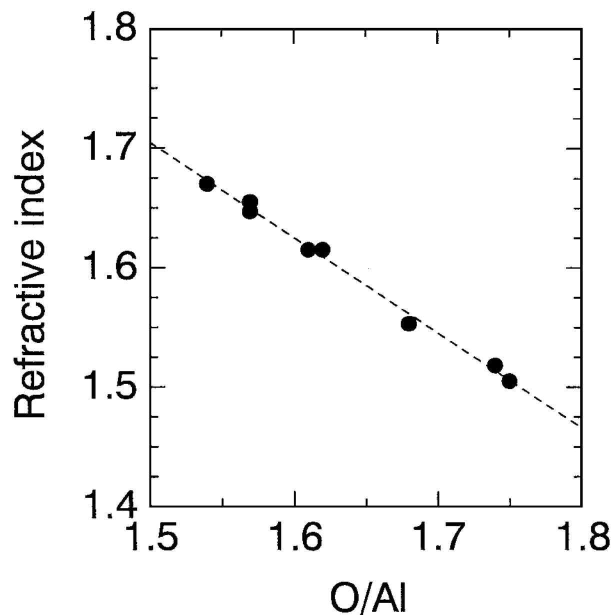


Figure 9 Refractive index of amorphous aluminum oxide films as a function of the atomic ratio, O/Al.

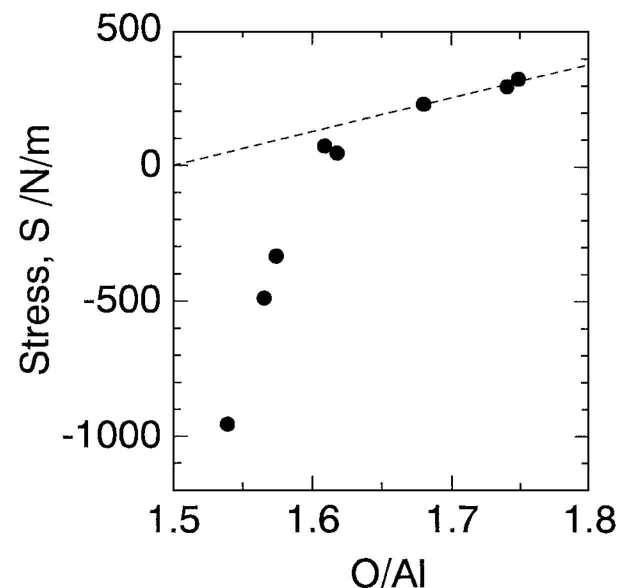


Figure 11 Stress, S of amorphous aluminum oxide films as a function of the atomic ratio, O/Al.

coefficient of fused silica substrate, α_s, and 122 GPa as Young's modulus, E_f [7], 0.22 as Poisson's ratio, ν_f [7], and $3.0 \times 10^{-6}/°C$ as the thermal expansion coefficient, α_f [18], σ_{th} is calculated using the Equation 2 to be $3.9 \times 10^5(T_d - T)(N/m^2)$. We have no data about T_d, but, from 30°C of the substrate temperature, we regarded $T_d - T$ as 100°C at the most, and calculated the thermal stress of the film with 1 μm thickness. The stress, $S_{th}(=\sigma_{th} \times t_f)$ was calculated to be 39 N/m, which would be negligible in this study.

From Fig. 4, it is found that the compressive stress was induced in the films prepared under the lower pressure, and decreased abruptly with increasing the pressure. It is known that the compressive stress induced in a sputtered film prepared under low pressure comes from the atomic peening effect [19, 20], which is caused by the attack of the sputtered particle having high kinetic energy to the film formed on a substrate. Many studies about this atomic peening effect have been done [21–23]. It is reasonable that the compressive stress induced in the present amorphous films prepared under the low pressure of the sputtering atmosphere is due to the atomic peening effect. Furthermore, the abrupt decrease of the compressive stress with an increase of the working pressure can be explained by the decrement of the atomic peening effect, which is due to the shortening of the mean free path of the sputtered particles with an increase of the pressure.

In Fig. 11, the stress, S of the present amorphous films is shown as a function of the atomic ratio, O/Al. For the films in which the tensile stress was induced, the stress increased linearly with increasing the O/Al ratio. The extrapolation of the tensile stress to 1.5 of the O/Al ratio gave a value close to 0 N/m. This result seems to indicate that the tensile stress of the films is induced by the deviation of the O/Al ratio to a bigger value than 1.5

(called "compositional effect" in this study), and that the stress changes in proportional to the O/Al ratio.

From above discussions, the dependence of the stress on the pressure of sputtering atmosphere may be explained by the followings. When the pressure of sputtering atmosphere is low, the compressive stress produces in the films so that the atomic peening effect is superior to the "compositional effect". As the pressure increases, the peening effect weakens abruptly, thus, the "compositional effect" comes to govern the stress of the films, and thus the tensile stress appears in the films.

4.2. Characterization of films

From Fig. 5, it can be clarified that the present films have the absorption bands around 3450 and 3200 cm^{-1}. Characterization for α-Al_2O_3 and some hydrated aluminas by IR [24] and PAS (photoacoustic spectroscopy) [25] have been done. Gibbsite, boehmite, and bayerite showed different absorption patterns in the OH stretching. The spectrum of gibbsite consists of five main of stretching bands at 3616, 3518, 3428, 3378, and 3361 cm^{-1} by IR, while, at 3620, 3525, 3446, 3393, and 3379 cm^{-1} by PAS. The spectrum of boehmite has OH stretching band at 3262 and 3079 cm^{-1} by IR, while at 3260 and 3080 cm^{-1} by PAS. For bayerite, OH stretching bands were observed at 3533, 3518, 3454, and 3401 cm^{-1} by IR, while at 3654, 3620, 3550, 3460, 3424, and 3371 cm^{-1} by PAS. Compared with their results, the broad band at around 3450 cm^{-1} observed in this study seems to be attributed to the OH stretching due to gibbsite and/or bayerite, while, the band at around 3200 cm^{-1} due to boehmite. It can be concluded that the present aluminum oxide films contain OH groups, which are the similar form to those in gibbsite and/or bayerite, and boehmite. Furthermore, the content of OH group which is the similar form to those in gibbsite and/or bayerite increases with increasing the atomic ratio, O/Al.

From the SEM micrographs, it seems that the basic morphology of the films does not depend much on the pressure of sputtering atmosphere. It is observed, however, that the channel structure was formed especially for the films prepared at medium pressure, that is, for the films having the larger value of the atomic ratio, O/Al. The compositional dependence of the formation of the channel structure is similar to those of the physical properties. Thus, the channel structure seems to be the peculiar characteristic structure of the films having the larger value of the atomic ratio, O/Al. On the contrary, however, it may be thought that the formation and disappearance of the channel structure depending on the sputtering gas pressure result from the tensile and the compressive stress induced in the films deposited on the fused silica substrate mentioned in 4.1.2.

This paper was focused on the effect of the pressure of sputtering atmosphere on the physical properties of amorphous aluminum oxide films. Thus, we still leave many problems to be solved about the characterization of films, such as the quantitative analysis and the state analysis of H atoms containing in the films, and the relation between the microstructure and the physical properties of the films.

5. Summary

Amorphous aluminum oxide films were prepared by rf sputtering at various values of the pressure of sputtering atmosphere, and their density, refractive index, Young's modulus and internal stress were measured. It was found that the physical properties of the present films depended upon the pressure of sputtering atmosphere, which gave a large influence to the chemical compositions (the atomic ratio, O/Al) of the films. The density, refractive index, and Young's modulus decreased linearly with increasing the ratio, O/Al. The compressive stress and tensile stress induced in the films depending upon the pressure of sputtering atmosphere could be explained by the atomic peening effect and the so called "compositional effect". The presence of OH group in the films was verified by using FT-IR, and their microstructure was investigated by SEM study.

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