

## Formation process of Al<sub>2</sub>O<sub>3</sub> thin film by reactive sputtering

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### Abstract

Al and Al<sub>2</sub>O<sub>3</sub> films were deposited by RF magnetron sputtering using a mixed gas of Ar and O<sub>2</sub>. The surface of the Al target was changed from the metallic mode to the oxide mode at a critical O<sub>2</sub> flow ratio of 8%. The atomic ratio of sputtered Al atoms to supplied oxygen atoms was found to be approximately 2:3 at the critical O<sub>2</sub> flow ratio. The oxide layer thickness formed on the Al target was estimated to be 5-7 nm at an O<sub>2</sub> flow ratio of 100% by ellipsometry.

Keywords: reactive sputtering, plasma emission intensity, target voltage, aluminum oxide, gettering effect

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## 1. Introduction

Reactive sputtering is one of the most commonly used techniques for obtaining compound thin films by sputtering a metal target in reactive gas atmosphere [1]. It is well known that target mode change (target poisoning) is very important in reactive sputtering, because the change in the target surface state induces drastic changes in the deposition rate and the chemical composition of the deposited films. Some models of reactive sputtering have been proposed to explain effects of processing parameters on the hysteresis effect, the change in deposition rate, and the critical amount of reactive gas [2-7]. However, values of some parameters, such as sputtering yields, sticking coefficients, pumping speed and target ion current, have to be assumed to fit the theoretical data with the experimental results, and many researchers still need to find appropriate conditions for their own sputtering systems experimentally. Furthermore, quantitative discussion on the target surface compound layers has not been studied in detail, in spite of the importance of information on the target surface state.

We studied the processes of reactive sputtering for Ti-O<sub>2</sub>, Si-O<sub>2</sub>, and Si-N<sub>2</sub> systems experimentally [8-10], and clarified the critical conditions for compound film formation and the thicknesses of the compound layer at the target surface. However, several different oxide or nitride, such as TiO, Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, could be formed for these systems, and this may cause ambiguity for the analyses. In this study, the formation process of Al<sub>2</sub>O<sub>3</sub> thin films was studied, because Al<sub>2</sub>O<sub>3</sub> is the only oxide of Al and we expect that more reliable data could be obtained. We examined the critical condition to form Al<sub>2</sub>O<sub>3</sub> thin films and the compound layer thickness formed at the surface of a metal target.

## 2. Experimental

Al and Al<sub>2</sub>O<sub>3</sub> films were deposited by RF (13.56 MHz) magnetron sputtering, using an Al (99.99% purity) target with a diameter of 2 inches. Corning #7059 glass and Si wafer were used as substrates. An Al model target (a 1- $\mu$ m-thick Al film sputter deposited on the surface of the Si wafer) was used as the sputtering target for the measurement of target surface oxide layer thickness. A mixed gas of Ar and O<sub>2</sub> was used for sputtering, and the O<sub>2</sub> flow ratio was varied from 0% to 100%. The total gas pressure, total gas flow rate, RF input power, and substrate temperature were fixed at 0.67Pa, 5ccm (mL/min at 25°C, 101.3kPa), 50W, and room temperature, respectively. The thickness of the deposited films was approximately 100nm. The flow rates of Ar and O<sub>2</sub> gases were controlled by mass flow controllers.

The crystal structure of the deposited films was evaluated by X-ray diffraction (XRD) with Cu K $\alpha$  radiation. The electrical resistivity was measured by a four-point probe method. The transmittance was examined by a multi-channel charge-coupled device (CCD) detector. The refractive index of the films and the oxide layer thickness formed at the surface of the model target were examined by ellipsometry using a He-Ne laser (633nm). The plasma condition during sputtering was evaluated by plasma emission spectroscopy, and the target surface state was verified by target self-bias voltage. The amount of Al atoms sputtered from the Al target was estimated using the same method as given in ref. 11.

## 3. Results and discussion

First, the effects of the O<sub>2</sub> flow ratio on the formation of Al<sub>2</sub>O<sub>3</sub> films were studied. The

transmittance of the films at a wavelength  $\lambda$  of 600nm is plotted as a function of O<sub>2</sub> flow ratio in Figure 1. The transmittance is very low for the films deposited at O<sub>2</sub> flow ratios of 0-6% and increases to 95-100% at O<sub>2</sub> flow ratios above 8%. The refractive index of the transparent films at a wavelength of 633nm was 1.50-1.66, which agrees well with the value of Al<sub>2</sub>O<sub>3</sub> (1.54-1.78) [12, 13]. The resistivity of the film was approximately 4 $\mu\Omega$ cm at an O<sub>2</sub> flow ratio of 0% and increased to 18 $\mu\Omega$ cm at an O<sub>2</sub> flow ratio of 6%. At oxygen flow ratios above 8%, the resistivity increased so high that it could not be measured by the four point probe method. XRD peaks due to Al(111) were observed for the films deposited at O<sub>2</sub> flow ratios of 0-6%. However, amorphous films were formed at 8-100%. From these results it is thought that Al films were formed at O<sub>2</sub> flow ratios below 8% and that Al<sub>2</sub>O<sub>3</sub> films were formed at O<sub>2</sub> flow ratios above 8%.

The plasma emission intensity of oxygen atoms [14] is shown as a function of O<sub>2</sub> flow ratio in Figure 2(a), which shows that the emission intensity of oxygen atoms is very small at O<sub>2</sub> flow ratios below 8%, and it begins to increase at 10%. It is thought that oxygen molecules are getterred by Al atoms deposited on the sputtering chamber wall and the substrate, and the oxygen density in the plasma is very low at O<sub>2</sub> flow ratios of 0-8%. Due to the oxygen insufficiency, Al films are formed. Above the critical O<sub>2</sub> flow ratios of 8%, the amount of supplied O<sub>2</sub> molecules is supposed to exceed the gettering effect and the oxygen density in the plasma begins to increase. As a result, Al<sub>2</sub>O<sub>3</sub> films are formed. Figure 2(b) shows the change of the deposition rate as a function of the O<sub>2</sub> flow ratio. The deposition rate decreases abruptly above the critical O<sub>2</sub> flow ratio. Figure 2(c) shows the change of the target self-bias voltage as a function of O<sub>2</sub> flow ratio. The target voltage also decreases abruptly above the critical O<sub>2</sub> flow ratio. These phenomena are attributed to a change of the target mode [1].

At the critical O<sub>2</sub> flow ratio of 8%, the amount of supplied O<sub>2</sub> molecules was calculated to be  $1.8 \times 10^{-5}$  mol/min, and that of sputtered Al atoms was estimated to be  $2.3 \times 10^{-5}$  mol/min from the

mass of the deposited Al film on a symmetrically-arranged foil substrate [11]. This means that the ratio of the number of sputtered Al atoms to that of supplied oxygen atoms becomes the stoichiometric ratio of 2:3 at the critical O<sub>2</sub> flow ratio. A similar results were obtained for the Ti-O<sub>2</sub> system [8], and a simple model similar to our results was proposed by Hohnke *et al.* [15]. The amount of reactive gas which is necessary to form compound films by reactive sputtering is predicted only from the amount of sputtered metal atoms under metallic target mode.

To confirm the target mode change, the surface oxide layer thickness formed on the Al model target was estimated by ellipsometry. Figure 3 shows the  $\Delta$ - $\Psi$  chart of the Al model target after sputtering at O<sub>2</sub> flow ratios of 0% and 100% for 3min. The data measured at various positions on the model target are indicated by open circles. The closed squares are the calculated data by assuming a refractive index of  $n = 1.63$  and an extinction coefficient of  $k = 0$  for Al<sub>2</sub>O<sub>3</sub>, and  $n = 1.49$  and  $k = 7.34$  for Al. The good agreement between the experimental and calculated values indicates the validity of the assumed optical constants. The oxide layer thickness formed at the target surface is plotted in Figure 4 as a function of the distance from the target center ( $x$ ), because reports on the variation of compound layer thickness on the target surface are scarce. The oxide layer thickness of 2-3 nm for the target sputtered at an O<sub>2</sub> flow ratio of 0% is thought to be caused by natural oxidation after the sample was taken out from the sputtering chamber. The oxide layer thickness of 5-7 nm for the target sputtered at an O<sub>2</sub> flow ratio of 100% is thought to be caused by plasma oxidation. The oxide layer thickness is close to that obtained by dynamic Monte Carlo simulations for Al-O<sub>2</sub> systems [16, 17]. Although the variation of the oxide layer thickness is small, the thickness at the erosion region ( $x=10-15$  mm), which is the area sputtered faster than the other area, is slightly thinner than that at the other regions. The higher sputter etching rate at the erosion region is thought to be the reason for the thinner oxide layer [2, 9].

#### **4. Conclusion**

The formation process of Al and Al<sub>2</sub>O<sub>3</sub> films was classified into two regions: (a) a metal target mode region and (b) an oxide target mode region. At a critical O<sub>2</sub> flow ratio of 8%, where the target mode changed from the metal mode to the oxide mode, it was found that the ratio of the amount of sputtered Al atoms to that of supplied oxygen atoms became the stoichiometric ratio of 2:3. The oxide layer thickness formed on the model target was estimated to be 5-7 nm at O<sub>2</sub> flow ratio of 100% by ellipsometry.

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## Figure captions

- Fig. 1 Transmittance ( $\lambda = 600\text{nm}$ ) and refractive index ( $\lambda = 633\text{nm}$ ) of the films as a function of  $\text{O}_2$  flow ratio.
- Fig. 2 (a) Plasma emission intensity of oxygen atoms ( $\lambda = 777\text{nm}$ ), (b) deposition rate of the films, and (c) target voltage as a function of  $\text{O}_2$  flow ratio.
- Fig. 3  $\Delta$ - $\Psi$  chart of Al targets after sputtering at  $\text{O}_2$  flow ratios of 0% and 100% as measured by ellipsometry. Open circles and closed squares indicate experimental and calculated values, respectively.
- Fig. 4 Thickness of the surface oxide layer formed on Al model targets after sputtering at  $\text{O}_2$  flow ratios of 0% and 100% as functions of the distance from the target center.



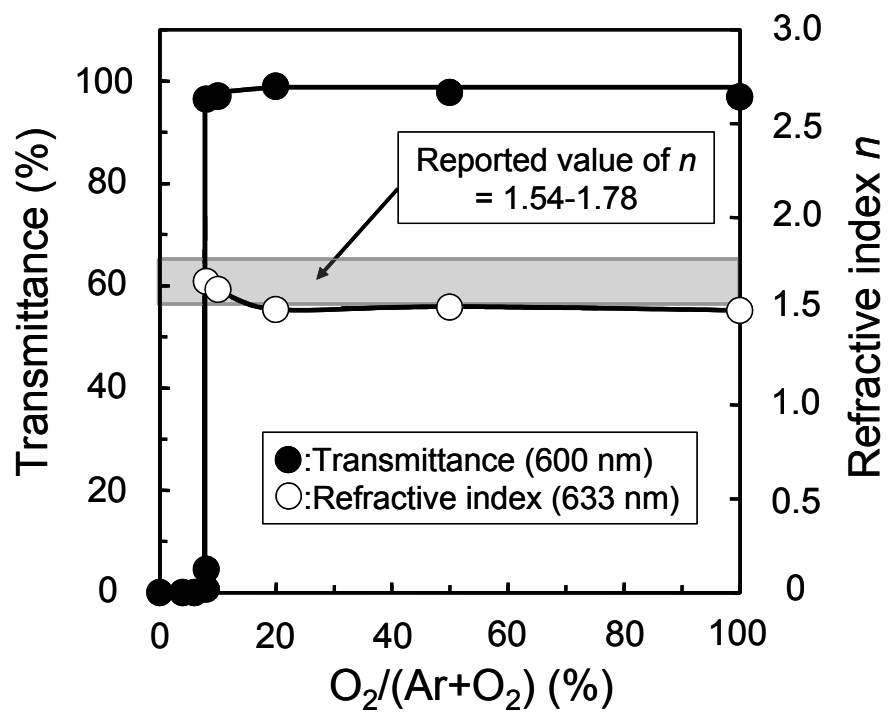


Fig. 1

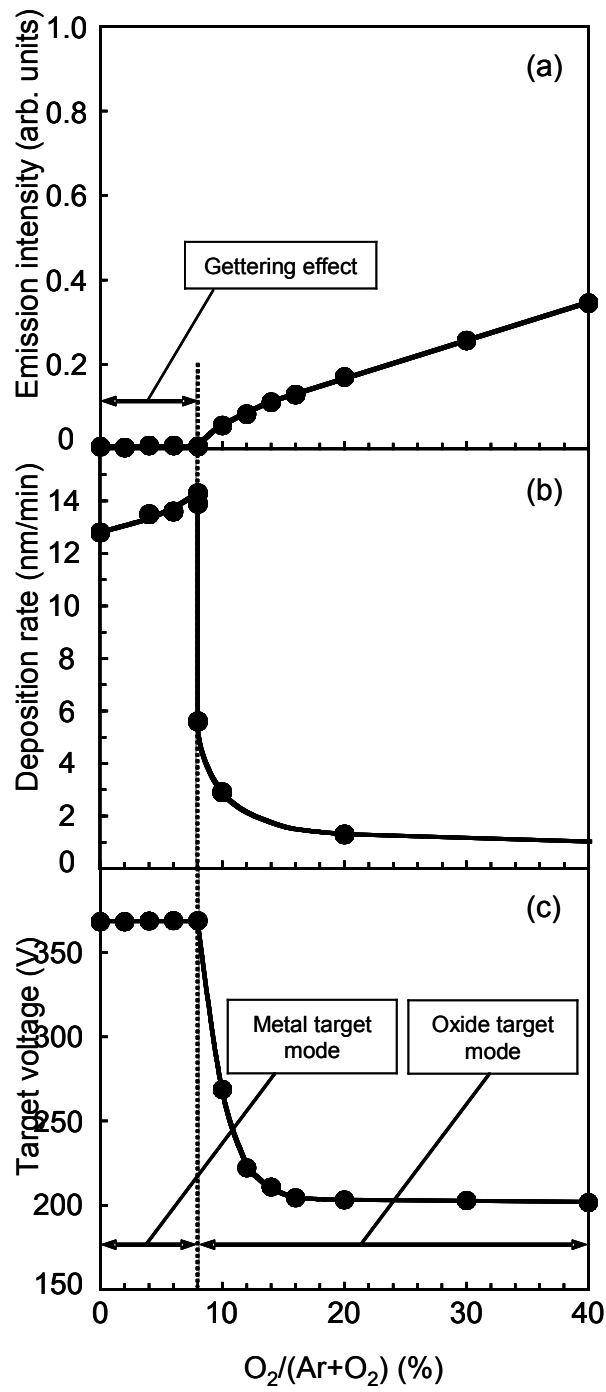


Fig. 2

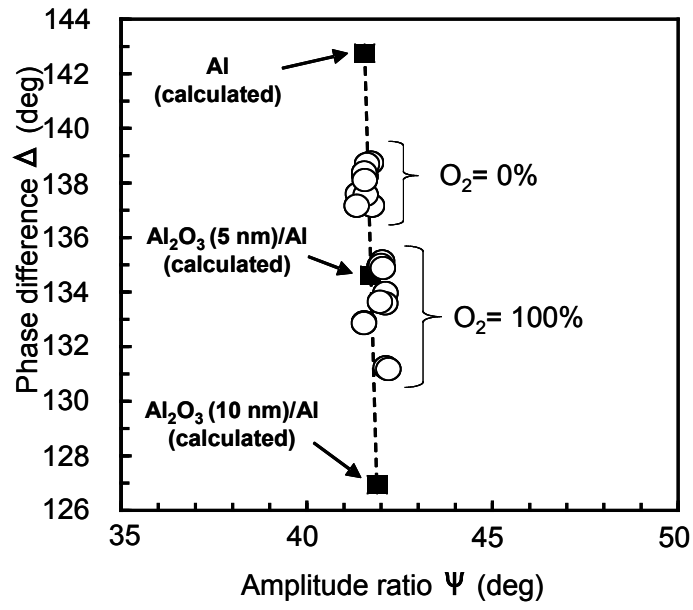


Fig. 3

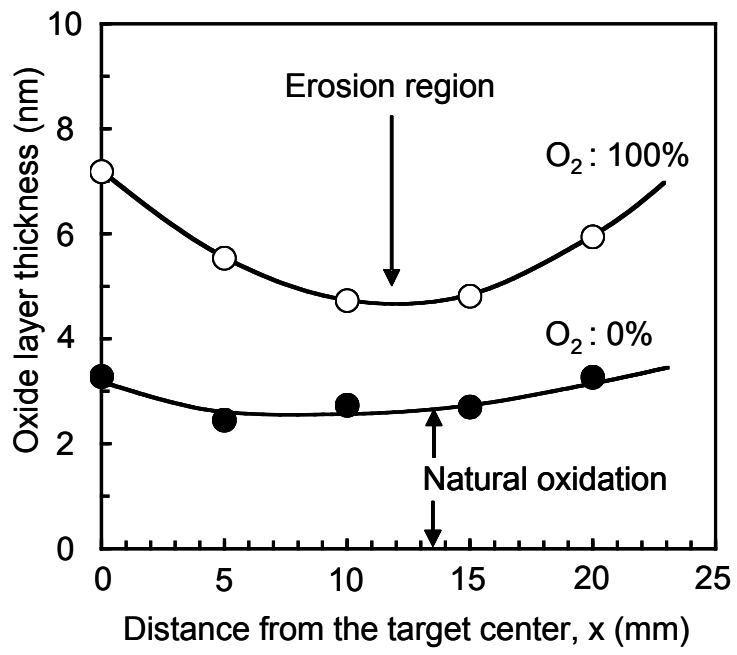


Fig. 4