

# Time-dependent variation of the target mode in reactive sputtering of Al–O<sub>2</sub> system

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## Abstract

Reactive sputtering techniques have been widely used for forming compound thin films. In this study, the time-dependent variation of the target mode of an Al–O<sub>2</sub> system was investigated by measuring the target voltage for various reactive O<sub>2</sub> gas flow ratios and presputtering (i.e., sputtering in pure Ar gas to clean the target surface) times. The Al target remains in metallic mode for a certain period of time after being exposed to an Ar–O<sub>2</sub> plasma before it begins to be oxidized. This period increases with decreasing O<sub>2</sub> flow ratio and with increasing the presputtering time. It is considered that the period is caused by the gettering of O<sub>2</sub> gas by Al films deposited on the substrate and the chamber wall during presputtering.

Keywords: target surface state, gettering effect, target voltage, chamber pressure

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## 1. Introduction

Reactive sputtering techniques have been widely used for forming compound thin films [1–3]. Usually, the formation of a compound layer on the surface of a metal target (i.e., the target mode variation) is closely related to the deposition of a compound thin film. Therefore, sputtering parameters such as the partial pressure of the reactive gas and the sputtering power are carefully controlled to maintain the target surface in an appropriate state. In addition to static control of the sputtering parameters, recent sputtering techniques employ dynamical control of the sputtering parameters enabling high deposition rates of compound thin films to be achieved [4,5]. Therefore, both the static target surface states and the dynamic behavior of the target modes should be clarified [6,7].

In the present study, the time-dependent target mode variation of an Al–O<sub>2</sub> system was investigated by measuring the target voltage for various reactive O<sub>2</sub> gas flow ratios and presputtering times.

## 2. Experimental procedure

The target mode variation during reactive sputtering of an Al–O<sub>2</sub> system was investigated using an RF magnetron sputtering system. A 2-inch-diameter Al target (99.9% purity) was sputtered in Ar and O<sub>2</sub> mixed gases. The Ar and O<sub>2</sub> flow rates were controlled by mass flow controllers and sputtering was carried out for various O<sub>2</sub> flow ratios. The presputtering time was also varied as a parameter. The total gas flow rate and RF power during sputtering were kept constant at 1 cm<sup>3</sup>/min and 50 W, respectively.

The surface oxidation states of the Al target were studied by measuring the target self-bias voltage [8,9]. The total gas pressure and the O<sub>2</sub> partial pressure in the sputtering chamber were

measured by a capacitance manometer and a quadrupole mass spectrometer (QMS), respectively.

Process flow diagrams for this study are shown in Fig. 1. The Al target was first presputtered in pure Ar gas to clean the target surface and ensure a metallic mode. Next, the flow rates of Ar and O<sub>2</sub> gases were adjusted for sputtering, and an Ar–O<sub>2</sub> plasma was generated by applying RF power to the target. The target voltage and chamber pressure were measured during sputtering.

### **3. Results and discussion**

The target voltage as a function of the O<sub>2</sub> flow ratio is shown in Fig. 2. It was measured by gradually increasing/decreasing the O<sub>2</sub> flow ratio while the plasma was on. In pure Ar gas, the target voltage is high (about 300 V), which means that the Al target is in metallic mode. The target voltage remains high up to an O<sub>2</sub> flow ratio of 33% and it then decreases abruptly to about 200 V when the O<sub>2</sub> flow ratio is increased gradually above this value. This means that the target surface state changes from metallic mode to oxide mode at a critical O<sub>2</sub> flow ratio of 33%. In the oxide target mode, the surface of the Al target is covered by a thin layer of Al oxide [10]. The target voltage decreases on oxidation of the target due to Al oxide having a higher secondary electron emission coefficient than Al. The target voltage returns to a high value when the O<sub>2</sub> flow ratio was gradually reduced to 12%, indicating that the target mode changes from being metallic to being an oxide mode. The hysteresis behavior of the target voltage shown in Fig. 2 has been commonly observed in reactive sputtering.

The target voltage and the chamber pressure during sputtering for various O<sub>2</sub> flow ratios after a constant presputtering time of 20 min (5 min at 20 W and 15 min at 50 W) are shown in Figs. 3(a) and (b). At O<sub>2</sub> flow ratios of 0 and 32%, the target voltage remains high because the Al target is in metallic mode at these O<sub>2</sub> flow rates. By contrast, at O<sub>2</sub> flow ratios of 40 and 50%, the target voltage remains high for a certain period of time and then abruptly decreases. This means

that the target remains in metallic mode for a period, which we term the incubation time ( $t_{\text{incu}}$ ), even although the  $\text{O}_2$  flow ratio exceeds the critical value for the target mode change (33%) shown in Fig. 2. The incubation time increases with decreasing  $\text{O}_2$  flow ratio. The decrease in the target voltage corresponds well with the increase in the chamber pressure. The sputtering rate of Al atoms in oxide target mode is much lower than that in metallic target mode. Therefore, the amount of gettered  $\text{O}_2$  gas decreases and the chamber pressure increases on target oxidation. The gettering of  $\text{O}_2$  gas during the incubation time was confirmed by the QMS measurements.

The target voltage and the chamber pressure during sputtering at an  $\text{O}_2$  flow ratio of 40% after presputtering in pure Ar gas at a constant RF power of 50 W for 0–20 min are shown in Figs. 4(a) and (b). These figures clearly show that the incubation time increases with increasing presputtering time.

In order to explain the effects of the  $\text{O}_2$  flow rate during sputtering and presputtering time on the incubation time, we propose the following simple model:

- 1) During presputtering, Al films are deposited on the surface of the substrate and the chamber wall.
- 2) If the amount of  $\text{O}_2$  molecules supplied to the sputtering chamber during sputtering exceeds that used for forming the  $\text{Al}_2\text{O}_3$  film, the excess  $\text{O}_2$  molecules oxidize the Al film deposited during presputtering.
- 3) After the Al film deposited during presputtering has been oxidized, the  $\text{O}_2$  partial pressure in the sputtering chamber increases and the target mode changes from metallic mode to oxide mode.

The number of oxygen atoms  $N_{\text{O}}$  that are introduced into the sputtering chamber during sputtering at an  $\text{O}_2$  flow rate of  $F_{\text{O}_2}$  ( $\text{cm}^3/\text{min}$ ) is

$$N_{\text{O}}=2 \times F_{\text{O}_2} \times 10^{-3} / 22.4 \text{ (mol/min)}. \quad (1)$$

The number of Al atoms deposited in metallic mode  $N_{Al}$  was estimated to be

$$N_{Al}=2.1 \times 10^{-5} \text{ (mol/min)} \quad (2)$$

in a previous paper by us when an RF power of 50 W was used [11]. Since two Al atoms sputtered from the target getter three O atoms to form  $Al_2O_3$ , the number of excess O atoms  $N_{O^*}$  is

$$N_{O^*}=N_O-3N_{Al}/2. \quad (3)$$

If we assume that all the excess O atoms are used to oxidize the Al films deposited during presputtering and the formation of  $Al_2O_3$ , the relationship between the presputtering time  $t_{pre}$  and the incubation time  $t_{incu}$  can be written as

$$3N_{Al} \times t_{pre}=2N_{O^*} \times t_{incu}. \quad (4)$$

The incubation time is calculated to be

$$t_{incu} = 3N_{Al} \times t_{pre}/(2N_{O^*})=7.5 \times t_{pre}, \quad (5)$$

for the experimental conditions shown in Fig. 4 ( $F_{O_2}=0.4 \text{ cm}^3/\text{min}$ ). In this model, we neglected the contribution of oxygen molecules that were pumped out from the chamber because it has been reported that more than 90% of the introduced oxygen gas was consumed by gettering in Ti- $O_2$  reactive sputtering process [12].

The solid and dotted lines shown in Fig. 5 indicate the experimentally measured and calculated incubation times, respectively. The simple model qualitatively explains the effect of

the presputtering time on the incubation time, and the slope of the experimental data for presputtering times in the range 2–5 min is in reasonably good agreement with that of the calculated line. However, the experimental incubation time does not increase linearly for incubation times in the range 0–1 min and the incubation time was shorter than predicted by the model for a longer presputtering time. These deviations are considered to be caused by 1) the target surface being oxidized prior to presputtering and 2) the thickness of the Al film deposited on the chamber wall and the substrate for presputtering times over 5 min being too thick to be completely oxidized. It seems that the incubation time in Fig. 5 approaches a constant value of approximately 20 min at a sufficiently long presputtering time, and the total amount of oxygen atoms supplied during the incubation time is calculated to be  $7 \times 10^{-4}$  mol. If we assume that the inner surface of the chamber (approximately  $0.85 \text{ m}^2$ ), which is covered by an Al layer with a density of  $2.7 \text{ g/cm}^3$ , is uniformly oxidized, the depth of the Al layer to be oxidized is estimated to be 5.5 nm. The increase in the incubation time with decreasing  $\text{O}_2$  flow ratio is explained by the decrease of  $N_{\text{O}^*}$  in Eq. (5).

#### **4. Conclusions**

Time-dependent target mode variation of Al– $\text{O}_2$  reactive sputtering was investigated and the incubation time, which is the period that the Al target remains in metallic mode, was measured. The incubation time increases with decreasing  $\text{O}_2$  flow ratio and with increasing presputtering time. A simple model that considers the gettering effect of the Al films deposited during presputtering qualitatively explains the incubation time dependence.

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## Figure captions

Fig. 1 Process flow diagrams of (a) gas flow rate and (b) RF power during presputtering and sputtering.

Fig. 2 Hysteresis behavior of target voltage as a function of O<sub>2</sub> flow ratio.

Fig. 3 Time dependence of (a) target voltage and (b) chamber pressure after exposure to Ar–O<sub>2</sub> plasma. O<sub>2</sub> flow ratio was varied as a parameter.

Fig. 4 Time dependence of (a) target voltage and (b) chamber pressure after exposure to Ar–O<sub>2</sub> plasma. Presputtering time was varied as a parameter.

Fig. 5 Incubation time as a function of presputtering time. The inset shows the definition of the incubation time.

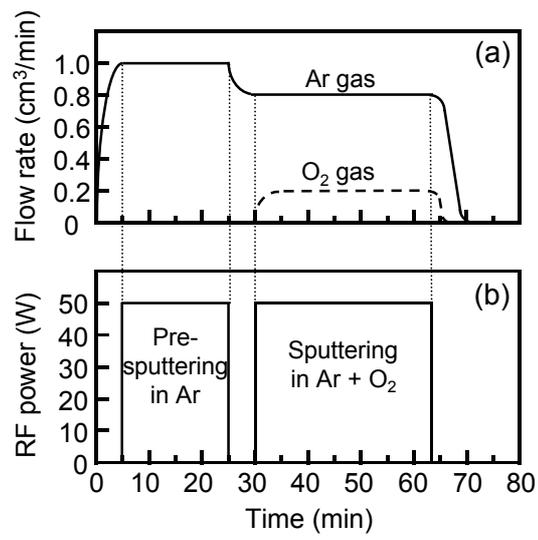


Fig. 1

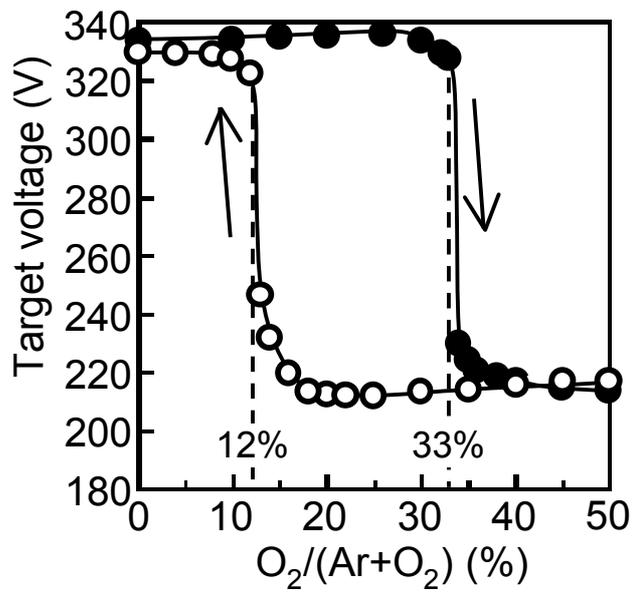


Fig. 2

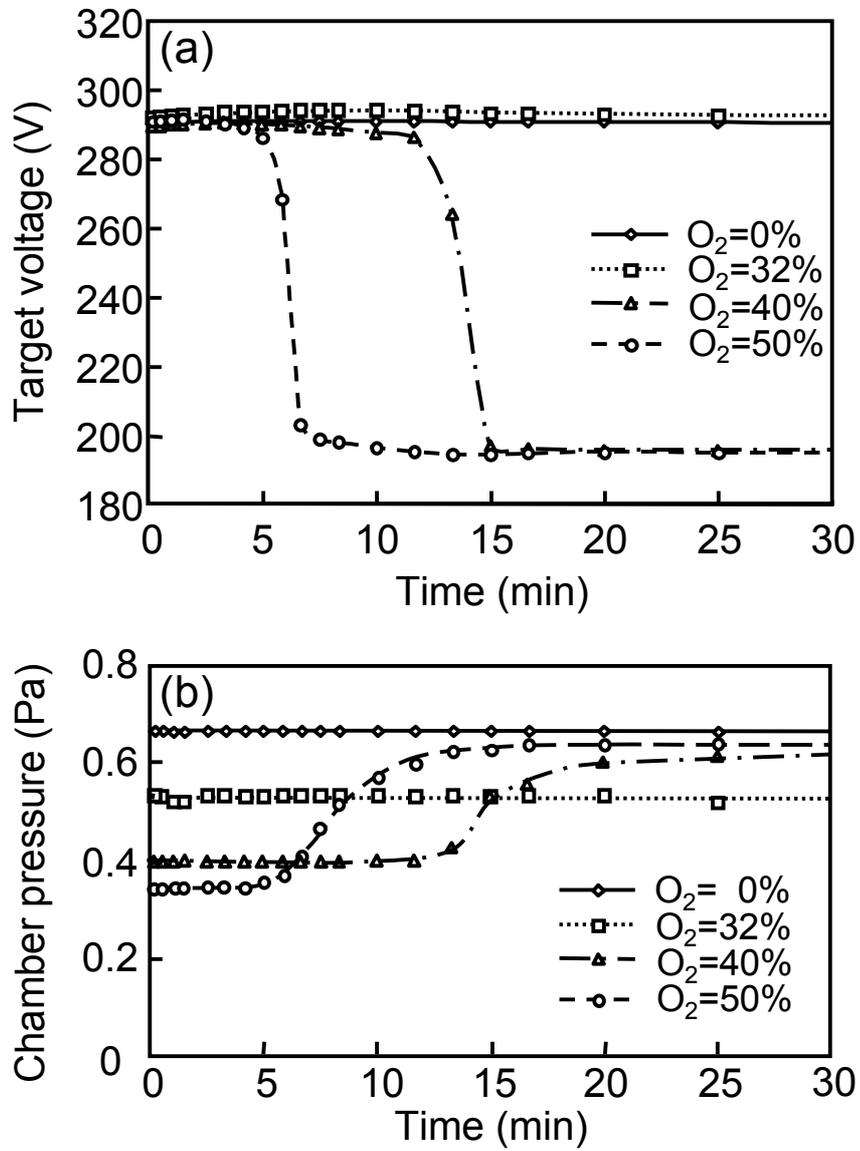


Fig. 3

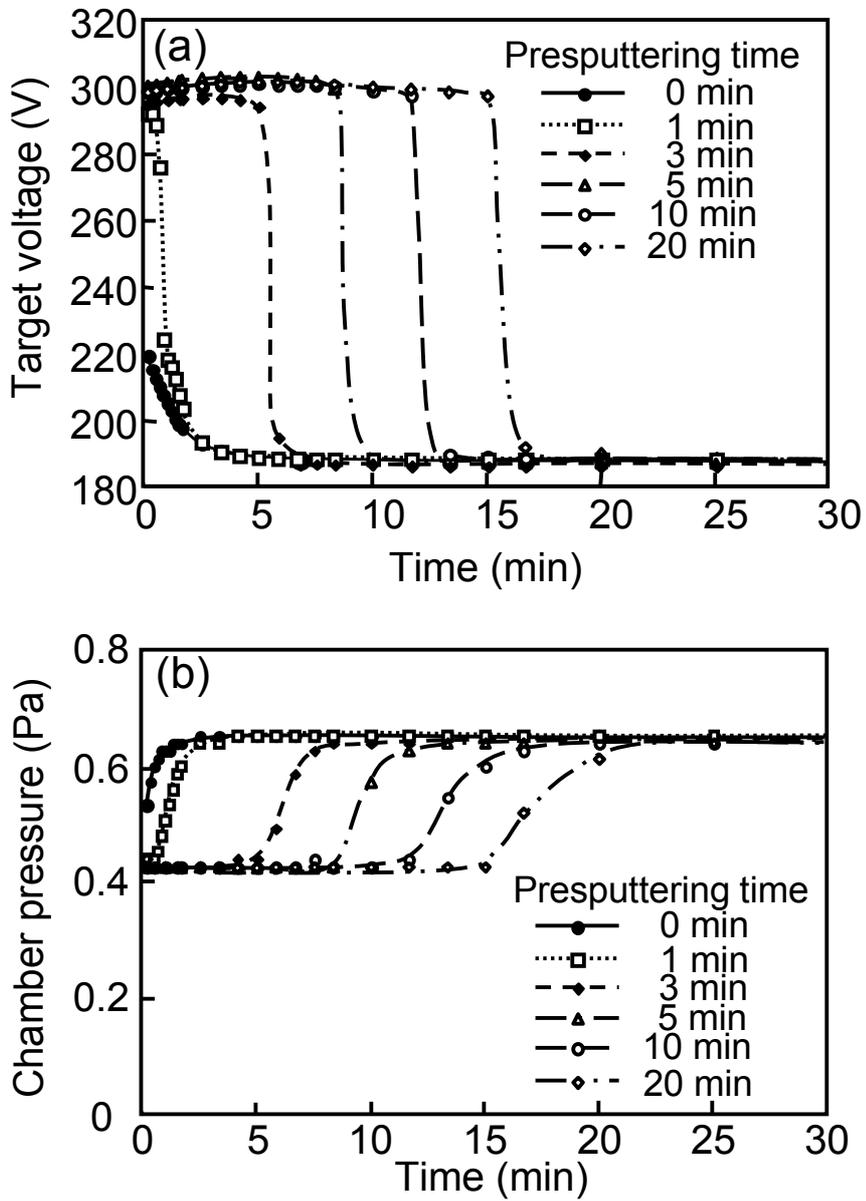


Fig. 4

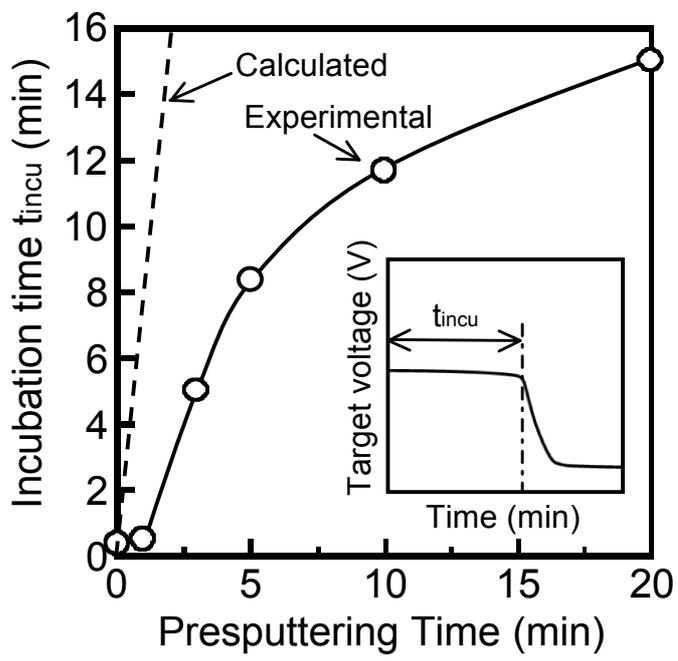


Fig. 5