Formation process of Al_2O_3 thin film by reactive sputtering

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Reactive sputtering is one of the widely used techniques to prepare compound thin films. In this study, Al and Al_2O_3 films were deposited by RF magnetron sputtering using mixed gas of Ar and O_2. The formation process of the Al_2O_3 films was studied by plasma emission spectroscopy and target voltage measurements. Al_2O_3 films with transmittance above 95% and refractive index of 1.50-1.66 were found to be formed at O_2 flow ratios above 8%. Plasma emission peaks of O atoms (777nm) were clearly seen at oxygen flow ratios above 8%, and target voltage decreased drastically at O_2 flow ratios above 8%. It is thought that the surface of Al target was changed from metallic mode into oxide mode at the O_2 flow ratios of 8%. The relationship between the amount of sputtered Al atoms and the amount of supplied O_2 molecules was studied, and the atomic ratio of sputtered Al atoms to supplied oxygen atoms was found to be approximately 2:3 at the critical O_2 flow ratio of 8%.

1. Introduction

Al_2O_3 films have attracted much attention for optical, and electrical applications due to their high dielectric constant and high mechanical, chemical and thermal stabilities.

Reactive sputtering is one of the most common techniques used for obtaining compound thin films. Al_2O_3 films have also been prepared by reactive sputtering and their formation process has been studied [1, 2]. However, quantitative discussions on the formation process of Al_2O_3 films and the target surface oxidation have not been reported in detail. The purpose of this study is to clarify the influence of O_2 flow ratio, which is necessary to form Al_2O_3 thin films, and the influence of O_2 flow ratio on the oxidation of an Al target. Optical and electrical properties of deposited films, plasma and target surface states were studied as a function of O_2 flow ratio.

2. Experimental

Al and Al_2O_3 films were deposited by RF (13.56 MHz) magnetron sputtering, using an Al (99.99% purity) target with 2-in diameter. Corning #7059 glass and Si were used as substrates. Mixed gas of Ar and O_2 was used for sputtering and the O_2 flow ratio was varied from 0% to 100%. Total gas pressure, total gas flow rate, RF input power, and substrate temperature were fixed at 5mTorr, 5cc/min, 50W, and room temperature, respectively. The thickness of the deposited films was about 100nm. The flow rates of Ar and O_2 gases were controlled by mass flow controllers.

The crystal structure of the films was evaluated by X-ray diffraction (XRD) with Cu Kα radiation. Electrical resistivity was measured by a four-point probe method. Transmittance was examined by a multi-channel charge-coupled device (CCD) detector. Refractive index of the films was examined by ellipsometry with a He-Ne laser (633nm). Plasma condition during sputtering was evaluated by plasma emission spectroscopy and target surface state was checked by target self-bias voltage. The amount of Al atoms sputtered from the Al target was estimated from the mass of deposited films.

3. Results and discussion

First, effects of O_2 flow ratio on the formation of Al_2O_3 films were studied. Transmittance of the films at a wavelength λ of 600nm is plotted as a function of O_2 flow ratio in Figure 1. The transmittance is very low for the films deposited at O_2 flow ratios of 0-6%, and it increases to 95-100% at O_2 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_2O_3 (1.54-1.78) [3, 4]. The resistivity of the film was about 4μΩcm at an O_2 flow ratio of 0% and it increased to 18μΩcm at that of 6%. The resistivity increased too high to measure by the four point probe method at oxygen flow ratios above 8%. XRD peaks due to Al(111) was observed for the films deposited at O_2 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_2 flow ratios below 8%, and Al_2O_3 films were formed at O_2 flow ratios above 8%.

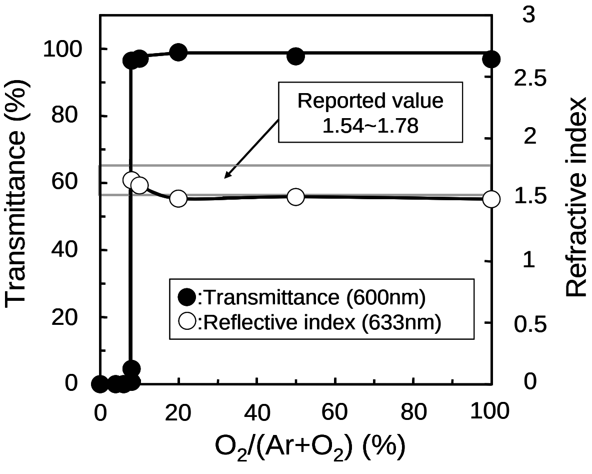


Figure 1. Transmittance (λ=600nm) and refractive index (λ=633nm) of the films as a function of O_2 flow ratio.

Plasma emission intensity of oxygen atoms [5] is shown as a function of O_2 flow ratio in Figure 2. From this figure, it is seen that the emission intensity of oxygen atoms is very small at O_2 flow ratios below 8%, and it begins to increase at 10%. It is thought that oxygen molecules are gettered by Al atoms deposited on the sputtering chamber wall and the substrate, and the oxygen density in the plasma are very low at O_2 flow ratios of 0-8%. Due to the very low density of oxygen in the plasma, Al films are formed. Above a critical O_2 flow ratio of 8% the amount of supplied O_2 molecules is supposed to exceed the gettering effect and oxygen density in the plasma beings to increase. As a result Al_2O_3 films are formed. At the critical O_2 flow ratio of 8%, the amount of supplied O_2 molecules was calculated to be 1.8×10^{-5} mol/min. And the amount of sputtered Al atoms was estimated to be 2.3×10^{-5} mol/min from the mass of the deposited Al film. 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_2 flow ratio.

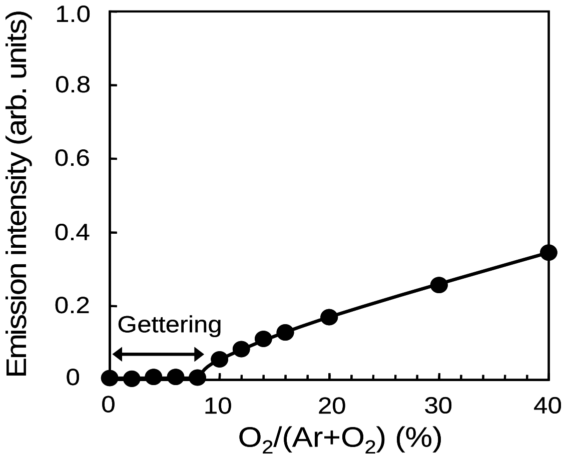


Figure 2. Plasma emission intensity of oxygen atoms (λ=777nm) as a function of O_2 flow ratio.

Figure 3 shows the change of the deposition rate as a function of O_2 flow ratio. It is clearly seen that the deposition rate decreases abruptly above the critical O_2 flow ratio of 8%. Figure 4 shows the change of the target self-bias voltage as a function of O_2 flow ratio. The target voltage also decreases abruptly above the critical O_2 flow ratio of 8%. These phenomena are attributed to a change of the target mode as shown in Figure 5. The formation process of Al and Al_2O_3 films is classified into the following two regions (a) metal target mode region at oxygen flow ratios below 8%, where Al films were formed at a high deposition rate of about 14nm/min, (b) oxide target mode region at oxygen flow ratios above 8%, where Al_2O_3 films were formed at a low deposition rate of about 1nm/min.

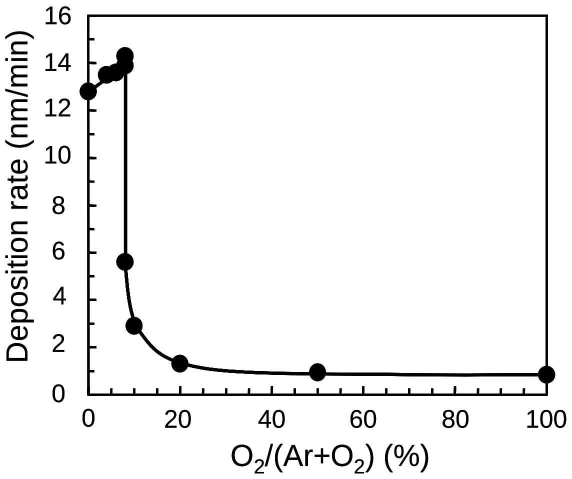


Figure 3. Deposition rate of the films as a function of O_2 flow ratio.

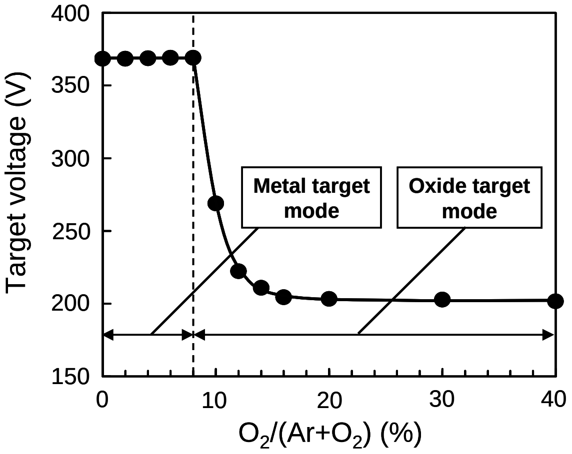
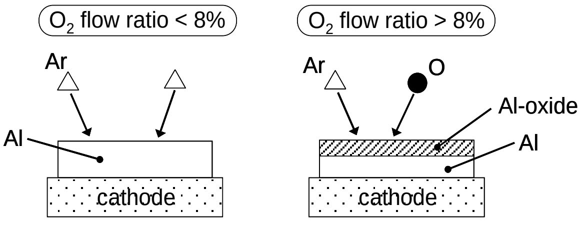


Figure 4. Target voltage as a function of O_2 flow ratio.



(a) Metal target mode (b) Oxide target mode

Figure 5. A model of target mode change.

4. Conclusion

The formation process of Al and Al_2O_3 films was classified into two regions; (a) metal target mode region, and (b) oxide target mode region. At a critical O_2 flow ratio of 8%, where the target mode changed from metal mode to 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. Al films were formed in the metal target mode region, because oxygen molecules supplied into the sputtering chamber were gettered and oxygen density in the plasma was very low. Above the critical O_2 flow ratio, the amount of supplied O_2 molecules exceeded the gettering effect and oxygen density in the plasma began to increase. As a result Al_2O_3 films were formed.

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