

Target-Surface Compound Layers Formed by Reactive Sputtering of Si Target in Ar+O₂ and Ar+N₂ Mixed Gases

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Abstract

Reactive sputtering is a very useful and widely used technique for preparing compound thin films, however, the target surface state is not fully understood. In this study, a Si wafer was used as a model sputtering target, and the thickness of the oxide and nitride layers formed on the target surface after sputtering in Ar+O₂ and Ar+N₂ mixed gases, respectively, was measured by ellipsometry. The maximum thicknesses of oxide and nitride layers were found to be approximately 7 nm in pure O₂ gas and 4 nm in pure N₂ gas, respectively. The oxidation rate of Si in oxygen plasma was thought to be higher than the nitridation rate of Si in nitrogen plasma.

KEYWORDS: reactive sputtering, Si model target, plasma oxidation and nitridation,
ellipsometry, target surface state

1. Introduction

Reactive sputtering is a very useful and widely used technique for preparing compound thin films.^{1,2)} Compound thin films with different chemical compositions are deposited by sputtering a metal target in reactive gas atmosphere. For example, sputtering a Ta target in Ar+O₂ gas produces a Ta₂O₅ film and that in Ar+N₂ gas produces a TaN film. It is well known that compound layer formation on the surface of the sputtering target induces a drastic decrease in the deposition rate and a change in the chemical composition of the deposited films. Some models of reactive sputtering have been proposed by Berg and coworkers³⁻⁵⁾ to explain the relationships between processing parameters and target mode changes. From practical viewpoints, a high thin film deposition rate is desired. However, compound layer formation at the surface of the target induces a drastic decrease in the deposition rate due to a decrease in the sputtering rate and an increase in the secondary electron emission coefficient. To realize high-rate sputter deposition of compound thin films, the target-surface compound layer should be eliminated and sputter deposition should be performed in the metallic target mode.⁶⁻⁹⁾ In spite of the importance of information on the target surface state, the thickness of the target-surface compound layers formed during sputtering is not fully understood. The reported thicknesses of target-surface

oxide layers for Fe-O₂, Al-O₂, and Ti-O₂ systems¹⁰⁻¹⁴⁾ vary widely from 1-2 nm to about 100 nm. In addition to the experimental studies, dynamic Monte Carlo simulations for Al-O₂ systems yield thicknesses of 3-5 nm.^{15,16)} Much less attention has been paid to target-surface nitride layers,^{17,18)} and the effects of reactive gas species on the thickness of target-surface compound layers have not been studied.

To clarify the thickness of the target-surface compound layers experimentally and directly, in our previous studies,^{19,20)} we measured the target-surface oxide layer thickness for a Ti-O₂ system by ellipsometry, and examined the effects of the processing parameters, including oxygen flow ratio, sputtering time, total gas pressure and RF power. The thickness of the TiO₂ layer formed at the surface of a Ti model target was found to vary from 2-3 nm to approximately 100 nm depending on the sputtering parameters. Since both SiO₂ and Si₃N₄ are transparent, we expect that the oxide and nitride layer thicknesses on a Si target can also be measured by ellipsometry. In this work, we study the thickness of the target-surface oxide layer for a Si-O₂ system and the target-surface nitride layer for a Si-N₂ system, and examine the effects of reactive gas species on the thickness of target-surface compound layers.

2. Experimental Procedure

An RF magnetron sputtering system was used for the experiment. A Si wafer with a thickness of 280 μm and a diameter of 2 in. was used as a model sputtering target for the measurement of the target surface state, because a sample with a flat surface is necessary for ellipsometry. The model target was bonded to a water-cooled Cu backing plate using Ag paste in order to avoid the increase of target temperature. A Si target with a thickness of 5 mm and a diameter of 2 in. was also used for thin film deposition on a glass substrate and plasma emission measurements. Mixed gases of Ar+O₂ and Ar+N₂ were used for the sputtering, and the O₂ and N₂ flow ratios were varied from 0 to 100%. The total gas pressure, total gas flow rate, and RF power were fixed at 0.7 Pa, 5 cm³/min, and 50 W, respectively. The flow rates of Ar, O₂, and N₂ gases were controlled with mass flow controllers, and the total pressure was measured with a capacitance manometer.

The thicknesses of oxide and nitride layers formed at the surface of the model target were measured by ellipsometry with a He-Ne laser (633 nm) at an incident angle of 70°. It was assumed that a thin layer of SiO₂ was formed at the surface of the Si model target after sputtering in Ar+O₂ gas and that of Si₃N₄ was formed in Ar+N₂ gas. The refractive index, n , and extinction coefficient, k , of the Si target, SiO₂ and Si₃N₄ layers were assumed to be

$n=3.882$ and $k=0.019$ for Si, $n=1.46$ and $k=0$ for SiO₂, and $n=2.02$ and $k=0$ for Si₃N₄.²¹⁾

Plasma emission spectra were measured using a charge coupled device (CCD) detector.

3. Results and Discussion

Figures 1(a) and 1(b) show the plasma emission intensities of oxygen atoms (777 nm) and nitrogen atoms (391 nm) as functions of O₂ and N₂ flow ratios, respectively. The emission intensity of oxygen atoms is very weak at O₂ flow ratios of 0-5 %, because most of the oxygen molecules introduced into the sputtering chamber are gettered and the density of oxygen molecules in the plasma is very low. However, the emission intensity of oxygen atoms begins to increase at an O₂ flow ratio of 6%, where the amount of supplied oxygen molecules exceeds that of gettered oxygen molecules. Corresponding to the increase of the emission intensity of oxygen atoms, the transmittance of the films deposited on glass substrates increases and transparent films (SiO₂) are formed at O₂ flow ratios of 8-100%. Similarly, the emission intensity of nitrogen atoms is very weak at N₂ flow ratios of 0 and 2%, and it begins to increase at 4%. Corresponding to the increase of the emission intensity of nitrogen atoms, the transmittance of the deposited films begins to increase and transparent films (Si₃N₄) are formed at N₂ flow ratios of 12-100%.

To clarify the effect of the plasma state on the target surface state, the thickness of the target-surface oxide and nitride layers was examined by ellipsometry. Figures 2(a) and 2(b) show the parameters obtained by ellipsometry of the Si model target after sputtering in O₂ flow ratios of 0–100% and N₂ flow ratios of 0–100%. Δ is the change in phase difference between the parallel component and the perpendicular component of the incident beam and the outgoing beam, and Ψ is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients. The measured and calculated values of Δ and Ψ are plotted by open and closed circles, respectively. The good agreement between the experimental and calculated values confirms the validity of the optical constants of the surface oxide and nitride layers used for the calculation. The sputtering time for the model target was varied from 1.5 to 15 min, and no marked change was observed in the thickness of target-surface oxide and nitride layers. Thus, in this study, the sputtering time was fixed at 3 min.

Figure 3 shows the thickness of the oxide and nitride layers at the target center as functions of O₂ and N₂ flow ratios. It is clear that the oxide and nitride layer thicknesses increase with increasing O₂ and N₂ flow ratios, and the oxide layer thickness is greater than the nitride layer thickness. The maximum layer thicknesses after sputtering in pure O₂ and pure N₂ were found to be approximately 7 and 4 nm, respectively. These values are similar

to the oxide layer thickness (5–6 nm) for the Ti-O₂ system, which was obtained under the same sputtering conditions.¹⁹⁾

In this study, we used a magnetron cathode, which confines electrons using a magnetic field and generates a high-density plasma in an erosion region (the area sputtered faster than other areas). It is expected that the compound layer thickness depends on the position on the target, because of the nonuniformity of the plasma density and sputtering rate. Figure 4 shows the oxide and nitride layer thicknesses as a function of the distance from the target center. The highest ion flux density is expected at the erosion region, which is a circular region with a radius of 10-15 mm when using our sputtering system. However, no marked differences in the compound layer thicknesses depending on the target position are seen in this figure.

Next, we discuss the effect of reactive gas species on the compound layer thickness formed at the surface of the Si model target. Heller¹⁰⁾ proposed a model for reactive sputtering that described the thickness of the target-surface oxide layer. At the surface of the sputtering target, oxygen ions impinge on the target surface and induce oxidation of the target, as shown in Fig. 5(a). The oxygen ions sputter-etch the target surface simultaneously. The steady-state oxide layer thickness is determined from the point where the

sputter-etching rate and oxidation rate are in balance, as shown in Fig. 5(b). Heller's model provides qualitative insight on the target-surface compound layer thickness, however, numerical calculation of the compound layer thickness is very difficult, because parameters that describe the oxidation and sputtering processes are not clear. To obtain information on the difference in the oxide and nitride layer thicknesses shown in Figs. 3 and 4, the deposition rates of SiO₂ and Si₃N₄ thin films on glass substrates were measured. The deposition rate of a SiO₂ film formed in pure O₂ and that of a Si₃N₄ film formed in pure N₂ were found to be 1.85 nm/min and 1.1 nm/min, respectively. If we assume that the densities of the SiO₂ and Si₃N₄ thin films are the same as those of bulk SiO₂ (2.2 g/cm³) and Si₃N₄ (3.1 g/cm³), respectively, the number of Si atoms in a cube (1 cm³) of SiO₂ is 2.2×10^{22} cm⁻³ and that in a cube of Si₃N₄ is 2.2×10^{22} cm⁻³. The number of Si atoms in the SiO₂ film with a unit area (1 cm²) deposited on the substrate in a unit time (1 min) is calculated to be 4.1×10^{15} atoms/(min·cm²) in pure O₂, and that in the Si₃N₄ film is calculated to be 4.4×10^{15} atoms/(min·cm²) in pure N₂. This estimate suggests that the sputter etching rates of the Si target in pure O₂ and pure N₂ gases are nearly the same. We assumed that the sputter etching rates of the Si target in pure O₂ and pure N₂ gases to be functions of the compound layer thickness that can be represented by a single line (solid line), and the oxidation rate of

the Si target in pure O₂ gas (dashed line) is higher than the nitridation rate in pure N₂ gas (dash-dot line), as shown in Fig. 5(b). Then, the thickness of the oxide layer, which is given at the cross point of the curves of the sputter etching rate and the oxidation rate, is expected to be thicker than that of the nitride layer, which is given at the cross point of the curves of the sputter etching rate and the nitridation rate. Therefore, the thicker oxide layer than the nitride layer on the Si model target is ascribed to the higher oxidation rate of Si in oxygen plasma than the nitridation rate in nitrogen plasma.

4. Conclusions

A Si model target was sputtered in Ar+O₂ and Ar+N₂ mixed gases and the thicknesses of the oxide and nitride layers formed on the target surface were measured by ellipsometry. The oxide and nitride layer thicknesses increased with increasing O₂ and N₂ flow ratios, and the maximum thicknesses of approximately 7 nm and 4 nm were obtained in pure O₂ and pure N₂ gases, respectively. On the basis of the Heller model, the oxidation rate of the Si target in oxygen plasma was thought to be higher than the nitridation rate in nitrogen plasma.

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Figure captions

Fig. 1. Plasma emission intensity of (a) oxygen atoms for Si-O₂ system and (b) nitrogen atoms for Si-N₂ system.

Fig. 2. Δ - Ψ chart of Si model target measured by ellipsometry after sputtering for 3 min (a) in various O₂ flow ratios and (b) in various N₂ flow ratios. Experimental and calculated data are plotted by open and closed circles, respectively.

Fig. 3. Thicknesses of oxide layer (open circles) and nitride layer (closed circles) formed on a Si model target as functions of O₂ and N₂ flow ratios. Ellipsometry measurements were carried out at the target center.

Fig. 4. Thicknesses of oxide layer (open circles) and nitride layer (closed circles) formed on a Si model target as a function of the distance from the target center. O₂ and N₂ flow ratios were 100%.

Fig. 5. (a) Schematic diagram of oxidation, nitridation and sputter etching of a target surface. (b) Oxidation, nitridation and sputter etching rates as functions of compound layer thickness (see ref. 10).

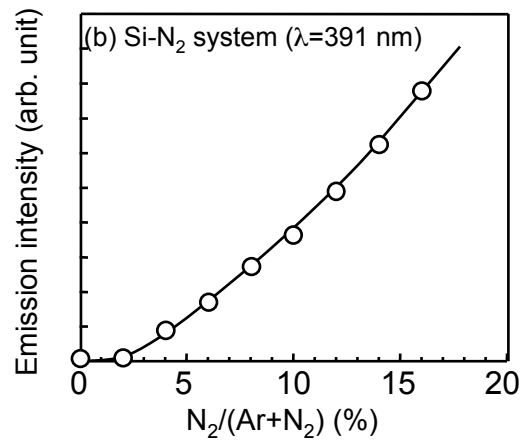
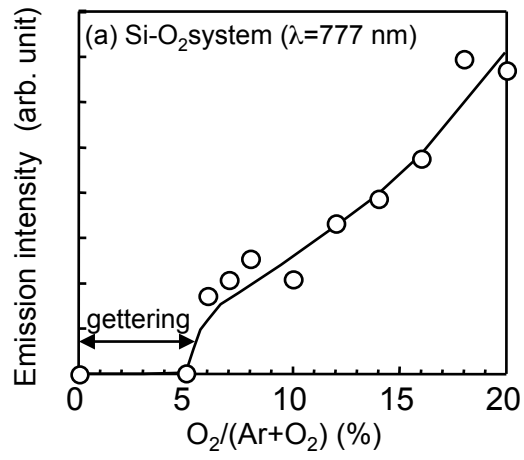


Fig. 1

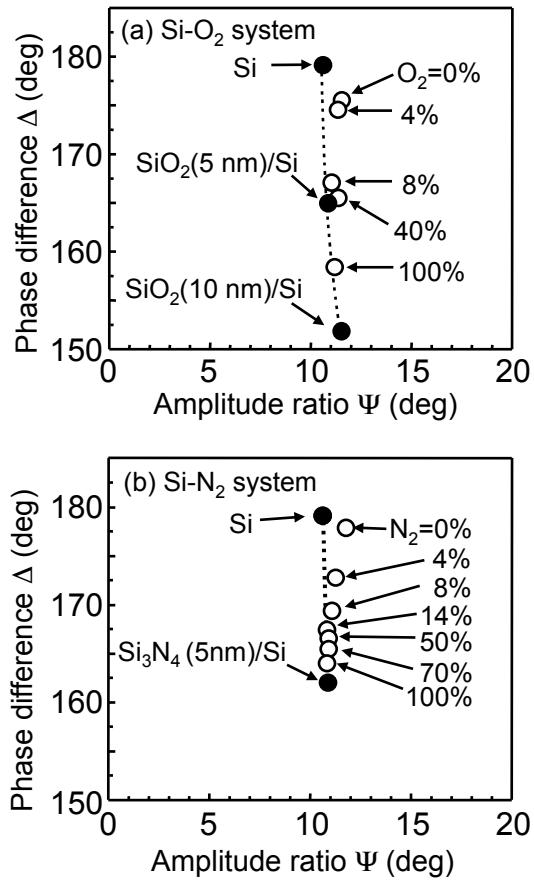


Fig. 2

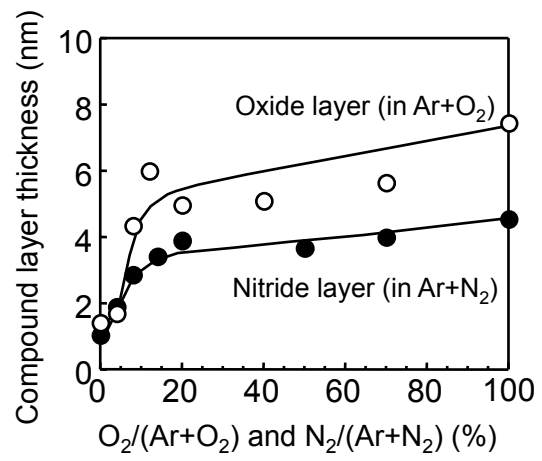


Fig. 4

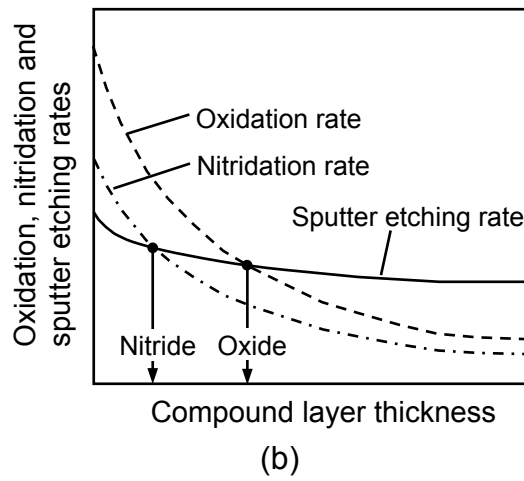
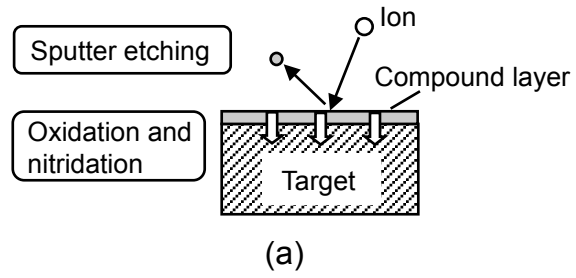


Fig. 5