Target surface oxide layer formed by reactive sputtering of Ti target in $Ar+O_2$ mixed gas

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Reactive sputtering is one of the most widely used techniques for preparing compound thin films. In this study, a Ti model target, a 1 μm thick Ti film sputter deposited on a Si wafer, was used as the sputtering target. The thickness of the oxide layer formed on the surface of the model target after sputtering in an $Ar+O_2$ mixed gas atmosphere was measured by ellipsometry under various varying processing parameters including oxygen flow ratio, sputtering time, rf power, and total gas pressure. The oxide layer thickness was varied from a few nanometers to approximately 100 nm by changing the parameters, and a nonuniform oxide layer thickness was observed on the target surface. © *2005 American Vacuum Society.* [DOI: 10.1116/1.2006135]

I. INTRODUCTION

Reactive sputtering is one of the most widely used techniques for preparing compound thin films by sputtering metal targets in an active gas atmosphere.[1,2] It is well known that compound layer formation on the surfaces of the sputtering targets is very important in reactive sputtering. The change on the target surface from a metal target mode to a compound target mode has a remarkable effect on the deposition rate and chemical composition of the deposited films. Different models of reactive sputtering have been proposed by Berg *et al.*,[3] Jonsson *et al.*,[4] and Berg and Nyberg[5] to explain the relationships between the processing parameters. From a practical viewpoint, a high deposition rate is desirable. However, compound layer formation at the target surface 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 a high rate of sputter deposition, some techniques of reactive sputtering under a metallic target mode have been reported.[6–9] In spite of the importance of information on the target surface state, quantitative studies have been relatively scarce thus far. Oxide layer thicknesses of several nanometers were reported by Heller[10] for a $Fe-O_2$ system using plasma monitoring and by Jonsson *et al.*[11] for an $Al-O_2$ system using target voltage measurement, and nitride layer thicknesses of a few nanometers were reported for $Ti-N_2$ systems.[12,13] However, a much thicker oxide layer of about 100 nm was reported by Maniv and Westwood[14] for an $Al-O_2$ system considering the etching rate and etching time of the oxide layer, and by Kusano and Kinbara[15] for a $Ti-O_2$ system considering the O_2 mass balance. In addition to the experimental studies, several nanometers of target surface oxide layers were reported by recent simulation studies using a dynamic Monte Carlo program (TRIDYN) for $Al-O_2$ systems.[16,17] This large discrepancy between the thicknesses reported for the surface compound layers has not been studied in detail.

TiO_2 films have attracted much attention for optical, electrical, and environmental applications because of their high refractive index, high dielectric constant, and photocatalytic properties. Furthermore, a target mode change from a metallic mode to an oxide mode was clearly observed for the $Ti-O_2$ system,[18–20] making it suitable for studying the target surface state. In our previous article,[21] the thickness of the oxide layer formed at the surface of a Ti target by sputtering in an $Ar+O_2$ mixed gas was measured by ellipsometry, and oxide layer thicknesses of several nanometers were obtained. The purpose of this article is to clarify the effects of the processing parameters, including oxygen flow ratio, sputtering time, total gas pressure, and rf power, on the oxide layer thickness in more detail.

II. EXPERIMENT

Ti and TiO_2 films were deposited by rf magnetron sputtering on Corning No. 7059 glass substrates. A Ti (99.99% purity) target of 50 mm diameter and 5 mm thickness was used for the thin film deposition and plasma emission measurements. A Ti model target, a 1 μm thick Ti film sputter deposited on the surface of a Si wafer, was used as the sputtering target for the measurement of surface oxide layer thickness because a sample with a flat surface is necessary for ellipsometry. The model target was attached to a water-cooled Cu backing plate by: (1) mechanically clamping or (2) bonding using Ag paste. A mixed gas of Ar and O_2 was used for the sputtering, and the O_2 flow ratio and total gas pressure were varied from 0% to 100% and from 0.7 to 7 Pa, respectively. The total gas flow rate was fixed at 5 cm^3/min. The flow rates of Ar and O_2 gases were controlled by mass flow controllers, and the total pressure was measured by a capacitance manometer. Rf power was varied from 30 to 100 W. The distance between the substrate and the target was fixed at 55 mm, and no intentional substrate heating was carried out.

The oxide layer thickness formed at the surface of the model target was measured by ellipsometry with a He–Ne laser (633 nm) and by reflectance measurements in a wave-

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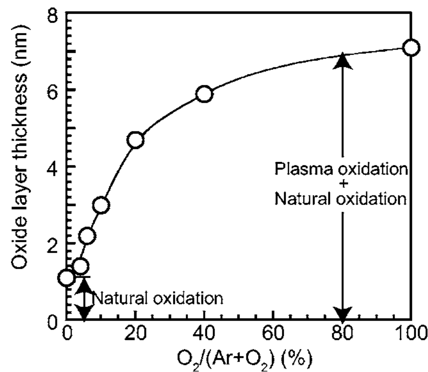

FIG. 1. Thickness of the surface oxide layer formed on the Ti model target as a function of the O_2 flow ratio. Rf power, total gas pressure, and sputtering time were kept constant at 50 W, 0.7 Pa, and 5 min, respectively, and ellipsometry measurements were carried out at the target center. The Ti model target was mechanically clamped to a water-cooled Cu backing plate.

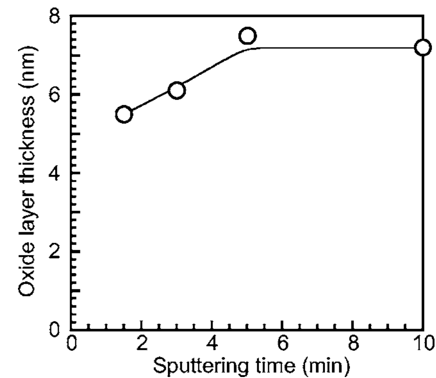

FIG. 2. Thickness of the surface oxide layer formed on the Ti model target as a function of sputtering time. The O_2 flow ratio, rf power, and total gas pressure were kept constant at 100%, 50 W, and 0.7 Pa, respectively, and ellipsometry measurements were carried out at the target center. The Ti model target was mechanically clamped to a water-cooled Cu backing plate.

length region between 350 and 800 nm. It is assumed that a thin layer of TiO_2, which is the most stable oxide of Ti, is formed at the surface of the Ti model target after sputtering. The refractive index, n, and extinction coefficient, k, of the Ti and TiO_2 layers are assumed to be $n=2.95$ and $k=3.75$ for Ti, and $n=2.6$ and $k=0$ for TiO_2, respectively.[21] Plasma conditions during sputtering were evaluated by plasma emission spectroscopy.

III. RESULTS AND DISCUSSION

First, the change in deposition rate and plasma emission intensity of oxygen atoms with O_2 flow ratio was studied at constant rf power and total gas pressure of 50 W and 0.7 Pa, respectively.[21] At low O_2 flow ratios, a high deposition rate of approximately 5 nm/min was obtained, and the deposition rate decreased abruptly to 0.4 nm/min above a critical O_2 flow ratio of 7%. The plasma emission intensity (777 nm) of oxygen atoms began to increase above the critical O_2 flow ratio. Corresponding to the change in the deposition rate and the plasma emission intensity, the film properties changed from metallic to insulating and transparent, which indicates that metal Ti films were formed below the critical O_2 flow ratio and TiO_2 films were formed above it. Similar results have been observed for reactive sputtering of a Ti target in an $Ar+O_2$ mixed gas, and are considered to be caused by the target mode change from a metallic target mode to an oxide target mode.[18–20]

Next, the thickness of the oxide layer formed at the target surface was studied by reflectance measurements and ellipsometry. Figure 1 shows the oxide layer thickness on the surface of the Ti model target measured by ellipsometry as a function of the O_2 flow ratio. At oxygen flow ratios of 0% and 4%, the oxide layer thickness is approximately 1 nm, which is thought to be caused by natural oxidation after the samples were taken out from the sputtering chamber because native oxide with thicknesses of 1–2 nm were reported for Ti–W alloy and Bi films.[22] The oxide layer thickness increases from 2 nm at an O_2 flow ratio of 6% to 7 nm at an oxygen flow ratio of 100%. This increase in the oxide layer thickness is thought to be caused by plasma oxidation. Good agreement was obtained between TiO_2 thicknesses estimated from ellipsometry and reflectance measurements (results are not shown). Furthermore, the oxide layer thicknesses of 2–7 nm agree well with those (several nanometers) reported by Heller,[10] Jonsson *et al.*,[11] and the simulation studies[16,17] in spite of the difference of target materials. It can be concluded that the deposition rate decreases abruptly on the formation of the surface oxide layer with a thickness of only a few nanometers.

Figure 2 shows the oxide layer thickness as a function of sputtering time. Though the oxide layer thickness decreases slightly at short times, no remarkable change is observed from 5 to 10 min. Since the transition times for the target mode change were reported to be several tens of seconds,[23,24] the oxide layer thickness can be supposed to reach a steady state within a similar time frame. Fluctuations in the total pressure within the sputtering chamber after forming a glow discharge due to the gettering effect may affect the experimental results in the short time region of 1.5–3 min in Fig. 2 affecting the oxide layer thickness.

Figure 3 shows the oxide layer thickness as a function of rf power. The oxide layer thickness values are in the range of 5–15 nm when the Ti model target was bonded to the water cooled Cu backing plate using Ag paste. Though higher plasma densities are expected at higher rf power conditions, no major effects on oxide layer thickness were observed. However, the oxide layer thickness increased up to approximately 100 nm at a rf power of 100 W when the Ti model target was clamped mechanically to the water cooled Cu backing plate. This is likely due to the fact that the Ti model target was not cooled sufficiently by the mechanical clamping at high rf powers, whereas the target was fully cooled by using Ag paste for bonding. The thicker oxide layer for the mechanical clamped target is thought to be formed due to the increase in target temperature, which enhances the oxidation rate. The maximum oxide layer thickness of 100 nm is close to that reported by Maniv and Westwood,[14] and Kusano and Kinbara.[15]

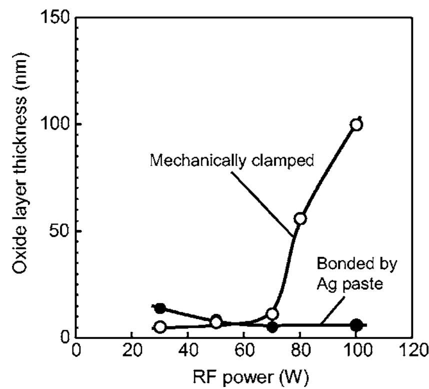

FIG. 3. Thickness of the surface oxide layer formed on the Ti model target as a function of rf power. The O_2 flow ratio, total gas pressure and sputtering time were kept constant at 100%, 0.7 Pa, and 5 min, respectively, and ellipsometry measurements were carried out at the target center. The Ti model target was either mechanically clamped or bonded using Ag paste to a water-cooled Cu backing plate.

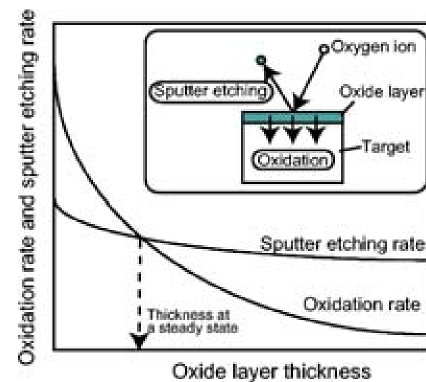

FIG. 5. Schematic diagram of the sputtering rate and the oxidation rate as functions of oxide layer thickness formed on the target surface (see Ref. 10).

A magnetron cathode, which was used in this study, confines electrons using a magnetic field and generates a high density plasma in the erosion region, which is the area sputtered faster than the other area. Figure 4 shows the oxide layer thickness after sputtering for total gas pressures of 0.7, 3, and 7 Pa in pure O_2 gas as a function of the distance (x) from the target center. The oxide layer thickness shows a minimum in the erosion region, $x=10-15$ nm. Though the oxide layer thickness remains nearly constant in the erosion region, it increases with increasing total gas pressure at the center of the target and the outer part of the erosion region.

At the surface of the sputtering target, oxygen ions impinge on the target surface and induce oxidation of the Ti target. In addition, the oxygen ions sputter etch the target surface simultaneously. Figure 5 shows the sputter-etching rate and the oxidation rate as functions of the oxide layer thickness proposed by Heller.[10] If the oxidation rate is higher than the sputter-etching rate, oxidation of the target surface is dominant. With increasing oxide layer thickness, the oxidation rate decreases and the oxide layer thickness reaches a steady state at a thickness where oxidation rate equals the sputter-etching rate. If the oxidation rate increases and the sputter-etching rate remains constant due to an increase in the target temperature, the steady-state oxide layer thickness is expected to increase as shown in Fig. 3. At high sputtering gas pressures, the mean free path of the sputtered particles decreases and a portion of the particles sputtered from the erosion region returns to the center of the target and the outer part of the erosion region, which is expected to cause a decrease in effective sputtering rate. The densities of the oxidizing species, such as excited and ionized oxygen molecules and atomic oxygen, may increase at high pressures, and the oxidation rate is expected to be enhanced. A low sputtering rate and a high oxidation rate can explain the thicker oxide layer formed at the center of the target and the outer part of the erosion region shown in Fig. 4. If the sputtering rate is higher than the oxidation rate, the oxide layer thickness decreases and finally the target surface returns to a metallic state.

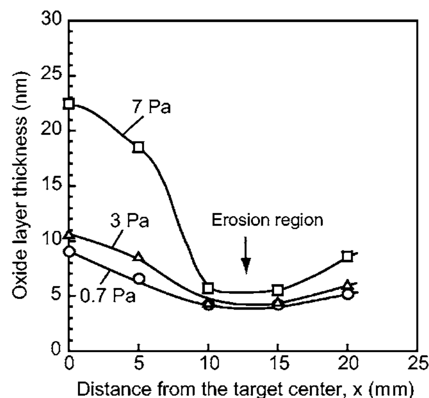

FIG. 4. Thickness of the surface oxide layer formed on the Ti model target for total gas pressures of 0.7, 3, and 7 Pa as functions of the distance from the target center. rf power, O_2 flow ratio, and the sputtering time were kept constant at 50 W, 100%, and 5 min, respectively. The Ti model target was bonded to a water-cooled Cu backing plate using Ag paste.

IV. CONCLUSIONS

The thickness of the oxide layer formed on the surface of a Ti target was estimated by ellipsometry. The oxide layer thickness varied from a few nanometers to approximately 100 nm by changing some of the processing parameters. An oxide layer thickness of only a few nanometers was found to cause a drastic decrease in the deposition rate. An increase in the target temperature is suggested to increase the oxidation rate and increase the oxide layer thickness. A nonuniform oxide layer thickness was also observed on the target surface.

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