Structure of MgO Films Prepared by Ion Beam Sputtering

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イオンビームスパッタリングにより作製した MgO 膜の構造

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Preferred orientation and microstructure of MgO films prepared by ion beam sputtering were investigated. The crystallographic orientation of MgO films was a function of the substrate angle (δ), O_2 gas partial pressure (P_{O_2}) and the substrate temperature (T_s). As δ changed from 90° to 0° , the transmission electron diffraction (TED) pattern of the films deposited in P_{O_2} of 1×10^{-4} Torr at $T_s = R. T.$ changed from a random orientation to the (111) preferred orientation in which the crystallographic (111) plane was parallel to the substrate surface. An increase in P_{O_2} from 0.1×10^{-4} to 10×10^{-4} Torr caused the (111) preferred orientation. At $T_s > 100^\circ C$, the TED pattern of the films on NaCl (200) deposited with $\delta = 90^\circ$ showed epitaxial growth in contrast with a random orientation at $T_s < 100^\circ C$. Annealing below $500^\circ C$ did not change the orientation and size of the crystallite. Annealing above $1000^\circ C$ for 30 min, however, caused crystallite growth from 5 nm to 20 nm without any change in orientation. This size is still smaller than that of the crystallites deposited on a heated substrate. The origin of the crystallographic preferred orientation of the MgO thin film deposited by ion beam sputtering was explained in terms of the growth competition. The (111) preferred orientation becomes predominant in the growth competition over others with decreasing the arrival ratio of Mg/O.

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1. Introduction

MgO film has recently been investigated⁽¹⁾⁻⁽⁹⁾ with special attention to the excellent high temperature chemical stability, electrical insulating property, optical property and thermal conductance. Many electron and X-ray diffraction investigations have shown that the crystal orientation of vapor deposited MgO films depends on deposition process.

Chemical vapor deposition (CVD) processes⁽¹⁾ have been developed using organometallic compounds for depositing MgO. The crystallite of MgO films deposited at $310^\circ C$ or above by CVD was found to possess a (200) preferred orientation in which the crystallographic (200) plane is parallel to the substrate surface.

The crystal orientation of MgO films by thermal evaporation onto amorphous and single crystal substrates varied with film thickness. According to the studies by Aboelfotoh et al. on amorphous substrates, the MgO films initially nucleate in a random orientation. As the film thickness increases, a (111) preferred orientation develops on the surface.^{(2), (3), (5)} On single crystal substrates, the orientation of crystallite in thin films (below 3 nm) depends on the crystal face and temperature of the substrates. In the range of thickness from 3 to 50 nm, the crystallite tends to

orient randomly, and in thick films (above 50 nm) the surface structure has a (111) preferred orientation independent of the substrate orientation and temperature.^{(4), (6)}

MgO film formed by rf-sputtering of MgO target was found to have a strong tendency to form a columnar structure of the (200) orientation normal to the substrate. However, by decreasing the sputtering pressure less oriented coatings of denser structure can be obtained at a moderate temperature.^{(7), (8)}

Reactive ion beam sputter deposition (RIBSD) method⁽⁹⁾ using a magnesium target was found to produce smooth MgO film dielectrics with low electrical loss, good mechanical stability, and excellent reproducibility.⁽⁹⁾ This technique has received attention with respect to the low temperature production of ceramic thin films for recent ten years. However, microstructure and preferred orientation of the MgO film deposited by RIBSD have not been investigated yet, although these are the important aspects of the thin film.

In this study, we report on the influence of preparation conditions of MgO films on the crystallographic orientation and on the microstructure of the film in comparison with the previously reported results.

2. Experimental

MgO films were prepared by a Koon Denki ion beam sputtering apparatus. The apparatus and preparation condition were described in Fig. 1 and Table 1. The magnesium target was a metallic disk of 4 N grade with 100 mm diameter and 5 mm thickness. Argon ion beam generated in a Kaufman-type ion gun was accelerated to 4-5 kV energy with 10-12 mA current and sputtered the target at an incident angle of 30° . The target was located at a distance of 200 mm from the acceleration grids of the 40 mm-diameter ion source. An aluminum plate with a 40 mm-diameter hole was placed between the ion gun and the target to

Table 1. Deposition conditions.

Target	Mg(99.99%) 100 ϕ X 5T
Ar ⁺ ion beam	
pressure	1.0×10^{-4} Torr
accelerated voltage	4-6 kV
current	10-12 mA
spot size	elliptic with its major axis
on the target	of about 60mm and its minor
	axis of about 50mm
Reaction gas	
pressure	0.1×10^{-4} , 1.0×10^{-4} , 10×10^{-4} Torr
Substrate	
material	collodion membrane, NaCl(200)
temperature	R.T., 100, 200, 300°C

Fig. 1. Schematic diagram of the ion beam sputtering apparatus and relationship between δ and incident ion beam. 1: substrate heater; 2: thickness monitor; 3: Pirani gauge; 4: Penning's gauge; 5: molecular turbo pump; 6: rotary pump

reduce the ion beam spread. The ion beam spot on the target was elliptic with its major axis of about 60 mm and its minor axis of about 50 mm. The sputtering chamber was once evacuated to a pressure of 2×10^{-6} Torr, and then argon gas was introduced to a pressure of 1×10^{-4} Torr. During the deposition, oxygen gas was also introduced to the partial pressure (P_{O_2}) between 0.1×10^{-4} - 10×10^{-4} Torr. The resulting deposition rates were 0.05-0.3 nm/min. Film thickness was determined from crystal quartz thickness monitor readings. The thickness was 20-30 nm. The substrates used were collodion membrane on a Pt mesh and cleaved single crystal NaCl (200). The substrates were placed at an angle of 30° from the target normal and on the incident plane of the ion beam. The incident angles of sputtered particles measured from the substrate surface (or the substrate angle δ) were chosen to be 0° , 60° and 90° . In Fig. 1, δ is illustrated to be 90° . The distance between the target and the substrate was adjusted to be 50-70 mm. The substrate temperature (T_s) during film deposition was set at a room temperature (R.T.), 100° , 200° and 300°C . The microstructure and the crystallographic orientation of the MgO film were examined by an analytical electron microscope (JEOL 2000 FX). Possible impurities in the MgO films originated from the ion source, the aluminum plate and the other part of the apparatus such as the target holder were not detected by EDX detector. The reason why the impurities originated from the ion source were not detected is because of the use of a carbon electrode for a rf-electrode and an acceleration electrode.¹⁰⁾ The reason why the impurities originated from the hole edge of the aluminum plate were not detected is probably because of the low sputtering yield of an aluminum atom by an argon ion beam and the low current density of an argon ion near the aluminum hole edge.

3. Results

3.1 The effect of substrate angle on the diffraction patterns

Figure 2 shows the transmission electron diffraction (TED) patterns of films deposited on collodion membrane at $T_s = \text{R.T.}$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and each δ . All the diffraction patterns were not spots but continuous rings, indicating that the films consist of fine crystals. It is clear from these diffraction patterns that the crystallite orientation changes with δ . At $\delta = 0^\circ$ the TED pattern (Fig. 2(a)) showed a strong (220) diffraction ring and weak (111) and (200) diffraction rings. At $\delta = 60^\circ$ the relative intensity of the (111) and (200) diffraction rings (Fig. 2(b)) became

Fig. 2. TED patterns of MgO film deposited on collodion membrane at $T_s = R. T.$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and δ (a) 0° , (b) 60° and (c) 90° , (d) schematic representation of the diffraction pattern, (e) TED pattern of MgO fine powder.

Fig. 3. The relationship between TED patterns and preferred orientations in the case of face-centered cubic lattice.

stronger than in Fig. 2(a). At $\delta = 90^\circ$ the relative intensity of the diffraction rings (Fig. 2(c)) approached those of the random orientation such as MgO fine powder as shown in Fig. 2(e). Figure 3 shows the relationship between TED patterns and preferred orientations in the case of the face-centered cubic lattice. From Fig. 3 the MgO film of the TED pattern (Fig. 2(a)) is known to possess a (111) preferred orientation. On a cleaved NaCl (200) substrate, the TED patterns showed the same tendency. Therefore, the crystallographic orientation at $T_s = R. T.$ is not affected by substrates.

3.2 The effect of O_2 gas partial pressure on the diffraction patterns

Figure 4 shows TED patterns of films deposited on collodion membrane at $\delta = 60^\circ$, $T_s = R. T.$ and each P_{O_2} . At $P_{O_2} = 0.1 \times 10^{-4}$ Torr the TED pattern (Fig. 4(a)) showed diffraction rings assigned to a random orientation. On the other hand, in the TED pattern (Fig. 4(b)) of the film deposited at $P_{O_2} = 1.0 \times 10^{-4}$ Torr, the relative intensity of the (200) diffraction ring decreased, while that of the (220) diffraction ring increased. Further, at $P_{O_2} = 10 \times 10^{-4}$ Torr, only the (220) diffraction ring was observed. These results suggest that as P_{O_2} increases, the TED pattern changes from a random orientation to the (111) preferred orientation.

3.3 The effect of substrate temperature on the diffraction patterns

Figure 5 shows the TED patterns of films deposited on a cleaved NaCl (200) surface at $\delta = 60^\circ$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and each T_s . At $T_s = R. T.$ the TED pattern showed only diffraction rings assigned to a random orientation of crystallite as mentioned before. The TED pattern changed with increase in T_s . At $T_s = 100^\circ C$ the TED pattern showed both diffraction rings and spots. And then at $T_s = 200^\circ C$, the TED pattern

Fig. 4. TED patterns of MgO film deposited on collodion membrane at $T_s = R.T.$, $\delta = 60^\circ$ and P_{O_2} (a) 0.1×10^{-4} , (b) 1.0×10^{-4} and (c) 10×10^{-4} Torr.

Fig. 5. TED patterns of MgO film deposited on NaCl (200) at $\delta = 60^\circ$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and T_s (a) R.T., (b) 100°C , (c) 200°C and (d) 300°C , (e) interpretation of the diffraction pattern (d).

showed the diminution of diffraction rings, and further at $T_s = 300^\circ\text{C}$ it showed only diffraction spots. The TED pattern (Fig. 5(d)) shows epitaxial growth of MgO films on NaCl (200). From these results it is confirmed that the interaction between the substrate and MgO molecules becomes weak with T_s and then film grows epitaxially.

3.4 The effect of annealing of deposited film on the structure

The change of the preferred orientation and the crystallite size of the films subjected to the

annealing was examined. Figure 6 shows the TED patterns and high resolution electron microscope (HREM) images obtained from the film (a) at $\delta = 0^\circ$, $T_s = R.T.$ and $P_{O_2} = 1.0 \times 10^{-4}$ Torr deposited on collodion membrane and the films annealed for 30 min in air at (b) 500°C and (c) 1000°C . The as-deposited film appeared to be a continuous sheet, the average crystallite size being about 5 nm. The continuous rings of the TED patterns in Fig. 2 are attributed to these fine crystallites showing the (111) preferred orienta-

Fig. 6. HREM images and TED patterns of MgO film (a) deposited at $T_s = \text{R. T.}$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and $\delta = 60^\circ$, (b) annealed at 500°C , (c) annealed at 1000°C for 30 min in air and (d) deposited on cleaved NaCl (200) at 300°C . All micrographs in this figure are presented to the same magnification.

tion. The 500°C annealing did not cause any change in TED pattern. The HREM image showed that crystallite size did not change. However, Fig. 6(c) shows the 1000°C annealing caused no change in crystallographic orientation but a change from a continuous ring to a discrete ring. This change of the ring shape arises from the growth of the crystallite up to 20 nm in size which is observed in the HREM image in Fig. 6(c). The microstructure of the film annealed at 1000°C was different from the one deposited on cleaved NaCl (200) at $\delta = 60^\circ$, $P_{O_2} = 1.0 \times 10^{-4}$ Torr and $T_s = 300^\circ\text{C}$ (Fig. 6(d)).

4. Discussion

The (200) preferred orientation appeared in CVD or rf-sputtering MgO films has been explained by the Bravais's rule,^{1,7)} that is, the crystal orientation of a minimum energy configuration takes place. The (111) preferred orientation appeared in thermally evaporated films has been considered to be caused by the growth competition between differently oriented crystals.⁵⁾ The growth competition is due to the differences in the number of ions or molecules

condensing on differently oriented crystals. For example, the condensation rate on $\langle 111 \rangle$ oriented crystals is higher than that on $\langle 200 \rangle$ oriented crystals when the ions or molecules arrive at the substrate at the rate of 130–150 nm/min.⁵⁾

The (111) preferred orientation observed in the present experiment can be also explained by the growth competition scheme, judging from the resemblance of the δ dependence of the crystal orientation to its P_{O_2} dependence. The (111) preferred orientation took place at a small δ and a high P_{O_2} ; both of which are connected with the low value of the arrival ratio of Mg/O as shown in Fig. 7. The oxygen excess acts to the advantage of $\langle 111 \rangle$ oriented crystallites in the growth competition through the following mechanism; The creation ratio of crystalline nuclei with low surface free energy is larger than that of crystalline nuclei with high surface free energy as the magnesium particles energy lowers. The magnesium particles lose some of their excess energy by transferring it to the excess oxygen. $\langle 111 \rangle$ oriented crystallites develop in the growth competition as a (111) plane has minimum

Fig. 7. Schematic diagram of relationship between crystallite orientation, δ and P_{O_2} .

surface free energy. A similar result is found in the dynamic mixing method,¹¹⁾ that is, the preferred orientation of TiN films is dependent on the arrival ratio, Ti/N on the substrate. In their paper, it is considered that the variation of orientation arises from the variation of the energy deposition rate from the ion beam per a titanium atom. The energy deposition rate is determined by the arrival ratio. In this experiment, it is not clear whether the same energy deposition takes place in the low energy particles system. But, the change of preferred orientation with the arrival ratio resembles Sato's result.¹¹⁾

The small δ and high P_{O_2} are also connected with the low deposition rate, the former through the geometrical $\sin \delta$ scheme and the latter through the low sputtering rate of the oxidized target surface. The low deposition rate may act to the advantage of $\langle 111 \rangle$ oriented crystallites in the growth competition. But we don't think that the (111) preferred orientation arises only from the low deposition rate. If the (111) preferred orientation is caused by the low deposition rate, the size of crystallites should become large with decreasing the deposition rate. As shown in Fig. 6(a), however, all the films of the present experiment consisted of small crystallites regardless of both δ and P_{O_2} .

We deny the possibility that high energy species involved in this RIBSD process (such as energetic neutralized argons) might affect the

preferred orientation because no trace of the argon was detected in the film by the analytical electron microscope.

5. Conclusion

The orientation of MgO films prepared by ion beam sputtering was strongly influenced by the substrate angle (δ), O_2 gas partial pressure (P_{O_2}) and the substrate temperature (T_s). As δ changed from 0° to 90° , the TED pattern of the films changed from the (111) preferred orientation to a random orientation. As P_{O_2} increased from 0.1×10^{-4} to 10×10^{-4} Torr, the TED pattern changed from a random orientation to the (111) preferred orientation. At $T_s > 100^\circ\text{C}$, the TED pattern of the films on NaCl (200) showed epitaxial growth in contrast with a random orientation at $T_s < 100^\circ\text{C}$. Annealing below 500°C did not change the orientation and size of the crystallite. Annealing above 1000°C , however, caused crystallite growth from 5 nm to 20 nm in size without any change in orientation. This size is still smaller than that of the crystallites deposited on a heated substrate. The Mg/O ratio on the substrate at $T_s = R. T.$ was considered to be the most important factor to affect the crystallographic orientation of the MgO thin film.

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