Low Temperature Preparation of TiO₂ Thin Films by Plasma-Enhanced Chemical Vapor Deposition

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プラズマ CVD 法による TiO₂ 薄膜の低温合成

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Thin films of TiO₂ were prepared from gas mixtures of TiCl₄ and O₂ using rf glow discharge. TiO₂ films were grown on glass, Si, Ti and MgO substrates at temperatures as low as 200°C by applying an rf power of 10 W, although no film was deposited without glow discharge even at 470°C except on the Ti substrate. As the rf power was increased, the deposition rate increased and attained the maximum value which was more than five times as large as the initial deposition rate, but decreased in applying excessive rf powers. TiO₂ crystals of anatase phase were grown at temperatures lower than those for growth of rutile phase. The temperature at which the rutile phase formed depended on the substrate material. Rutile films which were grown on MgO (100) at temperatures above 300°C exhibited highly [110]-oriented crystal growth. For these films, the surface morphology and the degree of the orientation of polycrystallites in the [110] direction depended on the rf power.

Key-words: TiO₂ thin film, Plasma-enhanced CVD, Anatase, Rutile, Deposition rate, Crystal orientation, Surface morphology

1. Introduction

Titanium dioxide (TiO₂) is suitable for optical coating materials due to its high refractive index and excellent optical transmittance. It also possesses a high dielectric constant, and thus TiO₂ thin films have been studied for the dielectric layer of metal-insulator-semiconductor (MIS) structures or storage capacitors in microelectronics.¹⁻³⁾ TiO₂ is one of the best materials for the photoelectrolysis of water,⁴⁾ which causes interest in TiO₂ films for solar energy conversion.^{5,6)}

TiO₂ thin films have been prepared using several techniques such as reactive evaporation,^{7,8)} sputtering^{9,10)} and chemical vapor deposition (CVD).^{11,12)} Among these techniques, the CVD method is superior in a film deposition rate and uniformity of deposited layer over uneven surfaces. However, in the conventional CVD it is usually necessary to heat substrates up to relatively high temperatures. In practice, at temperatures below 500°C TiO₂ films can not be prepared from TiCl₄ and O₂ at reson-

able growth rates.¹¹⁾

If plasma is applied in CVD, source molecules or atoms collide with high-temperature ($\sim 10^4$ K) electrons,¹³⁾ and then reactive species such as excited molecules, excited atoms, radicals and ions are generated. Therefore, it is expected that the films of not only amorphous but also crystalline TiO₂ can be prepared at lower temperatures by plasma-enhanced CVD than by the conventional CVD.¹⁴⁾ It is also hopeful that well-controlled crystal growth of TiO₂ can be obtained at low temperatures by using plasma since highly oriented or epitaxial ZnO films have been grown at relatively low temperatures by plasma-enhanced CVD.¹⁵⁾

The present paper describes the effects of plasma application on the deposition temperature, the deposition rate, crystal structure and surface morphology of TiO₂ films prepared from TiCl₄ and O₂. Highly oriented crystal growth at low temperature is also described.

2. Experimental

TiO₂ thin films were prepared by plasma-enhanced CVD using TiCl₄ and O₂ as source gases. Figure 1 shows a schematic diagram of the plasma-enhanced CVD apparatus used in this study. The apparatus is a cold-wall type. The reactor chamber is constructed of quartz. The base pressure was about 5×10^{-6} Torr. TiCl₄ gas was supplied by vaporizing

Fig. 1. Schematic diagram of the plasma-enhanced CVD apparatus.

liquid TiCl_4 in a quartz flask which was held at 45°C in a water bath. No carrier gas was used for the supply of TiCl_4 . The supply line was heated to 60°C . Flow rates of TiCl_4 and O_2 were regulated with mass flow controllers in the range of 0.5–2.5 and 0.5–4.0 ml/min, respectively. Gas pressure is monitored with a capacitance manometer (MKS, Baratron 127A). The gas pressure increased from 0.04 to 0.07 Torr with an increase in the gas flow rates. TiCl_4 gas was mixed with O_2 gas, and then introduced into a space between two parallel-faced electrodes through the nozzles which were arranged by hollowing the bottom face of the top electrode at equal intervals.

Glow discharge was generated between the top and the bottom electrodes by applying radio frequency (rf) power. The distance between these electrodes is 4 cm. The operating frequency is 13.56 MHz. The bottom electrode with a diameter of 10 cm is grounded. Substrates were mounted on the bottom electrode, which was heated with a resistance heater. Substrate temperature was controlled in the range of 150°C to 600°C .

Glass (Corning, 7059), polycrystalline Ti, Si(100), Si(111) and MgO(100) were used as substrates. The substrates were cleaned in argon or oxygen plasma for 2–5 min before introducing source gases.

Crystallographic features of the films were evaluated with an X-ray diffractometer (Rigaku, RINT 1200) using $\text{Cu K}\alpha$ radiation. Surface morphology of the films was investigated with a scanning electron microscope (Hitachi, S-530). Deposition rate was determined from deposition time and film thickness which was measured using a stylus step gauge (Rank Taylor Hobson, Talystep).

3. Results and discussion

3.1 Deposition rate

TiO_2 films formed on every substrate at temperatures as low as 200°C by applying an rf power of 10 W. Without glow discharge, no film could be deposited on glass, Si or MgO substrate even at 470°C . In the case of Ti substrate, however, TiO_2 films were grown on it at 400°C without glow discharge. Their deposition rate was about one order of magnitude less than that of the films prepared using rf glow discharge. This indicates the positive effect of plasma application on the growth of TiO_2 films. When using rf glow discharge, the deposition rates of TiO_2 films were independent of substrate material, and increased scarcely with increasing temperature from 200°C to 500°C .

The dependence of the deposition rate on the rf power is shown in Fig. 2. In the range of low rf power, the deposition rate increases with an increase in the rf power. At any gas flow rate, the deposition rate decreases for excessive rf powers. This decrease is probably due to the following reasons: (1) the homogeneous formation of TiO_2 particles in the vapor phase exceeds the film growth on the sub-

Fig. 2. Dependence of the deposition rate of TiO_2 films on rf power. The films were deposited on MgO(100) at 470°C . Gas flow rates and total pressure were, ●: 0.5 ml/min (TiCl_4), 1.0 ml/min (O_2), 0.045 Torr; ○: 1.0 ml/min (TiCl_4), 2.0 ml/min (O_2), 0.07 Torr.

strate surface, (2) chemical etching of the film surface by ions or radicals, (3) mechanical sputtering of the film surface by high-energy particles. The TiO_2 films which had been deposited on MgO or Si substrates were sputtered at the rate of 0.7–2.4 nm/min in oxygen plasma at an rf power of 100 W. This sputtering rate is much smaller compared with the decrease in the deposition rate. The films may be sputtered at larger rates during the deposition because there are many weak bonds at the growing surface.

3.2 Crystalline phase of the deposited film

Crystalline TiO_2 exists in three phases: rutile, anatase and brookite. Among them rutile is the most stable phase. Amorphous films and crystalline films of rutile or anatase phase were obtained in this study. Figure 3 shows X-ray diffraction (XRD) patterns of TiO_2 films prepared with rf glow discharge. The crystalline phases of the films are summarized

Fig. 3. XRD patterns of (a) TiO_2 powder of rutile phase, (b) TiO_2 film on MgO(100) and (c) TiO_2 film on glass. Substrate temperature: 470°C , rf power: 50 W, R: rutile, A: anatase.

Table 1. Crystalline phase of the TiO₂ film deposited at an rf power of 10 W.

T _s	Substrate material			
	Glass	Si	Ti	MgO
200	N	N	A	N
300	A	A	A	R and A
400	A	A	R and A	R
500	A	A	R	R
600		A and R	R	R

T_s: substrate temperature (°C). N: no peak (amorphous).

A: anatase, R: rutile.

in Table 1. Films deposited at 200°C except on the Ti substrate are amorphous, and all films deposited at temperatures above 300°C are crystalline. The anatase phases were obtained at lower temperatures. The temperature at which rutile phase formed was dependent on the substrate material, but almost independent of the rf power.

The XRD pattern of the film deposited at 300°C on the (100) plane of MgO contained two strong peaks which were attributed to (110) and (220) of rutile, and a small one which was attributed to anatase (200). As shown in Fig. 3 (b), all the crystals which were grown on MgO(100) at temperatures above 400°C were rutile phase and highly oriented.

In regard to the deposition on glass, Si and Ti substrates, the temperature at which rutile crystals form is consistent with the result by Williams and Hess.¹⁴⁾ Most of anatase crystals which were deposited on glass or Si substrates showed random orientation. No difference was found between the crystal growth on Si(100) and on Si(111). The interaction between the TiO₂ crystal and the substrate Si lattice is probably weak since the surface of the substrate is easily oxidized in oxygen plasma and covered with SiO₂ thin layer even at the beginning of the film deposition.

Rutile crystals were grown on the Ti substrate at lower temperatures than on glass or Si substrate. There were some rutile crystals in the oxide layer of a Ti plate which was formed by exposing the plate to the oxygen plasma at 400°C. These fine rutile crystals may act as nuclei for the crystal growth of rutile when the film is deposited on Ti.

3.3 Crystal orientation and surface morphology

The crystal orientation and surface morphology have been investigated about the rutile films which were grown on MgO(100). As shown in Fig. 3(b), the [110] direction of polycrystallites is almost perpendicular to the substrate surface. The interplanar spacing for (110) planes of these rutile films was well consistent with the value reported in the powder diffraction file of JCPDS.¹⁶⁾ The distribution of the [110] direction of the crystals around the vertical axis to the substrate was evaluated with the X-ray rocking curve for the (110) peak. The dependence of the full width at half maximum (FWHM) of the rocking curve on the rf power is shown in Fig. 4. In

Fig. 4. Dependence of the full width at half maximum (FWHM) of X-ray rocking curves for the (110) peak on rf power. The films were deposited on MgO(100) at 470°C. Gas flow rates and total pressure were, ●: 0.5 ml/min (TiCl₄), 1.0 ml/min (O₂), 0.045 Torr; ○: 1.0 ml/min (TiCl₄), 2.0 ml/min (O₂), 0.07 Torr.

the case of lower gas flow rates, the width of the rocking curve is almost independent of the rf power, which indicates that well oriented crystals are grown at any rf power. When the gas flow rates are higher and the rf power is lower, the width of the rocking curve increases, which shows an increase in the fluctuation of the [110] direction of polycrystallites. Chemical etching, mechanical sputtering or enhancement of migration due to plasma application would play an important role in the crystal growth, as it removes the species adsorbed at irregular sites for lattice arrangement.¹⁷⁾ In the case of the high flow rates with low rf power, the source gas supply probably exceeds the removal rate of the species from the irregular sites, and consequently the crystal growth to the random orientation is not negligible.

The surface morphology of rutile films on MgO(100) varied greatly with an increase in the rf power. Figure 5 shows the surface appearance of these films observed by scanning electron microscopy. The grains are small at low rf power (Fig. 5(a)). Their size increases and becomes uniform as the rf power increases (Fig. 5(b)). However, the grain size decreases again at excess rf power (Fig. 5(c)). When the rf power is relatively high, as shown in Figs. 5(b) and (c), the grains are arranged with a preferred orientation as their edges are nearly parallel to the [011] or [0 $\bar{1}$ 1] direction of MgO (Fig. 5(b)), or to the [001] or [010] direction of MgO (Fig. 5(c)). The lattice mismatch between rutile (110) and MgO(100) is about 5 % when [001] of rutile is parallel to [001] of MgO, and about 9 % when [001] of rutile is parallel to [011] of MgO. Although these mismatches are comparatively large, there is still a possibility of the heteroepitaxial growth of TiO₂ on MgO(100), because the condition of the lattice matching is not so rigorous for ionic crystals.¹⁸⁾ The heteroepitaxial growth of rutile on MgO has been investigated using the conventional CVD at high temperatures with TiCl₄ and O₂.¹¹⁾ In that case, rutile (110) plane is parallel to MgO(100), and rutile [001] is parallel to MgO[011]. The results

Fig. 5. Scanning electron micrographs of the surface of rutile films deposited on MgO(100) at 470°C. rf power: 2 W (a), 20 W (b), 50 W (c). Gas flow rates: 0.5 ml/min (TiCl_4), 1.0 ml/min (O_2). Total pressure: 0.045 Torr.

Fig. 6. Dependence of the grain size for rutile films on rf power. The films were deposited on MgO(100) at 470°C. Gas flow rates and total pressure were, ●: 0.5 ml/min (TiCl_4), 1.0 ml/min (O_2), 0.045 Torr; ○: 1.0 ml/min (TiCl_4), 2.0 ml/min (O_2), 0.07 Torr.

in the present plasma-enhanced CVD as well as in the conventional CVD suggests that there exists some strong interaction between rutile crystals and the MgO surface. This interaction can be assisted by plasma which is effective for cleaning the substrate surface.

Figure 6 shows the dependence of the grain size on the rf power. In the case of high gas flow rates, the grain size varies greatly with an increase in the rf power. When gas flow rates are low, the grain size has a maximum value in the medium range of rf power, where the deposition rate is constant as shown in Fig. 2. The grain size is possibly affected by chemi-

cal etching, mechanical sputtering and migration of species. Furthermore, nucleation sites may increase at high rf power, which results in the decrease of the grain size.

4. Conclusions

TiO_2 thin films were prepared by plasma-enhanced CVD using TiCl_4 and O_2 as source gases. The rf glow discharge is effective in reducing deposition temperature. Films could be prepared on every substrate at temperatures as low as 200°C. The film deposition rate increased greatly with an increase in the applied rf power, but it decreased for excessive rf powers. Anatase phase crystals tended to grow on glass or Si substrate at temperatures below 500°C. Rutile phase crystals were easily grown on MgO(100) at temperatures above 300°C, and on Ti above 400°C. The temperature at which the rutile phase formed was scarcely influenced by the rf power.

The rutile crystals which were grown on MgO(100) were highly oriented with their (110) planes parallel to MgO(100). Plasma affected remarkably the crystal growth in preferred orientation and morphology especially when large amounts of source gases were supplied.

References

- 1) T. Fuyuki and H. Matsunami, *Jpn. J. Appl. Phys.*, **25**, 1288-91 (1986).
- 2) G. P. Burns, I. S. Baldwin, M. P. Hastings and J. G. Wilkes, *J. Appl. Phys.*, **66**, 2320-24 (1989).
- 3) T. Kamada, M. Kitagawa, M. Sibuya and T. Hirao, *Jpn. J. Appl. Phys.*, **30**, 3594-96 (1991).
- 4) A. Fujishima and K. Honda, *Nature*, **238**, 37-38 (1972).
- 5) Y. Takahashi, K. Tsuda, K. Sugiyama, H. Minoura, D. Makino and M. Tsuiki, *J. Chem. Soc., Faraday Trans. I*, **77**, 1051-57 (1981).
- 6) L. M. Williams and D. W. Hess, *Thin Solid Films*, **115**, 13-18 (1984).
- 7) E. Ritter, *J. Vac. Sci. Technol.*, **3**, 225-26 (1966).
- 8) W. Grossklaus and R. F. Bunshah, *J. Vac. Sci. Technol.*, **12**, 593-97 (1975).
- 9) K. G. Geraghty and L. F. Donaghey, *J. Electrochem. Soc.*, **123**, 1201-07 (1976).
- 10) M. H. Suhai, G. Mohan Rao and S. Mohan, *J. Appl. Phys.*, **71**, 1421-27 (1992).
- 11) R. N. Ghoshtagore and A. J. Noreika, *J. Electrochem. Soc.*, **117**, 1310-14 (1970).
- 12) K. L. Siefering and G. L. Griffin, *J. Electrochem. Soc.*, **137**, 814-18 (1990).
- 13) P. Kocian, *J. Non-Cryst. Solids*, **35 & 36**, 195-200 (1980).
- 14) L. M. Williams and D. W. Hess, *J. Vac. Sci. Technol. A*, **1**, 1810-19 (1983).
- 15) T. Shiosaki, T. Yamamoto, M. Yagi and A. Kawabata, *Appl. Phys. Lett.*, **39**, 399-401 (1981).
- 16) "Powder Diffraction File", JCPDS International Centre for Diffraction Data (1989) No. 21-1276.
- 17) J. E. Greene and S. A. Barnett, *J. Vac. Sci. Technol.*, **21**, 285-302 (1982).
- 18) K. Saiki, Y. Nakamura and A. Koma, *Surf. Sci.*, **250**, 27-32 (1991).