Effects of Oxygen Partial Pressure and Laser Energy Density on the Heteroepitaxial Growth of YSZ on Si(001) by Pulsed Laser Deposition

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パルスレーザー蒸着法による Si(001) 上への YSZ 薄膜のヘテロエピタキシャル成長に 及ぼす酸素分圧とレーザーエネルギー密度の影響

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Yttria-stabilized zirconia (YSZ) was deposited on hydrogen-terminated Si(001) by pulsed laser deposition (PLD) under various oxygen pressures (about $2\text{--}2 \times 10^{-4}$ Pa) and laser energy densities ($0.87\text{--}1.09$ J/cm²) at 800°C. The effects of O₂ pressure and laser energy density were found to be important to the formation of an epitaxial oxide thin film. With decreasing laser energy density, the O₂ pressure required to grow epitaxial YSZ films was shifted toward the lower region. Therefore, epitaxial growth of YSZ films could be achieved at a very low pressure of 2×10^{-4} Pa compared with the known O₂ pressure region used for epitaxial growth. The roughness of surfaces was very low, within 0.18–0.26 nm.

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1. Introduction

Metal/ferroelectric/semiconductor field-effect transistors (MFS-FETs) have been intensively studied for the coming generation's ferroelectric nonvolatile random access memory (FeRAM) and will replace the 1T-1C structure's FeRAM. However it is difficult to control the interface between a Si wafer and a ferroelectric layer from the viewpoint of ionic diffusion and incoherence. In addition, decreasing the cell size would bring about a problem of the size effect on the properties. In order to solve these problems, it is necessary to epitaxially grow an oxide film as a buffer layer between the Si wafer and the ferroelectric layer.¹⁾ The required properties of the buffer layer for MFS-FETs are as follows:

- high resistivity,
- epitaxial growth on Si for the realization of an epitaxially grown ferroelectric layer,
- prevention of ionic diffusion between Si and the ferroelectric layer,
- high relative dielectric constant, ϵ_r ,
- smooth surface.

Some oxides are known to grow epitaxially on Si.^{2),3)} Yttria-stabilized zirconia (YSZ) is one of these oxides and has high chemical stability and high relative dielectric constant ($\epsilon_r = 27$). The lattice mismatch between YSZ(001) and Si(001) is -5.34% at room temperature. YSZ films are grown epitaxially on Si(001) with the cube-on-cube relation (YSZ [100]//Si[100]) using, for example, pulsed laser deposition (PLD),^{4)–8)} electron-beam evaporation^{9),10)} and sputtering.^{11)–13)} It has been reported that the O₂ pressure during deposition strongly affects the epitaxy of YSZ films on Si(001).^{4),9)} In PLD, the optimum O₂ pressure for epitaxial growth lies between 2.6×10^{-2} and 9×10^{-2} Pa at the laser energy density of 1.3 J/cm², below which, YSZ films have a preferred (111) orientation.⁴⁾ It was also reported that the laser wavelength and repetition rate of the laser affect the orientation and the ω -rocking curve full-width at half maximum (FWHM).⁵⁾ This suggests that the crystal structure of YSZ films is affected by not only the O₂ pressure but also

the pulsed laser condition. In PLD, the laser energy density is one of the most important parameters, whereas the relationship between the laser energy density and the crystal structure of YSZ films has not yet been clarified. The purpose of this work is to clarify the effects of O₂ pressure and laser energy density on the crystal structure of YSZ films on Si(001).

2. Experimental

YSZ films were deposited on Si(001) by pulsed laser deposition (PLD) with a KrF excimer laser ($\lambda = 248$ nm). The laser beam was focused on the target at an angle of 45° and at a spot size of 0.09 cm² by a fused silica lens. The laser energy density was controlled within 0.87–1.09 J/cm². The laser was fired at a repetition rate of 7 Hz. The distance between the substrate and the target was maintained at 55 mm. The target was rotated continuously during deposition. The YSZ target was prepared by pressing YSZ powder (8 mol% yttria, Tosoh Corporation, Japan) and sintering for 2 h at 1500°C in air. Si substrates in size 10 × 10 mm² were cut from polished Si(001) wafers (n-type, 0.1–1.0 $\Omega \cdot \text{cm}$). In order to clean the Si surface, the substrates were degreased with 2-propanol and dipped in three solutions, NH₄OH : H₂O₂ : H₂O = 1 : 1 : 4 for 10 min at 80°C, HF : H₂O = 1 : 10 for 1 min at room temperature and HCl : H₂O₂ : H₂O = 1 : 1 : 4 for 10 min at 80°C. In addition, the substrates were dipped in diluted HF (HF : H₂O = 1 : 10) to remove the surface oxide and to terminate the surface with hydrogen, and then placed inside the deposition chamber. The substrates were heated to 800°C at the base pressure of $< 10^{-4}$ Pa to prevent the growth of silicon dioxide. O₂ gas was introduced and was maintained at the prescribed pressure from 30 s after the beginning of laser pulsing. The deposition time was 30 min.

The structural properties of the films were characterized by X-ray diffraction (XRD) using Cu K α radiation operated at 40 kV–45 mA (X'Pert-MPD (θ – θ , Open Eulerian Cradle), Phillips). The chemical composition of the film was detected using energy dispersive spectroscopy (EDS) and

wavelength dispersive spectroscopy (WDS). The measurement of film thickness was achieved using a surface profile method (Dektak³, Sloan). The surface morphology was observed by atomic force microscopy (AFM, Nanoscope III, Digital Instruments).

3. Result and discussion

Figure 1 shows the change of the deposition rate with O₂ pressure as a function of laser energy density. The deposition rate increased with increasing laser energy density. At the same laser energy density, below 10⁻² Pa O₂, the change of the deposition rate was almost constant. However, above 10⁻² Pa O₂, the deposition rate was significantly affected by O₂ pressure and decreased with increasing O₂ pressure.

The composition ratio of Y₂O₃/(Y₂O₃+ZrO₂) of YSZ films plotted against laser energy density is shown in Fig. 2. EDS and WDS were used to determine the chemical composition. In the figure, the composition ratio of Y₂O₃/(Y₂O₃+ZrO₂) was almost constant regardless of laser energy density.

In this work, (001)- and/or (111)-oriented YSZ films were obtained, as shown in Figs. 3(a) and (b). Figure 4(a) shows a pole figure for {110} planes of the (001)-oriented film, and Fig. 4(b) shows a pole figure for {100} planes of the (111)-oriented film. In Fig. 4(a), four poles are clearly observed every 90°. On the other hand, Fig. 4(b) shows a ring. Therefore these figures indicate that (001)-oriented YSZ films were grown epitaxially on Si(001) with the cube-on-cube relation (YSZ[100]//Si[100]); however, (111)-oriented YSZ films were grown without in-plane alignment.

Figure 5 shows the degree of orientation for the YSZ

(002) peak as functions of O₂ pressure and laser energy density. The degree of orientation for the YSZ(002) peak was defined according to the following equation. It should be noted that only (00 $\bar{l}$) and ($h\bar{h}h$) peaks were observed in this work.

Fig. 3. 2 θ scans of YSZ films: (a) preferred (001) orientation, (b) preferred (111) orientation.

Fig. 4. X-ray pole figures of YSZ films: (a) {110} planes of the (001)-orientated film, (b) {100} planes of the (111)-orientated film.

Fig. 1. Deposition rates with O₂ pressure as a function of laser energy density.

Fig. 2. Composition ratio of Y₂O₃/(Y₂O₃+ZrO₂) of YSZ films with laser energy density measured by EDS and WDS.

Fig. 5. Degree of orientation for YSZ (002) peak: YSZ films were deposited at 800°C on Si(001) over ranges of O₂ pressure and laser energy density. O₂ gas was introduced into the chamber at 1.3 $\times 10^{-3}$, 6.7 $\times 10^{-3}$, 7.3 $\times 10^{-2}$ and 2 Pa. The base pressure was 2 $\times 10^{-4}$ Pa. The variation of laser energy density at 7 Hz repetition rate was 0.87, 0.92, 1.00 and 1.09 J/cm², respectively.

$$\frac{(002)_{\text{int.}}}{(002)_{\text{int.}} + (111)_{\text{int.}}} \times 100(\%)$$

At high laser energy density (1.09 J/cm^2), at a pressure of $>10^{-2} \text{ Pa}$ O_2 , YSZ films were grown with (001) orientation; below this O_2 pressure, (111) orientation became strong. This result indicates that sufficient oxygen is necessary to grow YSZ films epitaxially, which almost agrees with the reported result.⁴⁾ On the other hand, at low laser energy density (0.87 J/cm^2), the optimum O_2 pressure for growth with (001) orientation was shifted to the lower O_2 pressure region. This finding shows that it is possible to realize epitaxial growth of YSZ film even in $2 \times 10^{-4} \text{ Pa}$ (i.e., base pressure). The reason for this was not completely clarified. However, the following two suggestions were made.

(1) The deposition rate increases with increasing laser energy density, as shown in Fig. 1. This means that the number of ablated species per pulse changes with laser energy density. Based on this point, it would be considered that the amount of O_2 gas necessary for epitaxial growth of YSZ films changes relative to the number of ablated species.

(2) Generally, the kinetic energy of species arriving at the substrate changes with distance between the substrate and the edge of the plume.^{14),15)} This distance increases with decreasing laser energy density and increasing O_2 pressure. Therefore, from this viewpoint, it would be considered that the O_2 pressure necessary for epitaxial growth of YSZ films changes with the laser energy density in order to keep the kinetic energy of arriving species at an optimum level.

The AFM images of YSZ films deposited in $2 \times 10^{-4} \text{ Pa}$ (i.e., base pressure) and 2 Pa O_2 are shown in Figs. 6(a) and (b), respectively. These films have the same thickness of 150 nm . Both surfaces were very smooth, and roughness was within $0.183\text{--}0.255 \text{ nm}$ over a $1 \mu\text{m} \times 1 \mu\text{m}$ area. Moreover, these images indicate that the surface morphology of the YSZ film grown at a base pressure is somewhat porous compared with that grown in 2 Pa O_2 . This suggests that the porous morphology is caused by oxygen defects (such as V_{O}) in the YSZ film.

4. Conclusion

The change of the crystal structure of YSZ films on Si (001) as functions of O_2 pressure and laser energy density in PLD was studied. The chemical composition was almost independent of the laser energy density. It was found that the optimum O_2 pressure for epitaxial growth of YSZ films decreased with decreasing laser energy density. In particular, it is possible to realize epitaxial growth even at a base pressure of $2 \times 10^{-4} \text{ Pa}$. The surface morphology of YSZ films was very smooth regardless of O_2 pressure during deposition; however, the surface of the YSZ film grown at low O_2 pressure was somewhat porous compared with that grown at high O_2 pressure.

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References

- 1) M. Suzuki, *J. Ceram. Soc. Japan*, **103**, 1099–111 (1995) [in Japanese].
- 2) E. J. Tarsa, K. L. McCormick and J. S. Speck, *Mater. Res. Soc. Symp. Proc.*, **341**, 73–85 (1994).

Fig. 6. AFM images of YSZ films over a $1 \times 1 \mu\text{m}$ area: (a) at 0.87 J/cm^2 in base pressure ($2 \times 10^{-4} \text{ Pa}$). (b) at 0.92 J/cm^2 in 2 Pa O_2 .

- 3) M. Suzuki and T. Ami, *Mater. Sci. Eng.*, **B41**, 166–73 (1996).
- 4) D. K. Fork, D. B. Fenner, G. A. N. Connel, J. M. Phillips and T. H. Geballe, *Appl. Phys. Lett.*, **57**, 1137–39 (1990).
- 5) R. Aguiar, V. Trtik, F. Sánchez, C. Ferrater and M. Varela, *Thin Solid Films*, **304**, 225–28 (1997).
- 6) D. B. Fenner, D. K. Fork, G. A. N. Connel, J. B. Boyce, F. A. Ponce, J. C. Tramontana, A. M. Viano and T. H. Geballe, *Mat. Res. Soc. Symp. Proc.*, **191**, 187–92 (1990).
- 7) R. Haakenaasen, D. K. Fork and J. A. Golovchenko, *Appl. Phys. Lett.*, **64**, 1573–75 (1994).
- 8) R. D. Vispute, S. M. Kanetkar, S. B. Ogale, K. C. Rajkumar, A. Madhukar, N. Parikh and B. Patnaik, *Physica C*, **199**, 59–64 (1992).
- 9) T. Hirai, K. Teramoto, H. Koike, K. Nagashima and Y. Tarui, *Jpn. J. Appl. Phys.*, **36**, 5253–58 (1997).
- 10) H. Fukumoto, T. Imura and Y. Osaka, *Jpn. J. Appl. Phys.*, **27**, L1404–05 (1988).
- 11) S. Horita, T. Tajima, M. Murakawa, T. Fujiyama and T. Hata, *Thin Solid Films*, **229**, 17–23 (1993).
- 12) W. C. Tsai and T. Y. Tseng, *Thin Solid Films*, **306**, 86–91 (1997).
- 13) P. Legagnuex, G. Garry, D. Dieumegard, C. Schwebel, C. Pellet, G. Gautherin and J. Siejka, *Appl. Phys. Lett.*, **53**, 1506–08 (1988).
- 14) D. B. Geohegan, *Appl. Phys. Lett.*, **60**, 2732–34 (1992).
- 15) A. Eulenburg, E. J. Romans, Y. C. Fan and C. M. Pegrum, *Physica C*, **312**, 91–104 (1999).