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Dielectric Constant Behavior of Oriented Tetragonal Zr-Si-O System

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1. Introduction

The first generation of the high-k dielectrics for gate insulator is considered to be based on hafnium oxides. However, looking to the future, higher dielectric constant is preferable for gate insulator. $LaAlO_3$ [1] show good electrical properties, however, great efforts may be required in order to achieve its CMOS process compatibility and realize practical application in LSIs. On the other hand, it was reported that the dielectric constant increased by the change of crystal structure of well-studied hafnium oxides from monoclinic to other polymorphs by the doping of N [2], Y, La, Ti [3], or Si [4]. In this report, we will show that another method to enhance the dielectric constant controlling the crystal orientation by Zr-Si-O system.

2. Experimental

ZrSiO films from 5 nm to 500 nm in thicknesses are reactively co-sputtered by zirconium target and silicon target on HF treated Si-substrate. Compositions are determined by RBS (Rutherford backscattering spectrometry), XPS (X-ray photoelectron spectroscopy), and TEM-EDX (energy dispersive X-ray spectroscopy). Dielectric constants were measured by making Au-electrodes on the ZrSiO films. Areas were measured by optical microscopy for each Au-electrode. Thicknesses of the ZrSiO thin films were estimated by cross-sectional TEM (transmission electron microscopy), SEM (scanning electron microscopy) and spectroscopic ellipsometry. Crystal structures were determined by XRD (X-ray diffraction) measurement using the thin film method and the in-plane method.

3. Results and Discussion

X-ray profiles for $Zr_{1-x}Si_xO_2$ films obtained by the thin film method are shown in Fig. 1 and Table 1. We changed the Si concentration of x, annealing atmosphere, temperature, and time. Several samples showing typical results are listed in Table 1. Their XRD profiles are shown in Fig. 1. We could make monoclinic, cubic, and amorphous but failed to make tetragonal crystal. We also tried to make tetragonal HfSiO but were similarly unsuccessful.

We report a solution for tetragonal, namely, to deposit $Zr_{1-x}Si_xO_{2-\delta}$ film with oxygen defect in the x range from 0.06 to 0.14. As-deposited $Zr_{0.86}Si_{0.14}O_{2-\delta}$ was amorphous, but it transformed to tetragonal $Zr_{0.86}Si_{0.14}O_2$ after annealing (Fig. 1, Table 1). Even 5 nm sample was clearly tetragonal in the case of using this method (Fig. 2).

The XPS result in Fig. 3 shows that the $Zr_{0.86}Si_{0.14}O_{2-\delta}$ sample has oxygen defect as indicated by the metallic Zr-Zr, Zr-Si peaks, but these metallic peaks vanished in the oxygen compensated $Zr_{0.86}Si_{0.14}O_2$ sample.

Additionally, a-axis oriented tetragonal $Zr_{0.90}Si_{0.10}O_2$, c-axis oriented tetragonal $Zr_{0.94}Si_{0.06}O_2$, and nonoriented tetragonal $Zr_{0.86}Si_{0.14}O_2$ were derived by this compensating method as shown in Figs. 4 and 5. We could not find localization of Si atom in $Zr_{0.90}Si_{0.10}O_2$ film by TEM-EDX measurement, indicating Si was at the Zr site in the crystal.

These orientations reappeared in the case of the same silicon concentration of ZrSiO sample in different sputtering process batches and in different compensating annealing process batches. Therefore, these orientational orders are considered to be physically inevitable.

Fig. 6 shows the dielectric constants of the oriented tetragonal ZrSiO films. Dielectric constant of a-axis oriented film was larger than that of c-axis oriented film. This magnitude relation qualitatively coincides with the first -principle calculation [5]. Fig. 7 shows that the molar volume (V_m) for tetragonal films differs less than 1% by the orientation; therefore, V_m is not the major cause of dielectric constant difference at Zr/(Zr+Si)=6~14 at.%.

We confirmed the dielectric constant of tetragonal films was kept up to the thin film of 5 nm in thickness (Fig. 8). Despite the crystallization anneal, no turbulence was observed in the layer stack structure (Fig. 9).

3. Conclusions

We established a process for oriented tetragonal ZrO_2 thin films by adding a small amount of Si, in which oxygen deficient film deposition is followed by post-deposition annealing. The dielectric constant of a-axis oriented film is higher than that of c-axis oriented film, mainly due to the polarization anisotropy of tetragonal ZrO_2.

Acknowledgements

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References

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Table I: Sample nomination.

As-depo.	Annealed	Si / (Zr+Si) [at.%]	Oxidative process
S00	**A00**	0	Stoichiometric deposition
S02	**A02**	2	Stoichiometric deposition
S13	**A13**	13	Stoichiometric deposition
D02	**C02**	2	Compensating anneal
D06	**C06**	6	Compensating anneal
D10	**C10**	10	Compensating anneal
D14	**C14**	14	Compensating anneal

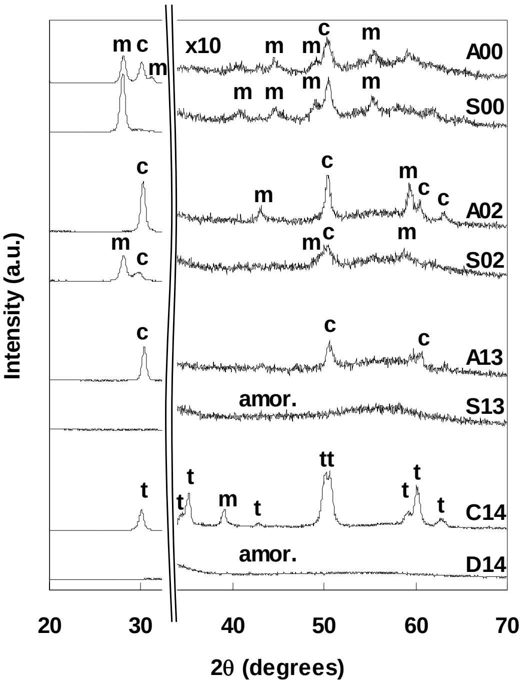

Fig. 1: Thin film XRD profiles of ZrSiO films given by oxygen stoichiometric process and oxygen deficient process.

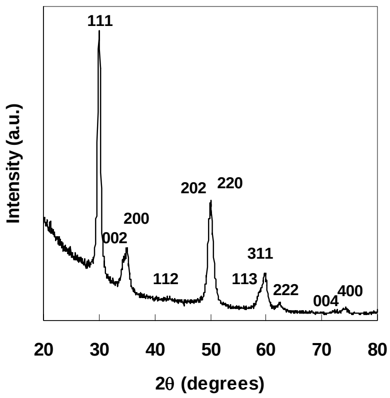

Fig. 2: In-plane XRD profile of 5 nm film. Other conditions are same to C14.

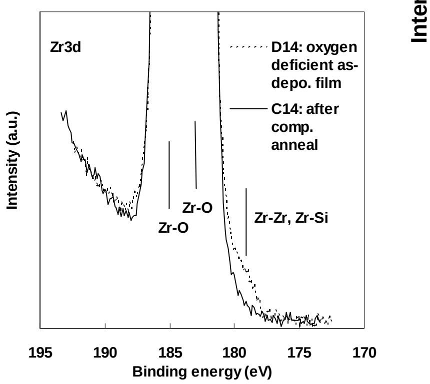

Fig. 3: XPS: D14 of oxygen deficiency is compensated in annealed C14.

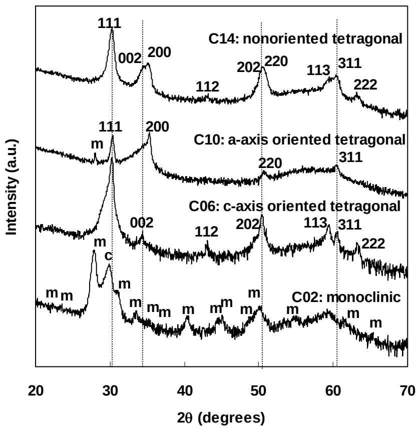

Fig. 4: Thin film XRD profiles of oriented tetragonal films.

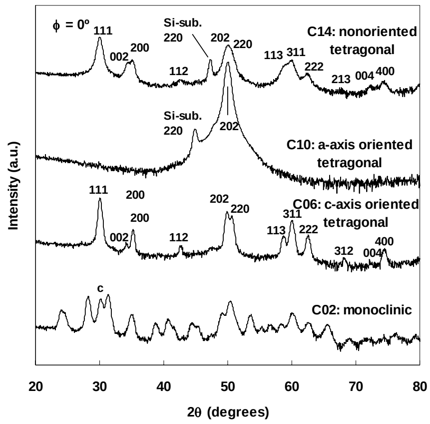

Fig. 5: In-plane XRD profiles of oriented tetragonal films.

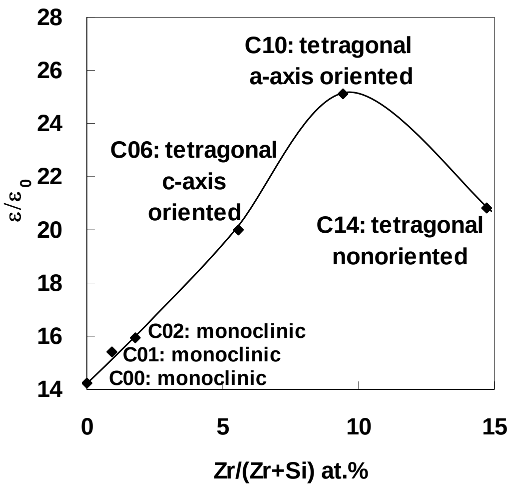

Fig. 6: Dielectric constant of oriented tetragonal film.

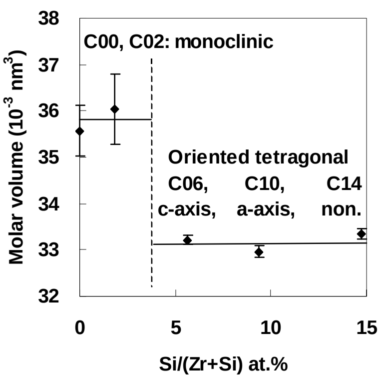

Fig. 7: Molar volume (V_m) of oriented tetragonal film.

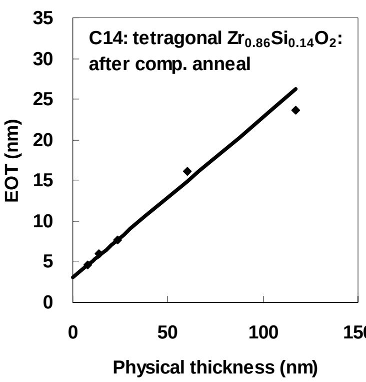

Fig. 8: EOT (equivalent oxide thickness) had linear relation to physical thickness.

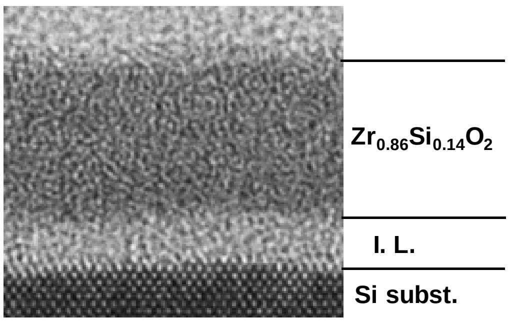

Fig. 9: Cross-sectional TEM photograph of compensating annealed $Zr_{0.86}Si_{0.14}O_2$ sample. Although crystalline array of atoms in $Zr_{0.86}Si_{0.14}O_2$ film was not clear, in-plane XRD profile showed clear tetragonal peaks (Fig.2).