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Phase Transformation Kinetics of Hf-Zr-O Thin Films Examined through Wide Ranges of Annealing Temperature and Annealing Time

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Abstract

Transformation of crystalline phases in 10-nm-thick Hf-Zr-O thin films is examined by investigations of crystalline structures and electrical properties. Through the survey of wide ranges of annealing conditions, from 200 °C to 1130 °C and from 10 ms to 4 days, it is elucidated that antiferroelectric phase appears before the emergence of ferroelectric phase. The antiferroelectric phase easily transforms to the ferroelectric phase at a little higher temperature and a longer annealing time. The ferroelectric phase is easily attainable, but it gradually transforms to the paraelectric phase. These results are instructive for the application of Hf-Zr-O ferroelectric films as memory devices in large-scale integrated circuits.

1. Introduction

Ferroelectric Hf-Zr-O thin films are considered as a promising material for the memory applications in large-scale integrated circuits (LSI). It is reported that the metal composition, Hf/Zr-ratio, is important to attain ferroelectricity [1]. HfO_2 film has a monoclinic structure and show paraelectric character. Hf-Zr-O films with appropriate compositions have orthorhombic structure and show ferroelectricity. The largest polarization is attainable at around 50/50 composition. When the films become Zr-rich, the structure changes to tetragonal and antiferroelectric nature appears. Although this trend is easily reproduced [2], there are another reports that ferroelectricity is confirmed in pure HfO_2 [3] and pure ZrO_2 [4] films. It seems that not only the metal composition but also another factor is driving the formation of ferroelectric films. In this work, through the investigation of phase transformation in $Hf_{0.5}Zr_{0.5}O_2$ films, we demonstrate that annealing temperature and time are important parameters for the control of ferroelectric property.

2. Experiment

Samples were prepared by the process flow shown in **Fig. 1**. Hf-Zr-O films were deposited by the co-sputtering of HfO_2 and ZrO_2 targets. In this work, chemical composition was adjusted to 50/50 and the film thickness was fixed to 10 nm. Crystallization anneal was performed using three kinds of annealing techniques, flash lamp annealing (FLA), rapid thermal annealing (RTA), and low-temperature and long-time anneal (LTLTA) using the horizontal furnace. FLA and RTA were processed in a vacuum condition. LTLTA was processed at 1 atm in a N_2 gas flow. After annealing, crystalline structures were examined using GIXRD system (Rigaku Smart Lab.) In the process of capacitors, TaN and aluminum film stacks were deposited on $Hf_{0.5}Zr_{0.5}O_2$ films. Top electrodes were defined by lithography and dry etching. Polarization characteristics were measured using the ferroelectric tester (Radiant Technologies Precision Premier II). The voltage and the frequency were set to 3 V and 1 kHz. The data were collected after applying 10^4 cycles of pulses.

3. Results and Discussion

Results of RTA samples are shown in **Fig. 2**. A good ferroelectric property is obtained by 700 °C annealing for 1 min. In the 800-°C-process, the polarization becomes small, and the crystal structure gradually transforms to the monoclinic phase by a long period annealing.

The impact of extremely short period anneal was examined by FLA, and the results are shown in **Fig. 3**. Because it is impossible to measure the peak temperatures during the FLA process (10 ms), they were estimated by the simulation of heat equation. Crystallization is partially progressing at 496 °C. Surprisingly, antiferroelectric behavior is observed by the sample processed at 749 °C. Furthermore, the 1130-°C-sample shows ferroelectric property. Although the GIXRD patterns of these films are similar, the electrical properties suggest the transformation of crystal structures from tetragonal to orthorhombic.

LTLTA is expected to decrease the reaction rate and facilitate the trace of transformation. The appearance of antiferroelectric and ferroelectric properties with annealing time at 500 °C (**Fig. 4**) clearly demonstrates the transformation from tetragonal to orthorhombic and monoclinic phases. Although it was impossible to form crystal film by 250 °C annealing for 4 days, the 300-°C-annealing promotes crystallization slowly (**Fig. 5**).

Phase transformation of 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ film is summarized in **Fig. 6**. The phase transformation occurs during anneal, and the rates strongly depend on the temperature. Those boundary lines may shift with the chemical composition, thickness, and mechanical stress.

4. Conclusions

The $Hf_{0.5}Zr_{0.5}O_2$ film is not always a ferroelectric. In the process of crystallization, the nature changes from antiferroelectric, ferroelectric, to paraelectric in accord with the transformation of crystal structures. This viewpoint is helpful for the integration of this material in LSI.

Acknowledgement
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References

[1] J. Müller *et al.*, *Nano Lett.* **12**, 4318 (2012).
[2] S. Migita *et al.*, *JJAP* **57**, 04FB01 (2018).
[3] T. Nishimura *et al.*, *JJAP* 55, 08PB01 (2016).
[4] S. Shibayama *et al.*, EDTM 2018.

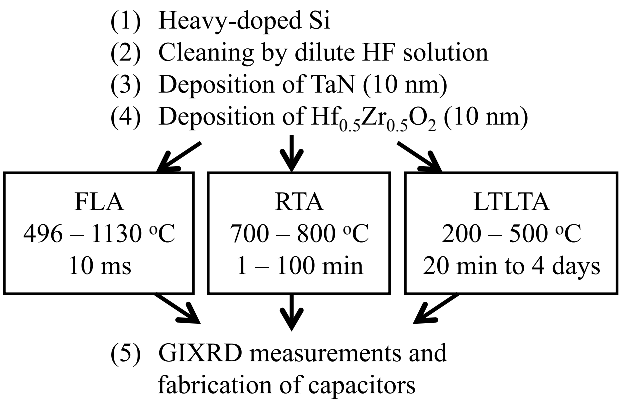

Fig. 1. Process flow to obtain crystalline films using flash lamp anneal (FLA), rapid thermal anneal (RTA), and low-temperature long-time anneal (LTLTA).

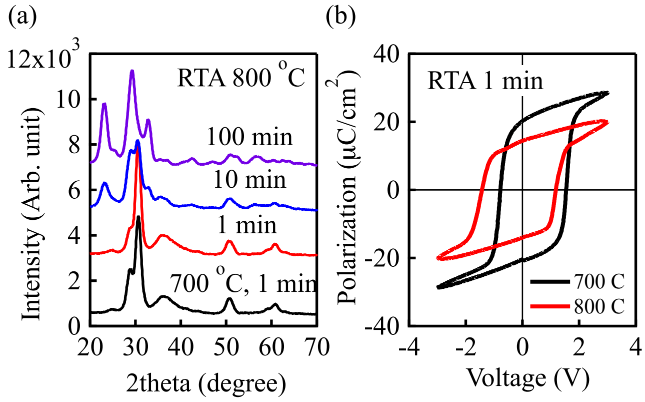

Fig. 2. 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films annealed by RTA process at 700 °C and 800 °C. (a) GIXRD patterns and (b) P-V characteristics.

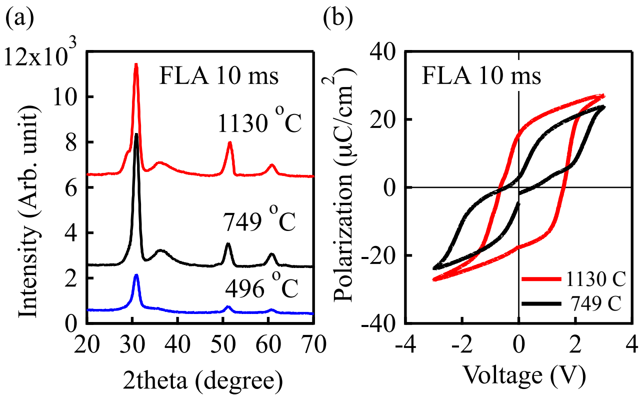

Fig. 3. 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films annealed by FLA process at 496, 749, and 1130 °C. (a) GIXRD patterns and (b) P-V characteristics.

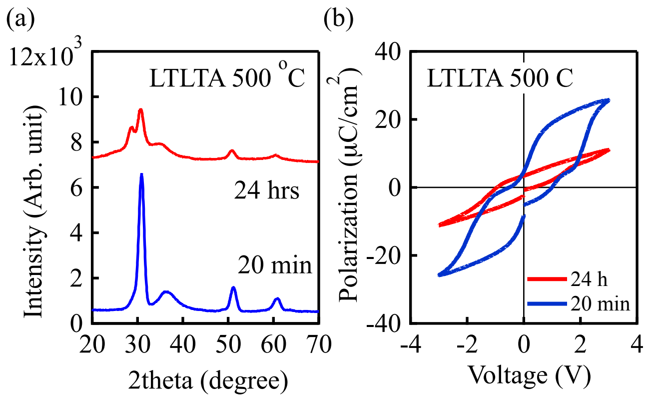

Fig. 4. 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films annealed by LTLTA process at 500 °C. (a) GIXRD patterns and (b) P-V characteristics.

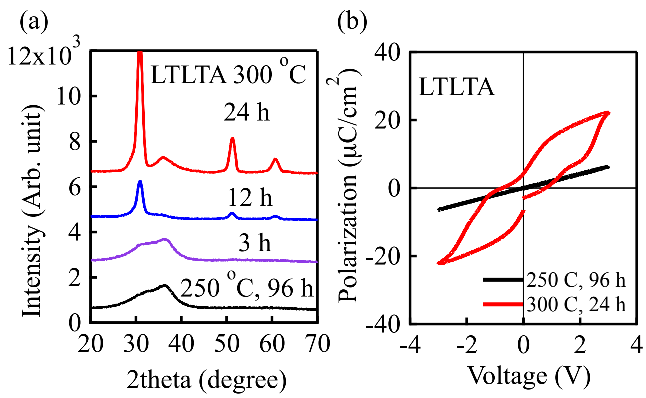

Fig. 5. 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films annealed by LTLTA process at 250, and 300 °C. (a) GIXRD patterns and (b) P-V characteristics.

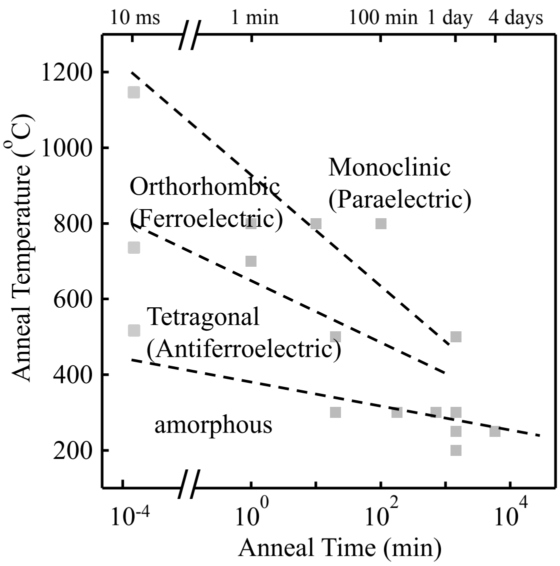

Fig. 6. Summary of phase transformation of 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films with annealing temperature and annealing time. The squares show the examined conditions. Because the crystalline films are not single phase and consist of mixed phases, and the indications of phases in the figure means the dominant components. It is difficult to distinguish between orthorhombic and tetragonal structures by GIXRD patterns, therefore, electrical properties are referred to determine the major structures in the films.