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Effect of Oxygen Partial Pressure under Heat Treatment on Ferroelectricity of $(Hf_{0.5}Zr_{0.5})O_2$ Thin Films

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Abstract

Ferroelectricity was investigated for 20-nm thick $(Hf_{0.5}Zr_{0.5})O_2$ thin films heat-treated under different oxygen partial pressure. Well saturated *P - E* hysteresis loops were observed irrespective of the heat-treatment atmosphere, measurement temperature, and frequency. These results indicate that the oxygen vacancies are not considered to be the origin of the *P- E* hysteresis loops.

1. Introduction

Ferroelectricity of thin films of HfO_2-based materials have been demonstrated by substituting various ions, such as Si, Y, Al, Zr, Gd, and Sr [1-3]. Most noticeable feature of these films compared to the previous ferroelectric films, such as $Pb(Zr, Ti)O_3$ and $SrBi_2Ta_2O_9$ films, is the appearance of ferroelectricity less than 10 nm in thickness even in polycrystalline film form. This feature possible to realize not only low voltage operation of capacitor-type ferroelectric memories due to the very thin film thickness, but also ferroelectric transistor-type one due to the good compatibility of HfO_2-based insulators with CMOS.

However, the most fundamental issue of the origin in ferroelectricity is still unknown that must make clear to realize ferroelectric memories with high reliability. It is pointed out that the ferroelectricity of these films is originated to the noncentrosymmetric orthorhombic phase [1-3]. However, the films consisting of single phase have not been reported and the analysis of the constituent phase of these films is still imperfect due to their thin film thickness as well as the existence of lots of crystal symmetry phases HfO_2-based materials. Therefore, the origin of the ferroelectricity is still under discussion.

One possibility of the hysteresis loops in polarization-electric field (*P* - *E*) curves is the movement of the oxygen vacancies in the films by the large electric field. The oxides materials having fluorite structure like HfO_2 and ZrO_2 is known to exhibit large ionic conductivity of oxygen at high temperature due to the relatively large amount of oxygen vacancies. This imagine us the possibility of oxygen ions movement by large electric field. In addition, almost all previous studies heat-treated the films under oxygen-poor reduction condition due to the use of TiN bottom electrodes. These pervious heat treatment conditions possible to introduce large amount of oxygen vacancies in the films and these oxygen vacancies are possible to migrate followed by the large electric field that results in ferroelectric-like *P* - *E* hysteresis.

To make clear the possibility of the oxygen vacancies migration by the electric field, the investigation of HfO_2-based ferroelectric films heat-treated under the oxygen atmosphere is essential. In the present study, *P* - *E* hysteresis loops were investigated for 20-nm thick $(Hf_{0.5}Zr_{0.5})O_2$ ferroelectric films sandwiched by the Pt-electrodes and heat-treated under various oxygen partial pressure.

2. Experimental Procedure

$(Hf_{0.5}Zr_{0.5})O_2$ thin films were prepared on the $Pt/TiO_2/SiO_2/Si$ substrates by pulsed metal organic chemical vapor deposition (MOCVD). $Hf(NMe_2)(C_8H_{17}N_2)$ (Tosoh Corp.) and $Zr(NMe_2)(C_8H_{17}N_2)$ (Tosoh Corp.) were supplied alternately as Hf and Zr source materials, respectively,. The substrate temperature and chamber pressure during film growth were maintained at 350 °C and 4 Torr, respectively. The Hf/Zr ratio in the films was checked by the wavelength dispersive X-ray fluorescence. Deposited films were heat-treated under atmospheric O_2 (higher oxygen partial pressure) and N_2 (lower oxygen partial pressure) atmosphere.

Crystal structural characterization was performed by grazing incident X-ray diffraction (GIXRD) method with Rigaku Smart Lab diffractometer and transmission electron microscopy (TEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) (JEM-ARM200F, JEOL). Electrical properties of the $(Hf_{0.5}Zr_{0.5})O_2$ films were investigated by the ferroelectric tester (Toyo Corp.) for *P* - *E* hysteresis measurement and by impedance analyzer (Agilent 4194A) for dielectric measurement. Low temperature measurement was performed using temperature-controlled prober station.

3. Results and Discussion

Figure 1(a) shows GIXRD patterns of as-deposited film, and films heat-treated under atmospheric N_2 and O_2. GIXRD pattern of the as-deposited film showed only the peaks from Pt electrode, indicating that the as-deposited film was amorphous phase. On the other hand, the peaks from crystalline $(Hf_{0.5}Zr_{0.5})O_2$ were observed on the GIXRD patterns of the films heat-treated under N_2 and O_2. Two distinct peaks corresponding to *111* reflection peak of tetragonal and/or orthorhombic phases and *11-1* reflection peak of monoclinic phase were observed. In the present study, volume fraction of the orthorhombic phase was not estimated because of the broadness of the peaks and closed positions of the *111* reflection from tetragonal and orthorhombic phases. However, these GIXRD patterns demonstrate that constituent phase of the present $(Hf_{0.5}Zr_{0.5})O_2$ films include unstable phases, in this case orthorhombic and/or tetragonal phases, as well as stable monoclinic phase. It must be noted that the significant difference in GIXRD patterns was not detected for these two films. This means that the heat-treated atmosphere was less affected to the constituent phase of the $(Hf_{0.5}Zr_{0.5})O_2$ films.

Figure 1(b) displays the HAADF-STEM image observed of the films heat-treated under O_2. The sharp interface between electrodes and $(Hf_{0.5}Zr_{0.5})O_2$ layers was observed in this figure. Magnified TEM image shown in Fig.1(c) ascertained the well crystallization of the deposited films as already ascertained by GIXRD pattern in Fig. 1(a).

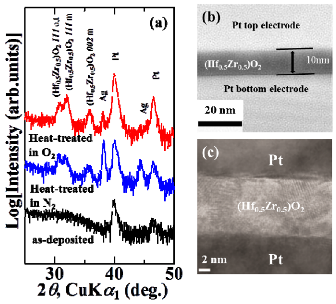

Fig. 1 (a) GIXRD patterns of as-deposited film, and films heat-treated under atmospheric N_2 and O_2. (b) HAADF-STEM images and (c) magnified TEM image for the films heat-treated under O_2.

Figures 2(a) and 2(b) show the room temperature *P* - *E* hysteresis loops measured at 10 kHz for $(Hf_{0.5}Zr_{0.5})O_2$ films heat-treated under atmospheric N_2 and O_2, respectively. Triangle wave electric field with 10 kHz was applied between top and bottom Pt electrodes. Ferroelectric-like hysteresis loops were observed for both films. Moreover, similar remanent polarization values of around 5 μC/cm^2 was obtained for both films, suggesting that the heat treatment condition weakly affected to the ferroelectric properties of the $(Hf_{0.5}Zr_{0.5})O_2$ films.

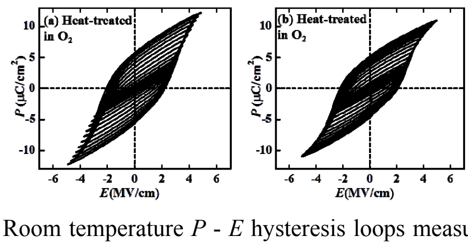

Fig. 2 Room temperature *P* - *E* hysteresis loops measured at 10 kHz for $(Hf_{0.5}Zr_{0.5})O_2$ films heat treated under atmospheric (a) O_2 and (b) N_2.

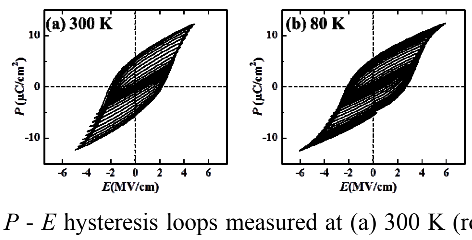

Fig. 3 *P* - *E* hysteresis loops measured at (a) 300 K (room temperature) and (b) 80 K for $(Hf_{0.5}Zr_{0.5})O_2$ films heat-treated under atmospheric O_2.

The *P*-*E* hysteresis loops measured at room temperature and 80 K are respective shown in Figs. 3(a) and 3(b) for $(Hf_{0.5}Zr_{0.5})O_2$ films heat-treated under atmospheric O_2. These figures reveal that the ferroelectric-like hysteresis loops appear even at 80 K, at which temperature the mobility of the oxygen ions should be decreased enough. In addition, well saturated *P* - *E* hysteresis loops against the maximum electric field were observed that were almost the same with the data measured at room temperature. This indicates that $(Hf_{0.5}Zr_{0.5})O_2$ films have typical ferroelectric characteristic irrespective of the measurement temperature. Small temperature dependence characteristics can be explained that the measurement temperature range is low enough from the Curie temperature.

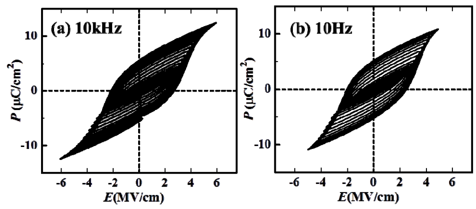

Fig. 4 *P* - *E* hysteresis loops measured at (a) 10 kHz and 10 Hz under 80K for $(Hf_{0.5}Zr_{0.5})O_2$ films heat-treated under atmospheric O_2.

Measurement frequency dependency in *P* - *E* hysteresis loops was measured at 80 K and is shown in Fig. 4. Well saturated loops were observed for both frequencies. In addition, similar values of around 5 μC/cm^2 and 3 MV/cm can be found for the remanent polarization and the coercive field, respectively for the results obtained at 10 kHz and 10 Hz. Well saturated characteristics were also observed even at lower frequency of 10 Hz. When the oxygen ions movement by the large electric field is the main origin of the *P* - *E* hysteresis loops, lower frequency measurement is possible to display small hysteresis loops. However, present result shows the almost frequency independent characteristics as shown in Fig. 4.

These results show that the origin of the ferroelectricity of the present films is not the oxygen vacancies movement by the electric field, but the ferroelectricity of the $(Hf_{0.5}Zr_{0.5})O_2$ films.

4. Conclusions

Ferroelectricity was investigated for 20-nm thick $(Hf_{0.5}Zr_{0.5})O_2$ thin films prepared on the $Pt/TiO_2/SiO_2/Si$ substrates and heat-treated under different oxygen partial pressure. Well saturated *P* - *E* hysteresis loops were observed irrespective of the heat-treatment atmosphere, measurement temperature, and frequency. These results indicated that the oxygen vacancies are not considered to be the origin of the *P*- *E* hysteresis loops.

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