Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp75-76

Antiferroelectricity and cycling behavior of ALD ZrO_2 ultra-thin films

Xuan Luo, Kasidit Toprasertpong, Mitsuru Takenaka and Shinichi Takagi

Department of Electrical Engineering and Information Systems, School of Engineering, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8654, Japan
E-mail: luo@mosfet.t.u-tokyo.ac.jp

Abstract

Antiferroelectricity (AFE) in ZrO_2 thin films is systematically investigated with different film thicknesses and PMA temperatures. Excellent AFE characteristics are observed for the ZrO_2 thickness from 5.3 to 9.5 nm. It is found that higher PMA temperature can provide better AFE properties in the thick ZrO_2 films, while the optimum temperature becomes lower in the thin films. In addition, the AFE ZrO_2 films are found to show a significant wake-up effect together with a reduction of the critical transition electric field during gate pulse cycling.

1. Introduction

ZrO_2 has been extensively studied as a high-k material in the past few years, while the discovery of the existence of antiferroelectricity (AFE) has given more choices on applications of this dielectric material [1]. Compared with its counterpart HfO_2 which has attracted much attention since the report of ferroelectricity (FE) in Si-doped ones [2], ZrO_2 possesses several superior properties such as the lower temperature crystallization, improved cycling endurance for non-volatile memory applications [3] and no need for dopants. Recently, scalability of AFE ZrO_2 has been proved in a wide thickness range (4.3-14.7 nm) [4], which strengthened the applicability to future CMOS devices. However, the AFE properties of ZrO_2 thin films including the effects of annealing and the cycling behaviors have less been studied so far.

In this work, we systematically examine factors that affect AFE in ZrO_2 thin films, including the film thickness and post metallization annealing (PMA) temperature. Besides, the cycling behavior of AFE ZrO_2 capacitors is studied with an emphasis on the wake-up effect of AFE in ultra-thin ZrO_2 films.

2. Experiment

The process flow is shown in **Fig. 1**. TiN/ZrO_2/TiN structure capacitors were prepared with changing the ZrO_2 film thickness from 3.7 nm to 9.5 nm. 32 nm TiN was sputtered on a heavily-p-doped Si substrate as the bottom electrode, followed by atomic layer deposition (ALD) of pure ZrO_2. Subsequently, 32 nm TiN was sputtered as the top electrode. PMA was then carried out at 400℃, 500℃ and 600℃ for 1 min in N_2 ambient.

3. Results and discussion

Antiferroelectricity in ALD ZrO_2 films

AFE characteristics were observed in ZrO_2 films from 5.3 nm with different PMA temperatures. In the present study, 3.7 nm and 4.2 nm ZrO_2 films are quite leaky and, thus, the AFE cannot be evaluated. **Fig. 2** shows P-E and I-E characteristics before and after gate pulse cycles of 10^4. We have observed symmetric and clear AFE P-E curves and clear switching current, compared with the results in the other recent report on AFE ZrO_2 [4]. **Fig. 3** summarizes the thickness dependence of (a) maximum polarization (P_{max}), (b) remnant polarization ($2P_r$), (c) critical transition electric field ($E_{AFE\text{-}FE}$, $E_{FE\text{-}AFE}$ and (d) the distance between $E_{AFE\text{-}FE}$ and $E_{FE\text{-}AFE}$ (ΔEc). The significant wake-up effect such as the increase of P_{max} and $2P_r$, and the decrease of the critical transition electric field, which has not been pointed out yet, are observed after 10^4 cycles. **Fig. 4** shows the amount of the hysteresis loop, ΔP, defined by the difference between the backward and forward polarization at a same electric field. The gate pulse cycle is found to open up the hysteresis loop in AFE.

Another finding in **Fig. 2** is the different trends of the PMA temperature dependence of AFE characteristics for the different film thickness. For 5.3 nm and 6 nm, lower PMA temperature (400℃) is enough to obtain strong AFE, while increasing PMA temperature leads to leaky P-V curves. On the other hand, the PMA temperature dependence is different for 9.5 nm ZrO_2, where the strongest AFE is obtained for 600℃ PMA and the films with lower PMA temperature show leaky P-V. This trend is quite consistent with the DC I-V characteristics that the gate current in 5.3 nm and 6 nm ZrO_2 increases with increasing PMA temperature, while that in the 9.5 nm one decreases in a relatively high electric field region. Thus, AFE characteristics were evaluated for the 5.3 and 6 nm ZrO_2 with 400℃ PMA and 9.5nm ZrO_2 with 600℃ PMA. As shown in **Fig. 4**, ΔP increases with increasing the film thickness. On the other hand, the distance between $E_{AFE\text{-}FE}$ and $E_{FE\text{-}AFE}$ also increases with the film thickness.

Cycling behavior of AFE ZrO_2 films

The cycling behavior and the wake-up effect in AFE ZrO_2 films have not been investigated yet so far, whereas it has been reported [5] that some doped-HfO_2 films need the wake-up process to obtain the ferroelectric properties from the pristine antiferroelectric-like characteristics. The cycling behavior is thus examined for the AFE ZrO_2 films in order to quantitatively evaluate the wake-up effect.

Fig. 5(a) and **(b)** show the cycling behaviors of P-E and switching I-E characteristics of 5.3 nm ZrO_2 films with 400℃ PMA up to 10^4 cycles. The emergence of AFE and a significant wake-up effect are clearly observed. **Fig. 5(c)** shows the ΔP-E characteristics as a parameter of the cycle number. All the above results have proved the existence of the wake-up effect in ultra-thin AFE ZrO_2 films. On the other hand, the critical electric field at which the switching current has a peak is reduced with an increase in the cycle number, as seen in **Fig. 5(d)**. This result suggests that the energy needed for the change from the tetragonal to the orthorhombic phase [6] can be smaller with increasing the cycles. The reduction of critical electric field is also observed in the other samples. Both

$E_{AFE\text{-}FE}$ and $E_{FE\text{-}AFE}$ in the positive gate voltage are reduced after 10^4 cycles. This fact suggests that the crystalline structure change of AFE ZrO_2 films might be easier during the cycling.

3. Conclusions

ZrO_2 films in the thickness range of 3.7-9.5 nm have been systematically studied form the viewpoint of AFE with an emphasis on the PMA condition. Clear AFE characteristics were observed for the thickness from 5.3 to 9.5 nm. The thinner ZrO_2 films show the AFE properties with low leakage current under lower thermal budget, while the thicker film tends to show a wider hysteresis loop under higher thermal budget. The strong wake-up effect has been observed in AFE ZrO_2 films together with a reduction of the critical transition electric field during cycling.

Acknowledgements This work was partially supported by JSPS KAKENHI Grant No. 17H06148.

References [1] J. Muller et al., Nano Lett. **12**, 4318 (2012).
[2] T. S. Boscke et al., Appl. Phys. Lett. **99,** 102903 (2011).
[3] M. Pesic et al., Adv. Funct. Mater. **26**, 7486 (2016).
[4] P. D. Lomenzo et al., IEEE International Memory Workshop (IMW), 5.2., (2020).
[5] M. Hoffmann et al., J. Appl. Phys. **118**, 072006 (2015).
[6] S. E. Reyes-Lillo et al., Phys. Rev. B **90**, 140103 (2014).

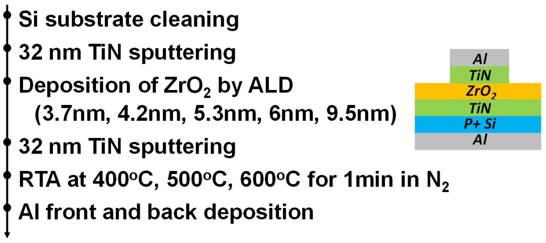

Fig. 1 Fabrication process flow.

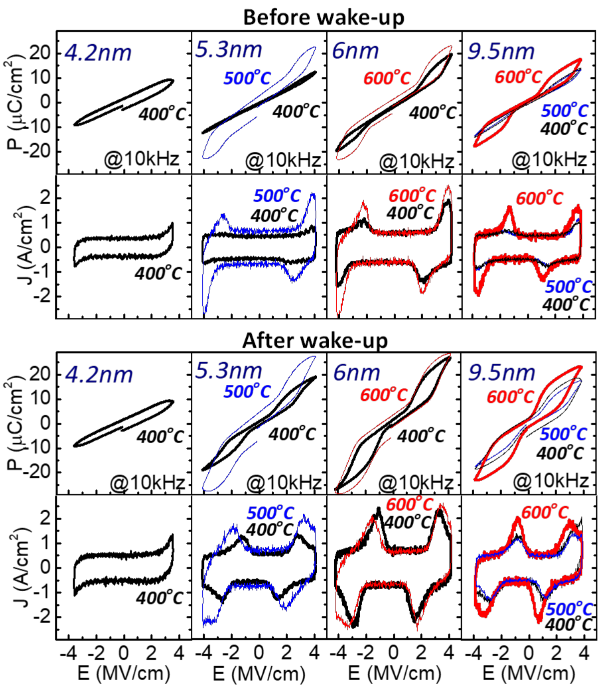

Fig. 2 P-V hysteresis loops and switching current characteristics for TiN/ZrO_2/TiN capacitors with different thicknesses measured before and after 10^4 gate pulse cycles for wake-up.

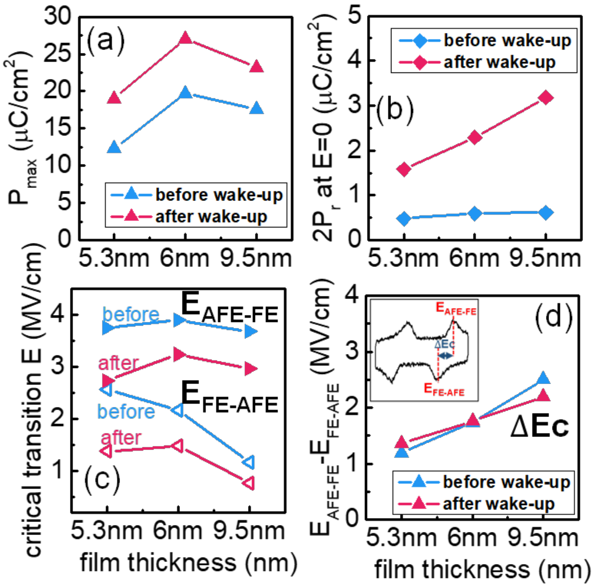

Fig. 3 Thickness dependence of (a) maximum polarization P_{max}, (b) remnant polarization $2P_r$, (c) critical transition E and (d) the distance between $E_{AFE\text{-}FE}$ and $E_{FE\text{-}AFE}$.

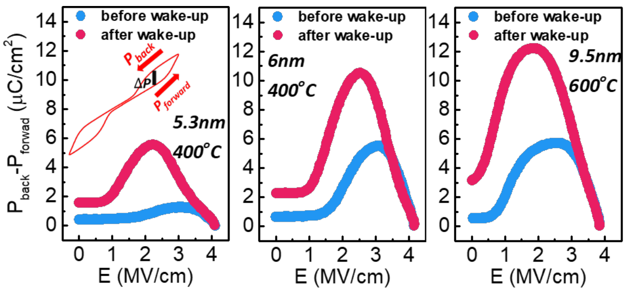

Fig. 4 The difference (ΔP) between backward polarization and forward polarization as a function of electric field for ZrO_2 films with different thicknesses.

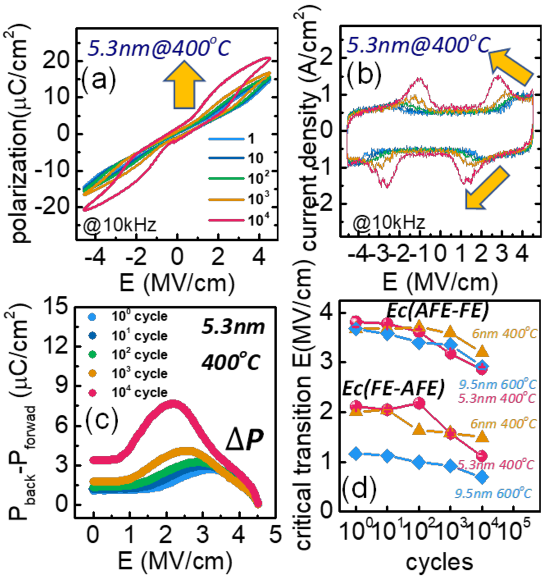

Fig. 5 Cycling behaviors of (a) P-V characteristics, (b) switching current characteristics, (c) ΔP for 5.3 nm ZrO_2 with 400 °C PMA. (d) critical transition E changed during cycling for ZrO_2 films with different thicknesses.