Antiferroelectric properties in ALD ZrO_2 ultra-thin films and their relations with the crystalline phases

Univ. of Tokyo, ○Xuan Luo, Kasidit Toprasertpong, Mitsuru Takenaka, Shinichi Takagi
E-mail: luo@mosfet.t.u-tokyo.ac.jp

Background: The discovery of antiferroelectric (AFE)-like properties in ZrO_2-based thin films has increased the options for their applications and the potential to contribute to future electronic devices [1-4]. However, the AFE-like properties of ZrO_2 thin films and how they correlate with the crystalline structure of the films have been less studied so far. In this work, the AFE-like properties and the crystalline structure of ZrO_2 thin films prepared by atomic layer deposition (ALD) with different film thicknesses and post metallization annealing (PMA) temperatures (T_{PMA}) are examined, based on which the relations between the AFE-like properties and the crystalline phase of the ZrO_2 films are discussed.

Experiment: TiN/ZrO_2/TiN capacitors were prepared with the ZrO_2 film thickness of 5.3 nm, 6 nm, and 9.5 nm [5, 6]. 32nm TiN was sputtered on a heavily doped P-Si substrate as the bottom electrode, followed by the growth of ZrO_2 through ALD, after which 32nm TiN was sputtered as the top electrode. Post metallization annealing (PMA) was then carried out at 400ºC and 600ºC for 1 min in N_2 ambient. The crystalline structure of the ZrO_2 films was analyzed by the ACOM-TEM technique [7], after removing the top TiN electrode by wet etching.

Results and discussion: The polarization-electric field (*P-E*) characteristics of the TiN/ZrO_2/TiN capacitors and the corresponding results of local crystalline phase mapping of ZrO_2 films with different film thicknesses and T_{PMA} are shown in Fig. 1. Note that the leakage current subtraction was conducted by using the dynamic leakage current compensation method [8] to exclude the effect of leakage current on the evaluation of the real *P-E* characteristics. It is found that the features of the AFE-like hysteresis loop are closely related to both the film thickness and T_{PMA}. In addition, it can be observed from the local crystalline phase mapping that, although the main phase in all the ZrO_2 films is the tetragonal (*t*) phase, the relative ratio of phases changes with varying the film thickness and T_{PMA}. For 5.3-nm-thick ZrO_2 with 400°C PMA, a large amount of the amorphous phase is observed, suggesting the necessity of higher T_{PMA} for the full crystallization. Also, the amounts of the monoclinic (*m*) phase and the orthorhombic (*o*) phase significantly increase with increasing the film thickness up to 9.5 nm. These differences in the crystalline structures can have a significant impact on the *P-E* characteristics.

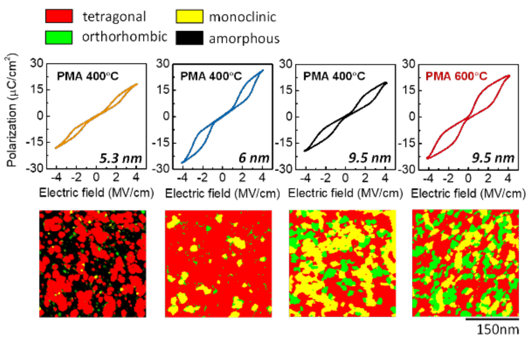

Fig. 1 P-E characteristics and the corresponding crystalline phase mapping of ZrO_2 films with different film thickness and PMA temperature.

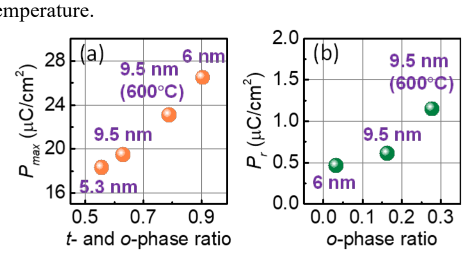

Fig. 2 The correlation between (a) P_{max} and the sum of the relative ratio of *t*- and *o*-phase, (b) P_r and the relative ratio of *o*-phase.

To directly clarify the correlation between the AFE-like properties and the crystalline phase properties of the ZrO_2 films, the relationships between the AFE parameters including the maximum polarization (P_{max}) and remanent polarization (P_r) extracted from the *P-E* characteristics, and the relative ratio of different phases evaluated from the local crystalline phase mapping were plotted in Fig. 2. Note that the small P_r shown in the AFE-like hysteresis loop of the ZrO_2 films after the subtraction of leakage current is attributable to the presence of the FE *o*-phase under zero field [9], which can contribute to P_{max}. As a result, both *t*-and *o*-phase are supposed to determine P_{max}. Thus, P_{max} was plotted in Fig. 2(a) as a function of the sum of the relative ratio of *t*- and *o*-phase. Also, P_r was plotted in Fig. 2(b) as a function of the relative ratio with only *o*-phase. Both P_{max} and P_r correlate well with the expected corresponding phase ratio. Especially, the correlation of P_{max} and *t*+*o* phase ratio is excellent. These strong correlations indicate that the change of the distributions of crystalline phases in the ZrO_2 films, led by the film thickness and T_{PMA}, can be a key factor that determining the AFE characteristics.

Conclusions: The impacts of film thickness and PMA temperature on the AFE characteristics of ALD ZrO_2 thin films, and their correlation with the crystalline structure have been studied. It has been found that the maximum polarization is in strong correlation with the sum of the relative ratio of both *t*- and *o*-phase, and the remanent polarization in correlation with that of only the *o*-phase.

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