Acta Materialia 115 (2016) 68–75

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Induction of ferroelectricity in nanoscale ZrO_2/HfO_2 bilayer thin films on $Pt/Ti/SiO_2/Si$ substrates

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ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
13 May 2016
Accepted 16 May 2016
Available online 4 June 2016

Keywords:
Hafnia
Zirconia
Ferroelectricity
Bilayer thin films
TEM

ABSTRACT

Large ferroelectricity has been demonstrated in nanoscale bilayer thin films consisting of undoped ZrO_2 and HfO_2 layers on conventional $Pt/Ti/SiO_2/Si$ substrates for the first time. The bilayer thin films had thicknesses between 7.5 and 18 nm and their crystalline phases, symmetry groups, polarization hystereses and composition depth profiles were characterized to understand the influence of the stacking order and thickness of the ZrO_2 and HfO_2 layers on ferroelectricity. Two factors: (1) effective confinement of the HfO_2 layer by the ZrO_2 layer and Si substrate to promote the ferroelectric orthorhombic phase and (2) reduction of the bulk characteristics of the ZrO_2 and HfO_2 layers to minimize the paraelectric monoclinic phase are the key to stable ferroelectricity with a large remanent polarization. These factors can be manipulated by the stacking order and thickness of the layers, and consequently, producing ferroelectric behaviors ranging from minor to fully developed hystereses. The undoped ZrO_2/HfO_2 bilayer thin film is a simpler design and can be fabricated more easily compared to the doped HfO_2 or solid solution $Hf_xZr_{1-x}O_2$ thin films reported in the literature, which require not only precise composition control but also the less available TiN electrodes for stable ferroelectricity. The chosen $Pt/Ti/SiO_2/Si$ substrate for the ZrO_2/HfO_2 bilayer thin films is readily available and has been widely used in MEMS applications. These advantages make the ZrO_2/HfO_2 bilayer thin films favorable for silicon-based device integration.

1. Introduction

Zirconia (ZrO_2) and hafnia (HfO_2) are important oxide materials for many industrial applications and have been studied for decades for their mechanical and electrical properties [1,2]. The discovery of toughening mechanism based on stress-induced tetragonal-to-monoclinic phase transformation has allowed partially stabilized ZrO_2 and HfO_2 to be used in load-bearing applications [2,3]. ZrO_2- and HfO_2-based materials are widely used in capacitors and transistors, especially in semiconductor devices, due to their high dielectric (high-κ) characteristics [4]. ZrO_2 and HfO_2 are similar in both physical and chemical senses. The similarity is related to the electron configurations of Zr ($[Kr]4d^25s^2$) and Hf ($[Xe]4f^{14}5d^26s^2$), which are both group IV elements. In terms of structural changes with increasing temperature, bulk ZrO_2 and HfO_2 transform from the low-temperature monoclinic (M) phase ($P2_1/c$) to the tetragonal (T) phase ($P4_2/nmc$) at around 1100 and 1720 °C, respectively, and further to the high-temperature cubic (C) phase ($Fm\bar{3}m$) at above 2370 and 2600 °C, respectively [2]. Additionally, three high-pressure orthorhombic phases – *Pbca*, *Pnma* and $Pbc2_1$ (denoted as O-I, O-II and O-III phases, respectively) – had been identified by neutron diffraction and simulation studies [5–8]. For ZrO_2 and HfO_2 nanocrystals, transformation between these polymorphic phases not only is influenced by the temperature and stress conditions, but also exhibits an intrinsic size dependence [2,9]. It has been shown that for ZrO_2 microcrystals, the reciprocal crystallite size is a linear function of the T-to-M transformation temperature [9]. For thin films of the same thickness, HfO_2 needs a higher temperature to crystallize than ZrO_2 [10].

The monoclinic $P2_1/c$, tetragonal $P4_2/nmc$, cubic $Fm\bar{3}m$, O-I and O-II phases of ZrO_2 and HfO_2 are centrosymmetric and therefore exhibit no ferroelectricity. The origin of ferroelectricity in nanoscale HfO_2-based thin films has been attributed to the presence of the noncentrosymmetric O-III phase, which is one of the high-pressure phases of HfO_2 [7,8,11–14]. Böscke et al. first proposed that the ferroelectric O-III phase in Si-doped HfO_2 thin films of thickness between 12 and 18 nm is induced by the mechanical confinement

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http://dx.doi.org/10.1016/j.actamat.2016.05.029
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of sandwiching titanium nitride (TiN) electrode layers and stabilized by the Si dopants [11]. The design of nanoscale TiN/doped-HfO_2/TiN thin films with post-metallization annealing would produce enough mechanical confinement to suppress the T-to-M transition in HfO_2 and promote the transformation to the high-pressure, ferroelectric O-III phase at room temperature [11–14]. Based on this approach, various dopants such as Y, Al, Gd, Sr and La were used to stabilize ferroelectricity in nanoscale HfO_2 thin films grown on or sandwiched between TiN electrodes [15–20]. A recent study showed that undoped nanoscale HfO_2 thin films capped between TiN electrodes in an amorphous state prior to crystallization could display ferroelectric properties comparable to those of doped HfO_2 thin films [21].

The evolution of ferroelectricity of the binary solid solutions of HfO_2 and ZrO_2, i.e., $Hf_xZr_{1\text{-}x}O_2$ (abbreviated as HZO), in the form of nanoscale thin films with different HfO_2-to-ZrO_2 ratios had also been studied — with increasing Zr content, the $Hf_xZr_{1\text{-}x}O_2$ thin film evolved from a paraelectric ($x = 1$; pure HfO_2) to a ferroelectric (e.g., $x = 0.5$) and then to an antiferroelectric ($x = 0$; pure ZrO_2) system [22–25]. Such evolution was observed for the films grown on the TiN electrodes, but not on the Pt electrodes [25]. Moreover, the antiferroelectricity of the ZrO_2 thin film ($x = 0$) was claimed based solely on the observed propeller-shaped polarization hysteresis without actual characterization of the film's atomic displacements or symmetry groups [22]. The insertion of Al_2O_3 interlayers into the $Hf_{0.5}Zr_{0.5}O_2$ thin films was adopted to inhibit the growth of HZO nanocrystals, which in turn promoted the formation of the ferroelectric O-III phase [26]. Overall, several parameters have been identified to influence the stability and amount of the O-III phase in nanoscale HZO thin films, including atmospheric conditions [27,28], annealing temperature [23,29] and grain size [26].

In this study, we demonstrate an alternative design for nanoscale ferroelectric thin films based on HfO_2. The design is a bilayer thin film of undoped ZrO_2 and HfO_2 fabricated on a conventional Pt/Ti/SiO_2/Si substrate using atomic layer deposition (ALD). The ferroelectric properties of the bilayer thin film can be tuned by changing the thickness or stacking order of the ZrO_2 and HfO_2 layers. Furthermore, the chosen substrate is Pt/Ti/SiO_2/Si, which is readily available and has been widely used in MEMS applications. The undoped ZrO_2/HfO_2 bilayer thin film is a simpler design and can be fabricated more easily compared to the doped HfO_2 or solid solution HZO thin films reported in the literature, which require not only precise composition control but also the less available TiN electrodes for stable ferroelectricity. Diffraction and hysteresis analyses were performed on the ZrO_2/HfO_2 bilayer thin films to shed light on the origin of their ferroelectricity.

For convenience in the following discussion, the thin film samples prepared in this study are denoted as: "Z#", "H#", "Z#H#" and "H#Z#", where Z or H and the number attached to it represent the film (material) type and film thickness, respectively. For example, Z12 and H6 represent 12-nm-thick ZrO_2 film and 6-nm-thick HfO_2 film, respectively. Z6H6 is a bilayer thin film consisting of a 6-nm-thick ZrO_2 layer on top of a 6-nm-thick HfO_2 layer; in other words, the HfO_2 layer is sandwiched between the ZrO_2 top layer and Pt/Ti/SiO_2/Si substrate. Fig. 1 shows the schematic and cross-sectional TEM image of the Z6H6 thin film, demonstrating the stacking of the ZrO_2 and HfO_2 layers. In contrast, H6Z6 is a bilayer thin film having the same thickness as Z6H6 but with a reserve stacking order, i.e., HfO_2 layer on ZrO_2 layer.

2. Experimental procedure

Nanoscale HfO_2 and ZrO_2 thin films and ZrO_2/HfO_2 bilayer thin films of thicknesses between 6 and 18 nm were deposited on Pt/Ti/SiO_2/Si substrates by ALD (Savannah 100, Cambridge NanoTech, USA) at a chamber temperature of 150 °C using Tetrakis(dimethylamido)hafnium(IV) (TDMAHf; Sigma-Aldrich, USA), tetrakis(dimethylamido)zirconium(IV) (TDMAZ; Sigma-Aldrich, USA) and H_2O vapor as the precursors. A growth rate of about 1 nm per 10 ALD cycles was set up for both the HfO_2 and ZrO_2 films (layers). Notice that in the initial stage of the ALD process, self-limiting reactions of the precursors on the hydrophobic Pt surface were difficult to achieve due to the lack of hydroxyl groups on the surface. To overcome this, the Pt surface was first exposed to 5 cycles of ZrO_2 to produce a sub-nanometer, discontinuous (i.e., island-like) adhesion layer before subsequent film deposition. The deposited films were then rapidly annealed at 600 °C for 20 s in the nitrogen atmosphere to achieve crystallization.

The crystalline phases of the thin films at room temperature were identified using grazing incidence X-ray diffraction (GIXRD; TTRAX III, Rigaku, Japan) with Cu Kα radiation operating at 50 kV and 250 mA. Structural analyses of the thin films were achieved by high-resolution transmission electron microscopy (HRTEM; 2010F, JEOL, Japan) and scanning transmission electron microscopy (STEM; Tecnai G2 F20, FEI, USA) operating at 200 kV. The latter was equipped with an energy-dispersive spectrometer (EDS; Link ISIS System, Oxford Instruments, UK) for micro-chemical analysis. The cross-sectional TEM specimens of the thin films were prepared using focused ion beam micromachining (FIB; Helios NanoLab 600i, FEI, USA). The contrast of HRTEM images was enhanced by fast Fourier transform (FFT) using software DigitalMicrograph (Gatan, USA). The polarization-electric field (*P-E*) hysteresis curves of the thin films were measured at room temperature using a ferroelectric analyzer (TF2000, aixACCT, Germany) operating at alternating electric fields of ±3–6 MV cm^{-1} and 2000 Hz. For the *P-E* hysteresis measurements, the Pt/Ti/SiO_2/Si substrate provided the bottom electrode, while, Au/Ni top electrodes were thermally evaporated and patterned into small circular dots (area $\approx 0.28\ mm^2$) onto the annealed thin films.

3. Results and discussion

3.1. Pure ZrO_2 and HfO_2 thin films

The GIXRD patterns of the pure ZrO_2 and HfO_2 thin films with different thicknesses are shown in Fig. 2a. H6 and H12 showed similar diffraction patterns and have been indexed as a monoclinic structure. As for Z6, Z12 and Z18, when the film thickness was increased, a symmetry-lowering, intrinsic size-dependent phase transition was detected by the splitting of the broad T/O (111) peak at $2\theta \approx 30.6°$ to form the M (111) peak at $2\theta \approx 31.4°$. The appearance of the paraelectric M phase with increasing film thickness would lead to a decrease in ferroelectricity. The polarization *P-E* hysteresis curves of H12 and Z12 are shown in Fig. 2b. H12 exhibited a paraelectric characteristic with no hysteresis. While, Z12 showed a propeller-shaped hysteresis with non-zero remanent polarization (P_r) — an antiferroelectric-like behavior which has been attributed to the electric field-induced T-to-O-III phase transition from a recent modeling study [24]. Another explanation for the propeller-shaped hysteresis may be the mixing of ferroelectric and non-ferroelectric phases. Such a mixed system, if possesses nano-domains of high coercivity from the ferroelectric phase and a strong depolarization effect at low electric fields due to the non-ferroelectric phase, could exhibit a propeller-shaped hysteresis [30]. Further diffraction studies of the crystalline phases, atomic displacements and symmetry groups of the nanoscale ZrO_2 thin films at various electric field strengths should reveal the origin of the propeller-shaped hysteresis.

The cross-sectional HRTEM images of H12, shown in Fig. 3a and b, reveal the monoclinic (002) and (111) planes with interplanar