

Structural properties of solution-processed $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films



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ABSTRACT

$\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) thin films were deposited on Si substrates with and without TiN seed layers using a simple and cost-effective solution synthesis. The crystalline quality of the as-deposited HZO films were improved through a post deposition annealing process. Cross-sectional transmission electron microscope analyses of HZO/TiN/Si structure revealed a clear and clean interface formation between HZO and TiN layers. X-ray diffraction and Raman analyses confirm that, after the post annealing process, HZO films deposited on bare Si substrate crystallized in monoclinic phase while the HZO films deposited on TiN/Si substrates tend to crystallize in tetragonal or orthorhombic crystal structure. Varying crystal structure through controlling the post deposition annealing temperature is a promising technique to manipulate the electrical properties of solution processed HZO thin films.

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1. Introduction

HfO_2 thin films have been extensively investigated for a wide range of applications such as high-k dielectric [1–6], ferroelectric transistors [7], field emission transistors [8], ultraviolet photodetectors [9], and memories [10–16]. For the niche applications such as gate dielectric in advanced transistors, smooth and dense ultra-thin films with high quality are required [5,17]. Since HfO_2 has four polymorphs namely cubic ($Fm\bar{3}m$), monoclinic ($P2_1/c$), tetragonal ($P4_2/nmc$), and orthorhombic ($Pbca$ and $Pnma$), electrical properties of HfO_2 can be easily tuned by varying the crystal structure. The cubic, tetragonal, and orthorhombic HfO_2 exhibit higher dielectric constant (>25) than that of monoclinic HfO_2 (16–20). Doping is one method, which is widely used to achieve desired crystal structure, in order to manipulate the dielectric properties of HfO_2 [18]. Undoped and doped HfO_2 with non-centrosymmetric orthorhombic structure exhibiting ferroelectricity/antiferroelectricity have been intensively studied [19–28]. Several dopants such as Si, Al, Ti, Ta, Zr, etc are used for tuning the dielectric properties [18]. Among these dopants, Zr is an attractive choice, since a solid solution is formed between ZrO_2 and HfO_2 in the whole composition range of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ [25,28]. Even though a solid solution is formed in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films, the crystal structure and hence the dielectric constant varies with Zr addition. The crystalline quality and phase of the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films also depends on the film thickness [29].

Previous reports suggests that the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films with a thickness less than 5 nm are amorphous [29]. Ferroelectricity has been observed in metastable orthorhombic phase (*o*-phase) of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ultra-thin films with thickness in the range 5–25 nm [29]. $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films with thickness greater than 25 nm crystallizes in the most stable monoclinic phase (*m*-phase) of HfO_2 [29]. The most stable phase of ZrO_2 is tetragonal (*t*-phase). Monoclinic $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films exhibit a low dielectric constant while the tetragonal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films exhibit the highest dielectric constant [25]. The tetragonal phase in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films can be partially stabilized by alloying ZrO_2 into HfO_2 [25]. Interestingly, tetragonal ZrO_2 thin films are easily crystallized, when grown on TiN seed layer; therefore TiN is generally used as a seed layer to grow tetragonal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films [30]. Even with a TiN seed layer, for achieving desired electrical properties, the crystal structure of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films need to be manipulated by controlling the deposition conditions or a post deposition annealing. It is quite challenging to grow $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films with desired crystal structure and mostly physical/chemical vapor deposition techniques such as electron beam evaporation, sputtering, chemical vapor deposition, and atomic layer deposition are being widely used to grow $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films. In most cases, thin films grown using physical/chemical vapor deposition techniques require post-deposition annealing at a high temperature ($>1000^\circ\text{C}$), to reduce the defect density in films. However, high temperature annealing commonly generates unwanted grain boundaries, high surface roughness, leakage current, and etc, leading to a poor device reliability [1]. Furthermore, the low growth rate, poor interface

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between film and substrate, the scarcity of appropriate precursors, requirement of vacuum environment, and high temperature ($\sim 1000^\circ\text{C}$) post-annealing are the limitations of the aforementioned techniques. It is highly desirable to grow high quality $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films using a facile method and at a lower post-annealing temperature ($<1000^\circ\text{C}$).

Solution processing is an inexpensive, vacuum free, and flexible deposition technique to deposit stoichiometric HfZrO_2 thin films. Here, we report the growth of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) thin films ($\sim 10\text{ nm}$) using solution processing. We observed a variation in the crystal structure with the post-annealing temperature ($<1000^\circ\text{C}$) of the as-deposited films.

2. Experiment

An equimolar ratio of precursors Hafnium isopropoxide isopropanol ($\text{C}_{15}\text{H}_{36}\text{O}_5\text{Hf}$, Sigma Aldrich) and Zirconium dinitrate oxide hydrate ($\text{N}_2\text{O}_7\text{Zr} \cdot x\text{H}_2\text{O}$, Sigma Aldrich) are dissolved in 2-methoxy ethanol for 8 h at 75°C . Prior to the deposition of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) thin films, nearly a 60 nm thick TiN is sputtered using a TiN target (purity 99.95%, Advanced Engineering Materials,

China) on to Si substrate at a sputtering power of 50 W and Ar gas pressure of 10 mTorr. The sputtering rate is $0.5\text{ \AA/s}$. The HZO thin films are spin casted on to TiN/Si substrates at a spin speed of 3000 rpm for 30 s. After the deposition, the HZO thin films are baked at 150°C for 10 min on a hot plate. The mixing of the precursor solution, spin coating, and baking processes are carried out inside a glove box. After baking, the films are post annealed in nitrogen ambient at a temperature ranging from 400 to 700°C for 1 h. In order to complete the capacitor, the Pt top electrode (60 nm) is evaporated using an electron beam evaporator. The thickness of the films is controlled by varying the molar concentration of the precursor solution. We used transmission electron microscopy (TEM, Tecnai G2 F30 S-Twin) to analyze the cross-section and interface quality of the fabricated capacitors. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) coupled to energy-dispersive X-ray spectroscopy (EDS) is performed at a voltage of 200 kV to analyze the elementary composition. The electron transparent cross-sectional TEM specimen is prepared using the focused ion beam (FIB) lift-out technique in a dual-beam SEM (FEI Versa 3D). The surface morphology and cross section of the films are also imaged using scanning electron

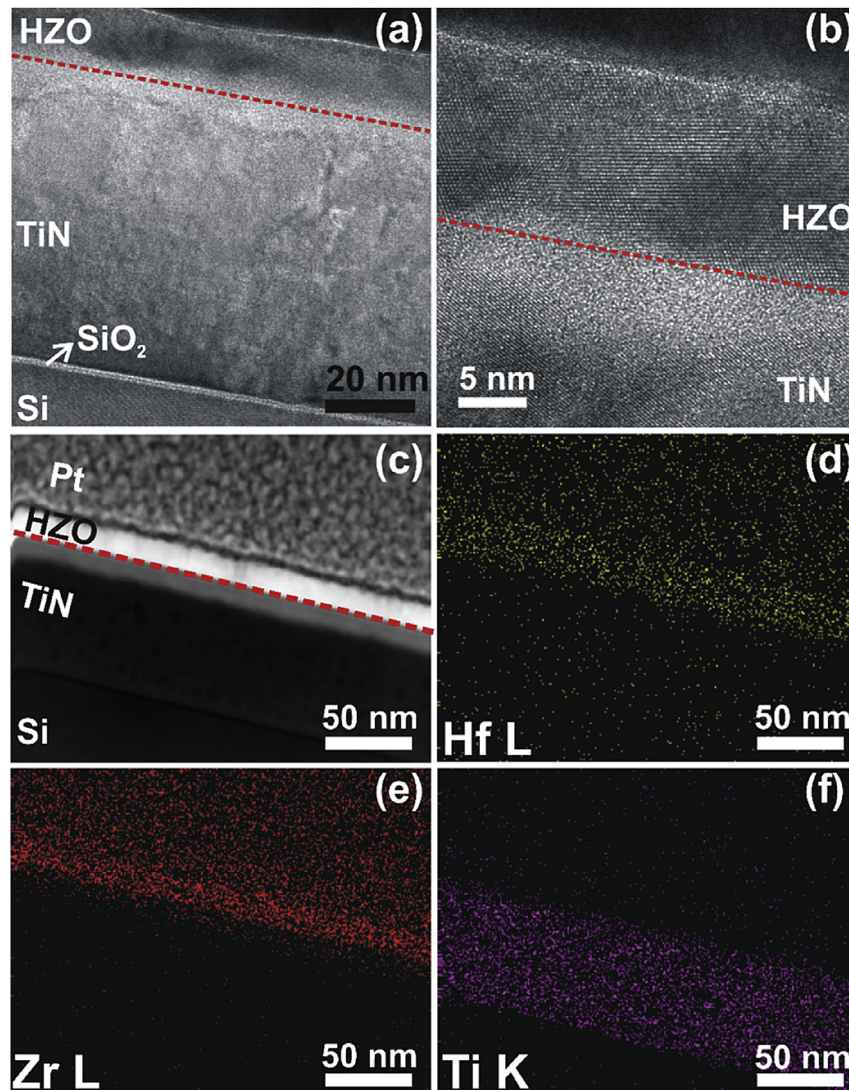


Fig. 1. (a–b) Cross-sectional TEM/HRTEM of Pt/HZO/TiN/Si device, (b) shows the magnified cross-sectional HRTEM of the TiN/HZO interface. (c) HAADF-STEM image, (d–f) STEM-EDS elemental mapping of Hf, Zr, and Ti.

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