

ALD Applications

Room Hall 3D - Session AA1-WeM

Flash and Ferroelectric Memories

Moderators: Haripin Chandra, EMD Electronics, USA, Matti Putkonen, University of Helsinki

8:00am AA1-WeM-1 Ferroelectric Doped HfO₂: From Ald Processing to Device Applications, Uwe Schroeder, NamLab, Germany **INVITED**

Extensive research and development have been conducted on doped HfO₂ or ZrO₂-based ferroelectric materials [1]. These unique fluorite-structured ferroelectrics have outstanding potential for commercial applications due to their scalability, CMOS compatibility, and ease of fabrication. Ferroelectric HfO₂ is particularly attractive for semiconductor memory applications because of its advantageous properties. The scientific community has made great efforts to improve and optimize the ferroelectric properties using a variety of approaches due to the wide range of conditions under which ferroelectricity can occur in thin films. Consequently, thin-film ferroelectric capacitor and memory array technologies are advancing quickly. But, researchers are still trying to elucidate the various causes of ferroelectricity in doped HfO₂ and ZrO₂ thin films in order to improve device performance.

Different chemical precursors for HfO₂ and ZrO₂ are compared for the best ALD process window [2]. The doping and oxygen content of the film are important for both the formation of the crystal phase and the performance of HfO₂-based devices [3]. It is crucial to consider all of these factors when designing and optimizing HfO₂-based devices. Other factors, such as interaction with electrode materials, crystallization anneals, and stress in the resulting film, can also significantly affect the ferroelectric properties. Once a ferroelectric phase is reached in thin films, it can be influenced by further thermal treatments and the application of an electric field. Recent piezo-force microscopy studies have confirmed a nanoscale electric field-induced phase transition from a non-polar tetragonal to a polar orthorhombic phase. This knowledge of phase transitions in doped HfO₂- and ZrO₂-based films is essential for the development of future ferroelectric devices.

The recently discovered properties of HfO₂, even at film thicknesses below 10 nm, have enabled a growing number of applications, such as high aspect ratio ferroelectric capacitors (FeCap) and field-effect transistors (FeFET) [4]. Additionally, other applications, such as ferroelectric tunnel junctions, neuromorphic, piezo-, and pyroelectric devices, are being discussed [4]. Many devices can now be realized on smaller technology nodes and in larger memory arrays. At the end of 2023, non-volatile FeCap based memory chips have been presented at conferences [5].

This review will cover recent results and provide an overview of the subject, starting with a discussion of the causes of ferroelectric properties and experimental reports on phase stabilization in doped HfO₂, as well as an introduction to recent semiconductor applications.

8:30am AA1-WeM-3 Interfacial Layer Engineering by Tungsten Oxide for Ferroelectric La-Doped Hf_{0.5}Zr_{0.5}O₂ Layer, Dae Seon Kwon, M. Popovici, J. Bizindavyi, imec, Belgium; G. De, A. Delabie, KU Leuven, imec, Belgium; A. Belmonte, G. Sankar Kar, imec, Belgium; J. Van Houdt, KU Leuven, imec, Belgium

In this work, the electrical performance of the ferroelectric La-doped Hf_{0.5}Zr_{0.5}O₂ (La:HZO) layer was optimized by interfacial engineering employing tungsten oxide with back-end-of-line (BEOL) compatibility, and the effect was investigated in detail. A major problematic issue arising when scaling down the physical thickness of the HZO for industrial applications is undesirable stabilization of non-ferroelectric tetragonal phase, especially at the interface between the TiN electrode and HZO layers due to a high defect level such as oxygen vacancy. This phenomenon was attributed to the oxygen scavenging effect by the TiN electrode, leading to the formation of oxygen vacancies throughout the HZO layer, and especially at the interfaces. In this study, to stabilize the ferroelectric orthorhombic phase, tungsten oxide was adopted as an oxygen donor for the HZO layer.

Tungsten oxide has numerous advantages, ranging from high compatibility with complementary metal-oxide-semiconductor (CMOS) technology to its various oxidation states, which can control the oxygen vacancy level in the HZO layer when used as an interfacial layer between the TiN electrode and HZO layer. First, the atomic layer deposition (ALD) process of the tungsten trioxide (WO₃) was established, and the characteristics as a potential interfacial layer were examined. Subsequently, all layers in metal-insulator-metal (MIM) capacitor were deposited via ALD. The oxygen supply

from reducible tungsten oxide, transitioning from WO₃ to WO_{3-x}, effectively annihilated oxygen vacancies in the HZO, leading to the promotion of the orthorhombic phase. Additionally, the possible distribution of the oxygen vacancies induced by the interfacial tungsten oxide layer and its effect was investigated depending on the device cycling through the imprint of the polarization-electric field (P-E) loop and the depth profile of the oxygen element. Appropriate control of oxygen vacancies via interfacial engineering with various seed and capping layer materials enabled the stabilization of the orthorhombic phase, thereby increasing the two remanent polarization (2P_r) value. Finally, the superior electrical performance of the improved 2P_r value with an endurance cycle number over 10⁹ cy was achieved with an optimized tri-layer stack consisting of seed TiO₂/La:HZO/capping WO₃. This interfacial engineering work is anticipated to provide a guideline for further engineering involving thickness, dopant, and functional layer in FeRAM capacitor.

8:45am AA1-WeM-4 Ultrathin HfO₂-ZrO₂ Multilayers Structures by ALD for Embedded Ferroelectric Non-Volatile Memories, Amanda Mallmann Tonelli, J. Mercier, N. Vaxelaire, Y. Mazel, Z. Saghi, N. Gauthier, S. Martin, L. Grenouillet, V. Jousseume, M. Bedjaoui, CEA-Leti, France

The rapid progress of nanoelectronic systems and miniaturized portable devices has increased the urgent demands for miniaturized and integrated circuit. Recently, the developed hafnium-oxide (HfO₂)-based ferroelectric films with CMOS-compatible process shows a great potential for advanced low-power device technology [1]. However, ultrathin HfO₂-based ferroelectric films are still in the risk of device failure due to the large leakage current, which makes it unstable and limits the device service life [2], [3]. On the other hand, a significant effort has been made to lower the ferroelectric film thickness below 10 nm while maintaining good ferroelectric properties. The multilayer approach can provide solutions to the problems of leakage current and endurance by blocking the electrons injected from the electrode, which provides a promising idea for the application of HfO₂ in electronic devices [4].

The aim of this study is to develop ultrathin ferroelectric layers by ALD for MFM (Metal-Ferroelectric-Metal) capacitors based non-volatile memories. Within this work, HfO₂-ZrO₂ multilayers consisting of stacked HfO₂ and ZrO₂ were developed and investigated. The objective of this project is i) to investigate the intrinsic characteristics of the material and its evolution at each stage of the MFM fabrication through different structural, physicochemical and image analyses and ii) correlate the structural properties to the electrical characteristics.

The experimental analysis of the 10 nm thick nanolaminates films allowed some preliminary conclusions. The x-ray diffraction results presented in (Fig. 1) reveal that the films are already crystalline after deposition of the TiN/W top electrodes, carried out at 380°C. The diffraction peaks around 30.5° stand for a mixture of tetragonal and orthorhombic phase and could be evidence of the beginning of crystallization of a ferroelectric material. Furthermore, after dry plasma etching of the top electrode, the chemical state of material was analyzed using x-ray photoelectron spectroscopy. In addition to the composition of the material, an estimation of the oxygen vacancies (V_o) was made, as V_o is supposed to play a crucial role in the ferroelectricity of HfO₂-based films (Fig. 2). After annealing, through electrical positive-up-negative-down (PUND) measurement, it was possible to obtain evidence of ferroelectricity of the structure (Fig. 3) The preliminary findings showed in this work seems favorable for the implementation of FE HfO₂-ZrO₂ multilayers in non-volatile memory devices.

9:00am AA1-WeM-5 Effects of Gamma Radiation on the Electrical and Structural Properties of Ferroelectric Hafnium Oxide-Based Capacitors, Samantha Jaszewski, M. Henry, Sandia National Laboratories

Ferroelectric hafnium oxide (HfO₂) presents opportunities for technological developments in microelectronics, such as scaling of ferroelectric random-access memory (FeRAM) and new devices such as ferroelectric field-effect transistors (FeFETs) and ferroelectric tunnel junctions (FTJs), that were not previously possible with conventional ferroelectrics. This is due to its compatibility with silicon and ability to exhibit a ferroelectric response in films as thin as 1 nm. Understanding the interaction between radiation and HfO₂-based ferroelectrics is necessary before this material can be utilized in devices facing radiation-hostile environments. In this work, the effects of varying doses of gamma radiation (1 to 8 Mrad) on the structural and electrical properties of metal-ferroelectric-metal capacitors fabricated with 17 nm thick hafnium zirconium oxide (HZO) layers is investigated.

Additionally different electrode materials, titanium nitride and tungsten, will be compared. Polarization-electric field, capacitance-voltage, and leakage current measurements were made after electric field cycling with voltages ranging from 2.6 to 4 V. It will be shown that the devices experience decreased endurance and a shift in the coercive voltage that scales with the applied gamma dose and depends on the electrode material. This work advances the understanding of the interaction between radiation and HfO₂-based ferroelectrics in order to probe the fundamental limits of radiation tolerance in this material.

9:15am **AA1-WeM-6 Enhancement of Ferroelectric Phase Formation of HfO₂/ZrO₂ Nanolaminate Films by Tuning HfO₂ and ZrO₂ Thicknesses Using Atomic Layer Deposition, Takashi Onaya, Y. Sakuragawa, K. Kita, The University of Tokyo, Japan**

Ferroelectric Hf_{1-x}Zr_xO₂ (HZO) thin films are typically fabricated by forming HfO₂/ZrO₂ nanolaminate films deposited by alternately depositing HfO₂ and ZrO₂ layers using atomic layer deposition (ALD). It has been reported that the remanent polarization of HfO₂/ZrO₂ nanolaminate films changed depending on each HfO₂ and ZrO₂ thickness [1]. However, it is still unclear how each HfO₂ and ZrO₂ thickness affect the formation of ferroelectric orthorhombic (O) phase. In this work, we studied the crystal structure of HfO₂/ZrO₂ nanolaminate films with various conditions using ALD.

A 10-nm-thick HfO₂/ZrO₂ nanolaminate film was deposited on a TiN/p-Si substrate by alternately depositing HfO₂ and ZrO₂ layers using ALD at 300°C. Hf[N(C₂H₅)CH₃]₄ and Zr[N(C₂H₅)CH₃]₄ precursors were used for HfO₂ and ZrO₂, respectively, and H₂O was used for an oxidant. The ALD cycle ratio was varied from HfO₂/ZrO₂=1/1 to 60/60 so that each HfO₂ and ZrO₂ thickness would be varied from 0.08 to 5 nm while keeping the total thickness of the nanolaminate film to 10 nm. Finally, post-deposition annealing was performed at 600°C for 1 min in a N₂ atmosphere. A 10-nm-thick HZO solid-solution film was also fabricated by ALD using a Hf/Zr[N(C₂H₅)CH₃]₄ cocktail precursor as a reference.

In grazing-incidence X-ray diffraction (GIXRD) spectra, all samples clearly showed the diffraction peak at ~30.7°, attributed to either O(111), tetragonal (T) (101), or cubic (C) (111) (O/T/C) phases. The peaks for HfO₂ and ZrO₂ are not distinguishable due to almost the same lattice constant. The O/T/C peak areas of the HfO₂/ZrO₂=6/6 and 12/12 films were ~1.4 times larger than that of the HZO solid-solution film, where each HfO₂ and ZrO₂ thickness was 0.5–1 nm (1–2 monolayers). On the other hand, the HfO₂/ZrO₂=1/1 and HZO solid-solution films showed similar O/T/C peak area, because Hf and Zr atoms could be uniformly mixed in the HfO₂/ZrO₂=1/1 film. In addition, the O/T/C peak area decreased by increasing ALD cycle ratio, such as the HfO₂/ZrO₂=20/20 and 60/60. We also found that the as-grown ZrO₂ film was already crystallized in O/T/C phases even without annealing, whereas the most of as-grown HfO₂ and HZO solid-solution films was amorphous [2]. Therefore, the ZrO₂ layers in HfO₂/ZrO₂ nanolaminate films should play a role to provide nuclei efficiently to enhance the O/T/C phase formation in the HfO₂/ZrO₂=6/6 and 12/12 films.

In conclusion, the O/T/C phase formation can be prompted by using HfO₂/ZrO₂ nanolaminate films with each HfO₂ and ZrO₂ thickness of 1–2 monolayers.

[1] J. Liao et al., IEEE Electron Device Lett. 40, 1868 (2019).

[2] T. Onaya et al., APL Mater. 7, 061107 (2019).

9:30am **AA1-WeM-7 Investigating the Impact of Process Parameters on the In-plane Strain of Ultra-Thin Hf_{1-x}Zr_xO₂ Films, Florian Wunderwald, Namlab, Germany; B. Xu, Namlab, China; P. Vishnumurthy, Namlab, India; S. Enghardt, TU Dresden, Germany; K. Holsgrave, Queen's University Belfast, UK; A. Kersch, University of Applied Sciences Munich, Germany; T. Mikolajick, U. Schroeder, Namlab, Germany**

Since the development of Atomic Layer Deposition (ALD) 50 years ago, the technique has improved the deposition of thin films [1]. The first hafnium oxide processes were developed in the mid-1990s, and the material has been in mass production for semiconductor devices since 2007 [2, 3]. Interestingly, in the same year, T. Boescke discovered ferroelectricity in doped hafnium oxide thin films [4]. The finding of ferroelectricity in a fluorite-structured material, which is simultaneously compatible with semiconductor processing, has generated significant interest in their use for cutting-edge technologies such as non-volatile memory applications, neuromorphic computing, and AI applications [5]. To achieve the desired industrial properties of the material, which include high remnant polarization, high endurance, and high retention, understanding the impact of ALD processing on the later properties is crucial. In addition to that, the thickness scaling and behavior of ultra-thin Hf_{1-x}Zr_xO₂ films are receiving

more attention from the industry [5]. However, there is a lack of studies that review the impact of the single-stack engineering steps, such as atomic layer deposition (ALD), interface engineering, and annealing conditions, on one of the key factors: biaxial in-plane strain and its influence on ferroelectric phase formation in ultra-thin Hf_{1-x}Zr_xO₂ films.

This study fills this gap and investigates the shortcomings mentioned above. To determine the biaxial in-plane strain, the lattice spacing was measured using the sin²Ψ-method [6]. The results in Figure 2 show a clear increase in in-plane strain for thinner films, indicating a stronger impact of interfacial crystal lattice misfits, which can be confirmed by TEM measurements. Changes in strain lead to phase transitions for thinner films. To determine the different phases Grating Incidence XRD (Figure 3) and EBSD (Figure 4) has been performed. For a deeper understanding and correlation, bipolar electric field cycling measurements were carried out to set the strain results in correlation with the electric switching field.

This study aims to enhance the knowledge of the influence of ALD process parameters on the in-plane strain in thin and ultra-thin Hf_{1-x}Zr_xO₂ films. The findings will provide a better understanding of processing and, thus, the establishment of Hf_{1-x}Zr_xO₂ films in non-volatile memory storage applications.

9:45am **AA1-WeM-8 Thermal ALD IGO Channel Layer with High-thermal Stability (> 800 °C) for New Hybrid (Poly-Si/IGO) Vertical 3D NAND Application, Su-Hwan Choi, J. Sim, Hanyang University, Korea; C. Park, Hanyang University, Korea, Republic of Korea [], Republic of Korea; Y. Song, J. Park, Hanyang University, Korea**

The oxide semiconductor (OS) channel materials represented by IGO have been attracting attention from memory devices such as DRAM and NAND flash applications because of their outstanding properties, such as high mobility, low off-current, and excellent uniformity. Especially for the NAND flash memory, high field-effect mobility OS is proposed as the channel layer. However, OS channel NAND has problems, such as the inability to erase operations and poor thermal stability. To improve the disadvantages of OS channel NAND, we proposed a hybrid channel (HC, Poly-Si/OS) for V-NAND flash memory in which a poly-Si and an OS channel coexist for the remaining gate-induced-drain leakage (GIDL) erase scheme and high mobility, respectively. In this study, we adopt the atomic layer deposition (ALD) method for depositing the OS channel. The ALD has great advantages, such as excellent step coverage and sub-nanometer-scale thickness control. Especially for hybrid channel structures, high step coverage properties of OS deposition are crucial because the aspect ratio is increased by Poly-Si channel deposition. This is because the hole diameter of the V-NAND string is decreased by poly-si thickness, whereas the hole height is similar.

In this study, we adopt the IGO for the hybrid channel structure (poly-Si/IGO). The DBADMI was adopted to deposit the InO, the mother material of IGO. As shown in **Fig 1 (a) and (b)**, the 250 °C deposited InO using ozone as a reactant easily crystallizes even at 3 nm thick with highly c-axis aligned Cubic (222) orientation, exhibiting superior electrical and stability properties. The TMGa was adopted to gallium doping for the InO channel using the super-cycle method. A thickness of IGO above 10 nm is needed to achieve high thermal stability after the post-annealing process at 800 °C for 3 hours because the thermal stability of IGO is related to crystallinity (**Fig 1 (c)**). The vertically structured HC NAND flash was successfully fabricated, as shown in **Fig 2**. The Schematic of the V-NAND flash memory structure for illustrating conventional poly-Si and the purpose of the hybrid-channel (HC) structure are summarized in **Fig 2(a)**. As shown in **Fig 3 (a)**, the GIDL current of HC channel NAND flash was achieved and confirmed as successfully operating the program and erase operation after the post-annealing process at 800 °C for 3 hours. We easily understand the conventional program, however, in the case of GIDL erase, through **Fig. 3(b)**, the proposed HC structure generates a band to band tunneling generation through a poly-Si channel, therefore the GIDL-assisted increasing channel potential can be confirmed through hole current generation.

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