ALD Applications
Room Hall 3D - Session AA1-WeM

Flash and Ferroelectric Memories

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

8:00am **AA1-WeM-1 Ferroelectric Doped HfO_2: From Ald Processing to Device Applications***, Uwe Schroeder,* Namlab, Germany **INVITED**

Extensive research and development have been conducted on doped HfO_2 or ZrO_2-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 HfO_2 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 HfO_2 and ZrO_2 thin films in order to improve device performance.

Different chemical precursors for HfO_2 and ZrO_2 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 HfO_2-based devices [3]. It is crucial to consider all of these factors when designing and optimizing HfO_2-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 HfO_2- and ZrO_2-based films is essential for the development of future ferroelectric devices.

The recently discovered properties of HfO_2, 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 HfO_2, as well as an introduction to recent semiconductor applications.

8:30am **AA1-WeM-3 Interfacial Layer Engineering by Tungsten Oxide for Ferroelectric La-Doped $Hf_{0.5}Zr_{0.5}O_2$ 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 $Hf_{0.5}Zr_{0.5}O_2$ (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 (WO_3) was established, and the characteristics as a potential interfacial layer were examined. Subsequentially, all layers in metal-insulator-metal (MIM) capacitor were deposited via ALD. The oxygen supply from reducible tungsten oxide, transitioning from WO_3 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 10^9 cy was achieved with an optimized tri-layer stack consisting of seed TiO_2/La:HZO/capping WO_3. 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 HfO_2–ZrO_2 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. Jousseaume, 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 developedhafnium-oxide (HfO_2)basedferroelectric filmswith CMOS-compatible process shows a great potential for advanced low-power device technology [1]. However, ultrathin HfO_2-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 provides 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 HfO_2 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, HfO_2-ZrO_2 multilayers consisting of stacked HfO_2 and ZrO_2 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 HfO_2-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 HfO_2-ZrO_2 multilayers in non-volatile memory devices.

9:00am **AA1-WeM-5 In-situ Crystallization of Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films with Record-high $2P_r$ (56μC/cm²) at Low Thermal Budget (300℃) Towards Full BEOL-compatibility***, P. Yuan,* Beijing Superstring Academy of Memory Technology, China*; L. Tai,* Shandong University, China*; X. Ma, J. Xiang,* Beijing Superstring Academy of Memory Technology, China*; G. Wang,* Shandong University, China*; J. Chen,* shandong University, China*; C. Zhao, **Yuting Chen**,* Beijing Superstring Academy of Memory Technology, China

In barely over a decade, HfO_2-based ferroelectric thin film went from the early research stage to possibly being integrated into backend- of-line (BEOL) and even industrialized. Acting as the dielectric layer in the 1T1C unit for ferroelectric random-access memory (FRAM) or Dynamic random-access memory (DRAM), HfO_2-based ferroelectric thin film should be compatible with the thermal budget (<400℃) of BEOL process, especially in advanced nodes. However, a high rapid thermal annealing (RTA)

temperature beyond 400℃ seems indispensable for HfO_2-based ferroelectric thin film. Nowadays, seeking a lower thermal budget (<400℃) has been a hot topic in the area of HfO2-based ferroelectric materials. A real sense of a low thermal budget for ferroelectric HfO2-based materials with both high $P_r$and endurance remains a great challenge.

In this work, we present a process solution in thermal ALD for fabricating ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) capacitors annealed at 300℃ with high remanent polarization (P_r) and good endurance for full compatibility with BEOL. Record-high $2P_r$ values in 300℃-annealed (56 μC/cm²) $Hf_{0.5}Zr_{0.5}O_2$ (HZO)-based metal-ferroelectric- metal (MFM) devices are demonstrated by using an in-situ crystallization process in atomic layer deposition, i.e., using TDMA-based precursors and interfacial O_3 engineering at a slightly higher temperature of 320℃. This work is believed to leading a trend in fabricating the fully BEOL-compatible HZO ferroelectric devices, especially for advanced nodes requiring a much lower thermal budget.

9:15am **AA1-WeM-6 Enhancement of Ferroelectric Phase Formation of HfO_2/ZrO_2 Nanolaminate Films by Tuning HfO_2 and ZrO_2 Thicknesses Using Atomic Layer Deposition**, ***Takashi Onaya***, *Y. Sakuragawa, K. Kita,* The University of Tokyo, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) thin films are typically fabricated by forming HfO_2/ZrO_2 nanolaminate films deposited by alternately depositing HfO_2 and ZrO_2 layers using atomic layer deposition (ALD). It has been reported that the remanent polarization of HfO_2/ZrO_2 nanolaminate films changed depending on each HfO_2 and ZrO_2 thickness [1]. However, it is still unclear how each HfO_2 and ZrO_2 thickness affect the formation of ferroelectric orthorhombic (O) phase. In this work, we studied the crystal structure of HfO_2/ZrO_2 nanolaminate films with various conditions using ALD.

A 10-nm-thick HfO_2/ZrO_2 nanolaminate film was deposited on a TiN/p-Si substrate by alternately depositing HfO_2 and ZrO_2 layers using ALD at 300℃. $Hf[N(C_2H_5)CH_3]_4$ and $Zr[N(C_2H_5)CH_3]_4$ precursors were used for HfO_2 and ZrO_2, respectively, and H_2O was used for an oxidant. The ALD cycle ratio was varied from HfO_2/ZrO_2=1/1 to 60/60 so that each HfO_2 and ZrO_2 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℃ for 1 min in a N_2 atmosphere. A 10-nm-thick HZO solid-solution film was also fabricated by ALD using a $Hf/Zr[N(C_2H_5)CH_3]_4$ 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 HfO_2 and ZrO_2 are not distinguishable due to almost the same lattice constant. The O/T/C peak areas of the HfO_2/ZrO_2=6/6 and 12/12 films were ~1.4 times larger than that of the HZO solid-solution film, where each HfO_2 and ZrO_2 thickness was 0.5−1 nm (1−2 monolayers). On the other hand, the HfO_2/ZrO_2=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 HfO_2/ZrO_2=1/1 film. In addition, the O/T/C peak area decreased by increasing ALD cycle ratio, such as the HfO_2/ZrO_2=20/20 and 60/60. We also found that the as-grown ZrO_2 film was already crystallized in O/T/C phases even without annealing, whereas the most of as-grown HfO_2 and HZO solid-solution films was amorphous [2]. Therefore, the ZrO_2 layers in HfO_2/ZrO_2 nanolaminate films should play a role to provide nuclei efficiently to enhance the O/T/C phase formation in the HfO_2/ZrO_2=6/6 and 12/12 films.

In conclusion, the O/T/C phase formation can be prompted by using HfO_2/ZrO_2 nanolaminate films with each HfO_2 and ZrO_2 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 H-$f_xZr_{1-x}O_2$ Films**, ***Florian Wunderwald,*** Namlab, Germany*; B. Xu,* Namlab, China*; P. Vishnumurthy,* Namlab, India*; S. Enghardt,* TU Dresden, Germany*; K. Holsgrove,* 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-$_xZr_{1-x}O_2$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 H-$f_xZr_{1-x}O_2$ 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 $\sin^2\Psi$-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 Gracing 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-$_xZr_{1-x}O_2$films. The findings will provide a better understanding of processing and, thus, the establishment of Hf-$_xZr_{1-x}O_2$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 IGZO 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 DBADMIn 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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