Thin Films
Room 115 - Session TF+EM-ThA

Thin Films for Microelectronics II: Ferroelectrics, Dielectrics, and Semiconductors

Moderators: Elton Graugnard, Boise State University, **Christophe Vallee**, University at Albany

2:15pm **TF+EM-ThA-1 Atomic Scale Control of Ferroelectric $HfZrO_x$ Thin Films through Atomic Layer Modulation**, ***Ngoc Le Trinh***, *C. Nguyen,* Incheon National University, Viet Nam; *B. Gu, B. Lee,* Incheon National University, Republic of Korea; *K. Yang,* Seoul National University, Republic of Korea; *H. Kim, H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea; *M. Park,* Seoul National University, Republic of Korea; *Y. Kang,* Incheon National University, Republic of Korea; *S. Kim,* Ulsan National Institute of Science & Technology, Republic of Korea; *H. Lee,* Incheon National University, Republic of Korea

Over the past few decades, atomic layer deposition (ALD) has become a key technique for the fabrication of multicomponent films in Si devices, such as 3D memory and logic devices. Conventionally, the formation of multilayers by supercycle method consisting of two or more ALD processes has been used, and the compositional ratio of the films could be controlled by cyclic ratio of two ALD processes. However, the supercycle method could not be applied to a few nanometers range in film thickness due to inconsistent surface reactions and low out-of-plane uniformity. Based on understanding of surface reactions mechanism in ALD, we have studied the concept of atomic layer modulation (ALM) for fabrication of the multicomponent thin film with atomic-scale control. The main key idea of ALM is that the compositional ratio is determined by the physical steric hindrance and the chemical reactivity of two precursors on the surface which can be predicted by theoretical calculations. We fabricated a $HfZrO_x$ multicomponent thin film with controllable dopant ratio using a Hf precursor, tetrakis(dimethylamido)-hafnium (TDMAH), and a Zr precursor, tetrakis(ethylmethylamido)-zirconium (TEMAZ). Due to the differences of steric hindrance and chemical reactivities, the stoichiometry of $HfZrO_x$ thin films is determined by the exposure sequence of precursors. Theoretical calculations were performed using Monte Carlo (MC) and density functional theory (DFT) to study physical and chemical reaction mechanisms. The theoretical results are consistent with the experiments analyzed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). From the ferroelectric property analysis, the ALM $HfZrO_x$ films showed superior properties than the others prepared by conventional supercycle method, such as higher 2Pr values of 39.4 μC/cm^2, which is 2 times higher than in supercycle ALD $HfZrO_x$ film. By enabling precise stoichiometric control at atomic level, the ALM method not only extends the potential for fabricating multicomponent oxide materials but also enhances the quality of the deposited films.

2:30pm **TF+EM-ThA-2 Plasma-Enhanced Atomic Layer Deposition Based Ferroelectric Field Effect Transistors**, ***Chinsung Park***, *P. Ravindran,* Georgia Institute of Technology, USA; *D. Das,* National Institute of Technology, India; *P. Ravikumar,* Georgia Institute of Technology, USA, Uganda; *w. chern, S. Yu, A. Khan,* Georgia Institute of Technology, USA

This presentation investigates the electrical characteristics of ferroelectric material $Hf_{0.5}Zr_{0.5}O_2$ (HZO) when deposited on Si using either thermal ALD or plasma ALD methods. Previous research has explored the differences in ALD deposition methods in metal-insulator-metal (MIM) capacitor structures with HZO deposited on metal. However, considering emerging non-volatile memory (eNVM) applications, a comparative evaluation based on Si substrates is necessary but has not yet been reported. We examined how the characteristics differ between thermal and plasma ALD deposition methods in metal-oxide-semiconductor (MOS) structures compared to MIM structures. Experiments were conducted by fabricating ferroelectric field-effect transistors (FEFETs) using thermal and plasma ALD deposition methods, followed by electrical characterization. The results showed that devices fabricated using plasma ALD exhibited similar results to MIM structures in MOS structures, including no wake-up effect, better endurance (one order higher), and a larger coercive voltage (V_c). Additionally, HR-TEM cross-sectional analysis revealed that plasma ALD requires a larger write voltage to achieve a given memory window due to the presence of a thicker SiO_2 interfacial layer. Through this study, it was observed that ferroelectric HZO devices fabricated using thermal ALD require wake-up and have one order lower endurance but offer the advantage of lower write voltage. On the other hand, devices fabricated using plasma ALD exhibit no wake-up effect, better endurance (one order higher), but have higher write voltage. Considering these characteristics, future device designs may benefit from taking into account the differences in characteristics based on ALD methods.

2:45pm **TF+EM-ThA-3 Effect of Annealing Temperature on the Electrical Characteristics of $Hf_{0.5}Zr_{0.5}O_2$/InGaZnO Ferroelectric Field-Effect Transistor**, ***Deokjoon Eom***, *H. Kim, W. Lee, J. Lee, C. Park, J. Park, H. Lee, Y. Kim, H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, amorphous-oxide-semiconductor (AOS) materials, such as InGaZnO (IGZO), InZnO, and InWO, have been widely studied as channel materials for ferroelectric field-effect transistors (FeFETs) with a $Hf_{0.5}Zr_{0.5}O_2$ (HZO) gate dielectric because of their superior interface properties compared to Si channel-based FeFETs [1]. Typically, the fabrication of bottom-gate FeFETs with an AOS channel requires post-deposition annealing (PDA) after channel formation, which induces the formation of the ferroelectric orthorhombic phase in the HZO film and activates the AOS channel layer [2]. Meanwhile, it was reported that hydrogen atoms incorporated within the high-k film during atomic layer deposition (ALD) diffuse towards the IGZO channel region under thermal annealing, resulting in a notable change in the transfer characteristics of AOS-based FETs [3]. However, there is still a lack of research observing the detailed changes in the chemical and electrical properties of AOS-based FeFETs as a function of the PDA temperature.

In this presentation, we study the effect of PDA temperature on the electrical properties of bottom-gate HZO/IGZO FeFETs, where the PDA temperature was varied from 300 ℃ to 600 ℃ using rapid thermal annealing. The HZO and IGZO films were deposited in series via ALD with a Hf:Zr cycle ratio of 1:1 and sputtering of an IGZO target (In:Ga:Zn=1:1:1), respectively. Microstructural analysis revealed that, despite a significant volume shrinkage, the IGZO film maintained its amorphous structure after PDA at 600 °C, while the ferroelectric phase emerged in the HZO films after PDA at 400−600 ℃. Distinct changes in hydrogen content within the IGZO/HZO stack were observed at different PDA temperatures. These changes in hydrogen content, along with the evolution of the ferroelectric phase, significantly influenced the transfer characteristics of the fabricated devices, including parameters such as the threshold voltage and hysteresis loop direction.

References

[1] J. Ajayan et al., Mater. Today Commun. **35**, 105591 (2023)

[2] F. Mo et al., IEEE J. Electron Devices Soc. **8**, 717 (2020)

[3] Y. Nam et al., RSC Adv. **8**, 5622 (2018)

3:00pm **TF+EM-ThA-4 Polarization Switching in Metal-Organic MBE-Grown Metal-Ferroelectric-Metal Heterostructures**, ***Anusha Kamath Manjeshwar***, *Z. Yang,* University of Minnesota; *A. Rao, G. Rojas,* University of Minnesota, USA; *J. Wen,* University of Minnesota; *C. Liao, S. Koester, R. James, B. Jalan,* University of Minnesota, USA

Metal-ferroelectric-metal heterostructures have diverse applications ranging from ferroelectric non-volatile memories and sensing to neuromorphic computing. Traditionally, lead-based perovskite oxide ferroelectrics such as PZT and PMN-PT have been leading contenders in some of these applications. However, the toxicity of lead has prompted a renewed interest in the latent potential of lead-free ferroelectrics such as $BaTiO_3$ within the perovskite oxide family.

A long-standing challenge to unlock the potential of $BaTiO_3$ is systematically isolating the effect of parameters such as epitaxial strain, stoichiometry, and dimensionality on the ferroelectric properties of $BaTiO_3$ films. Producing reliable thin-film metal-ferroelectric-metal heterostructures for these studies depends on the (1) degree of control in the synthesis of each layer and (2) the atomic sharpness of the metal-ferroelectric interfaces. Despite molecular beam epitaxy (MBE) being the preferred growth method for heterostructures due to the high quality of the constituent layers and abrupt interfaces, the growth of ferroelectric $BaTiO_3$ with $SrRuO_3$ as metallic electrodes has two key challenges. First, elemental Ru is simultaneously difficult to evaporate and oxidize, requiring the use of electron-beam evaporators and potent oxidants which complicate stoichiometry control. Second, balancing the retention of molecular flow and preserving ideal oxygen stoichiometry and, consequently, ferroelectricity restricts the oxygen background pressures to ~1-3 orders of magnitude lower than in other synthesis methods.

We present the growth of $SrRuO_3$ and $BaTiO_3$- films using metal-organic MBE, overcoming both challenges. Using a solid metal-organic precursor for

Ru, we show the presence of an adsorption-controlled growth window within which the films self-regulate their cation stoichiometry for $SrRuO_3$ films on $SrTiO_3$ (001) substrates. We grow phase-pure, epitaxial, single-crystalline $BaTiO_3$ on $SrRuO_3$-buffered $SrTiO_3$ (001) substrates and note polarization switching with piezoresponse force microscopy for an applied bias of ± 6 V for a ~36 nm $BaTiO_3$ film without any post-growth oxygen annealing. We extend this technique to grow $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructures on Nb-doped $SrTiO_3$ (001) substrates. For a ~40 nm $BaTiO_3$ layer, we observe a room-temperature static dielectric constant of ~400 and ideal capacitor-like behavior up to 1 kHz using impedance spectroscopy. We demonstrate hysteretic *P-E* curves with P_r ~ 17 μC cm^{-2} and an E_c ~ 221 kV cm^{-1} at f = 1 kHz. We will discuss the effect of stoichiometry, strain, and dimensionality on the structural and dielectric properties of metal-organic MBE-grown $BaTiO_3$.

3:15pm **TF+EM-ThA-5 Integration of Barium Titanate onto high-Al content AlGaN***, **Peter Dickens**, A. Allerman, C. Harris, B. Klein,* Sandia National Laboratories

Wide-bandgap transistor development for next generation power electronics is promising. This is due to their higher breakdown field and saturated electron velocity over traditional silicon insulated-gate bipolar-transistors, and within this development, a push towards wider bandgaps in the $Al_xGa_{1-x}N$ system by increasing the Al-content is desired to further improve breakdown strengths and power densities in devices.However, even with higher breakdown strength, electric field spikes between the gate-drain on high-electron-mobility-transistors can result in device failure far below the inherent breakdown strength of the semiconductor.This has led to the integration of high-permittivity dielectrics on top of the semiconductor to mitigate these spikes; $BaTiO_3$ has received much of the attention owing to its large dielectric constant.Here we will report on the integration of RF sputtered $BaTiO_3$ thin films onto $Al_{0.85}Ga_{0.15}N$ substrates with a focus on the film morphology under specific deposition conditions.Results will focus on film morphology (x-ray diffraction, scanning electron microscopy, and atomic force microscopy) and stoichiometry (electron microprobe and x-ray fluorescence).

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC (NTESS), a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525.

3:30pm **TF+EM-ThA-6 Understanding the Crystallization of $BaTiO_3$ Thin Films Prepared by Atomic Layer Deposition***, **Jiayi Chen**,* Georgia Institute of Technology, USA, China*; A. Khan, M. Losego,* Georgia Institute of Technology, USA

This talk will discuss our work to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ thin films.Ferroelectric materials are the potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials HfO_2 and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields which makes it difficult to lower switching voltages to below 1V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V.However, such a ferroelectric needs to be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory and unfortunately, the deposition of multicomponent, stoichiometric crystalline phases by ALD is extremely challenging.In this talk we will discuss our efforts to achieve ALD of $BaTiO_3$ and discuss its microstructure, chemistry, and electrical properties.Specifically we will discuss variations caused by the use of different titanium precursors and their potential to lead to reduced oxidation states, hydrated phases, or carbon contamination that can prevent crystallization.We will also discuss the influence of these chemistries on stoichiometry and the ability to get pure crystalline phases.

3:45pm **TF+EM-ThA-7 Thermal and Plasma ALD BN for Low-k Applications***, **Pegah Bagheri**, M. Konh, R. Pearlstein, X. Lei, H. Chandra,* EMD Electronics, USA

Integration of low dielectric constant thin films in transistors and memories is a crucial step in realization of high speed, low-power and high-performance switches with lower parasite capacitance. Dielectric films, such as SiO_2 and Si_3N_4 and amorphous films deposited via Atomic Layer Deposition (ALD), were studied extensively providing a wide range of dielectric constants from 4.0 to 7.0. However, next generation of low-K spacer films targeting low-power high-performance applications requires conformal films on patterned structures with dielectric constant below silicon oxide (< 4.0) with good leakage current as low as <10^{-7} A.cm^2 at 1 MV/cm. Moreover, these thin films are expected to show high stability and high resistance to etching after exposure to HF which are typical integration steps in semiconductor device processing. Boron nitride is a new materials system in which lower dielectric constant than SiO_2 and Si_3N_4 is expected.-Previous study demonstrated PECVD boron nitride films with k as low as 2.0. Deposition of amorphous BN via ALD seems to be a superb candidate for the next generation of low-K spacer materials with dielectric constant below 3.0.

In this work, BN deposition was studied by use of BCl_3 and NH_3 as Boron and Nitrogen sources. NH_3 reacted with BCl_3 via surface-controlled reactions both thermally at 300°C, 400°C and 500°C and through NH_3 plasma generation at 200W and 300°C. ALD-deposited BN films showed uniformity of below 5% and thickness of 200Å measured by ellipsometer. Furthermore, electrical performance of BN films was measured by Capacitance-Voltage and Current-Voltage in Metal-Insulator-Semiconductor (MIS) structure using Mercury probe. To understand the incorporation of B and N and other elements such as C, O and Cl, crystallinity degree of the films and B-N bonding structures, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were utilized. Finally, the stability and resistance of ALD BN films to HF exposure was measured and monitored with time.

It was shown that amorphization degree increases at lower temperature and use of NH_3 plasma. However, thermally deposited BN at lower temperature showed high oxygen incorporation leading to degraded properties such as instability, low resistance to etching and poor electrical performances. Plasma ALD BN showed the lowest dielectric constant at 3.4 and wet etch rate below 0.03 time of the thermal oxide. Nevertheless, all BN films deposited with BCl_3 and NH_3 resulted in B/N~1.3 indicative of poor network formation. This led to formation of instable films with rough surfaces and degradation of bulk properties overtime.

4:00pm **TF+EM-ThA-8 Quantum Chemical Analysis for Effects of Carbon and/or Nitrogen Bond-Types on Dielectric Constant and Leakage Current in Low-K Dielectric SiOCN Film***, **Hu Li**, J. Zhao, P. Ventzek,* Tokyo Electron America, Inc.

Silicon Oxycarbon nitride (SiOCN) films are promising low dielectric(low-*k*) materials in semiconductor devices. The SiOCN film is fabricated using various fabrication technologies, that is, atomic layer deposition (ALD) and chemical vapor deposition (CVD), for specific applications such as inner spacers, gate spacers, and bottom contact etch stop layers (BCESL) in the deposition processes. Film deposition requires atomically precise control, with an increasing demand for nanoscale multilayer architectures. To further develop the SiOCN film properties and deposition processes, precise control of the bond-types in the fabrication process is required to maintain a low-k film property without increasing the risk of leakage current and/or decreasing the film density, particularly in a plasma enhanced ALD (PEALD) process. Chemically reactive species, such as radicals and energetic ions, generated in the plasma easily affect the film properties during plasma treatment by modifying the bond-types or surface structures. However, neither the effects of the reactive species on the formation of specific bond-types nor the effects of these bond types on the film properties are fully understood. Therefore, in this study, we examined the effects of various -Si-M-Si- bond-types ($M=C_xN_yH_z$) on the dielectric constant and leakage current using quantum chemical simulation. Our simulation modeling is based on experimental observations (XPS and FTIR). We found that when a carbon atom was present in a film with dangling bonds strongly affects the *k* values. The simulation results also showed that the Si-C-Si bond formed a mid-gap state, resulting in leakage current. When a carbon atom exists in the form of Si-CH_2-Si, no mid-gap state was observed, and such bond-type lowers the k value of the film. These results suggest that hydrogen plasma treatment may effectively prevent leakage current and yield low-k film structures. The effects of other bond-types and their concentrations on the k values and leakage currentare discussed in this presentation.

4:15pm **TF+EM-ThA-9 Electrical Measurement of in-situ Boron-Doped Epitaxial $Si_{1-x}Ge_x$ Films with Crystalline Defects***, **Hyung Chul Shin**, D. Eom,* Sungkyunkwan University (SKKU), Republic of Korea*; D. Yoon,* Yonsei University, Republic of Korea*; K. Kim, H. Yoo,* Samsung Electronics Co., Republic of Korea*; D. Ko,* Yonsei University, Republic of Korea*; H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Since its introduction as a channel-strain inducer in the early 2000s [1], in-situ epitaxial $Si_{1-x}Ge_x$ films doped with boron (B) have been continuously

employed as source and drain (S/D) regions in high-performance p-channel transistors, including the most advanced devices with a gate-all-around structure [2]. However, when the B doping concentration exceeds 10^{21} atoms/cm^3 in the $Si_{1-x}Ge_x$ film, the B atoms may partially occupy interstitial sites or form clusters, producing defects that can reduce the electrical activation ratio [3]. Therefore, it is crucial to assess these defects through electrical characterization because they can significantly impact the final device performance [4]. Furthermore, while the effect of defects on the electrical properties of $Si_{1-x}Ge_x$/Si p^+−n diode has been studied in the context of their application to S/D regions [5], there remains a need for a more extensive study, including further investigation of their effect on the contact properties of $Si_{1-x}Ge_x$ to the overlaid metals.

This presentation discusses various electrical properties of in-situ B-doped $Si_{1-x}Ge_x$ films epitaxially grown on n-type Si substrates, where crystalline defects are intentionally induced by varying the thickness and doping concentration. Various electrical parameters, such as reverse leakage current, on/off ratio, ideality factor, and activation energy, were extracted from the current−voltage characteristics of the p^+−n diodes. These parameters' changes were correlated with the presence of defects in the $Si_{1-x}Ge_x$ film. In addition, the contact resistivity values measured by a circular transmission line method also exhibited a similar trend, demonstrating reliable results regarding the effect of these defects.

[1] S. Thompson et al., 2002 IEEE International Electron Devices Meeting (IEDM) 61−64

[2] S. Barraud et al., 2016 IEEE International Electron Devices Meeting (IEDM) 17.6.1−17.6.4

[3] A. Moriya et al., Thin Solid Films 343-344, 541−544 (1999)

[4] T. Bhat et al., IEEE Trans. Semicond. Manuf. 33, 291 (2020)

[5] H. Huang et al., J. Appl. Phys. 89, 5133−5137 (2001)

Author Index

Bold page numbers indicate presenter

— A —
Allerman, A.: TF+EM-ThA-5, 2
— B —
Bagheri, P.: TF+EM-ThA-7, **2**
— C —
Chandra, H.: TF+EM-ThA-7, 2
Chen, J.: TF+EM-ThA-6, **2**
chern, w.: TF+EM-ThA-2, 1
— D —
Das, D.: TF+EM-ThA-2, 1
Dickens, P.: TF+EM-ThA-5, **2**
— E —
Eom, D.: TF+EM-ThA-3, **1**; TF+EM-ThA-9, 2
— G —
Gu, B.: TF+EM-ThA-1, 1
— H —
Harris, C.: TF+EM-ThA-5, 2
— J —
Jalan, B.: TF+EM-ThA-4, 1
James, R.: TF+EM-ThA-4, 1
— K —
Kamath Manjeshwar, A.: TF+EM-ThA-4, **1**
Kang, Y.: TF+EM-ThA-1, 1
Khan, A.: TF+EM-ThA-2, 1; TF+EM-ThA-6, 2
Kim, H.: TF+EM-ThA-1, 1; TF+EM-ThA-3, 1; TF+EM-ThA-9, 2
Kim, K.: TF+EM-ThA-9, 2
Kim, S.: TF+EM-ThA-1, 1
Kim, Y.: TF+EM-ThA-3, 1
Klein, B.: TF+EM-ThA-5, 2
Ko, D.: TF+EM-ThA-9, 2
Koester, S.: TF+EM-ThA-4, 1
Konh, M.: TF+EM-ThA-7, 2
— L —
Lee, B.: TF+EM-ThA-1, 1
Lee, H.: TF+EM-ThA-1, 1; TF+EM-ThA-3, 1
Lee, J.: TF+EM-ThA-3, 1
Lee, W.: TF+EM-ThA-3, 1
Lei, X.: TF+EM-ThA-7, 2
Li, H.: TF+EM-ThA-8, **2**
Liao, C.: TF+EM-ThA-4, 1
Losego, M.: TF+EM-ThA-6, 2
— N —
Nguyen, C.: TF+EM-ThA-1, 1
— P —
Park, C.: TF+EM-ThA-2, **1**; TF+EM-ThA-3, 1
Park, J.: TF+EM-ThA-3, 1
Park, M.: TF+EM-ThA-1, 1
Pearlstein, R.: TF+EM-ThA-7, 2
— R —
Rao, A.: TF+EM-ThA-4, 1
Ravikumar, P.: TF+EM-ThA-2, 1
Ravindran, P.: TF+EM-ThA-2, 1
Rojas, G.: TF+EM-ThA-4, 1
— S —
Shin, H.: TF+EM-ThA-9, **2**
— T —
Trinh, N.: TF+EM-ThA-1, **1**
— V —
Ventzek, P.: TF+EM-ThA-8, 2
— W —
Wen, J.: TF+EM-ThA-4, 1
— Y —
Yang, K.: TF+EM-ThA-1, 1
Yang, Z.: TF+EM-ThA-4, 1
Yoo, H.: TF+EM-ThA-9, 2
Yoon, D.: TF+EM-ThA-9, 2
Yu, S.: TF+EM-ThA-2, 1
— Z —
Zhao, J.: TF+EM-ThA-8, 2