

ALD Applications

Room Van Rysselberghe - Session AA1-WeA

ALD for Memory Applications II

Moderators: Nouredine Adjeroud, Luxembourg Institute of Science and Technology (LIST), Christian Wenger, IHP - Leibniz Institut fuer innovative Mikroelektronik

1:30pm AA1-WeA-1 Effects of Ultra-thin Atomic Layer Deposited MgO Buffer Layer on Structural and Electrical Properties of BeO and HfO₂ Films for Dynamic Random Access Memory Capacitors, Bo Wen Wang, H. Song, S. Byun, D. Kwon, J. Lim, H. Seo, T. Kim, H. Paik, J. Shin, C. Hwang, Seoul National University, Korea (Republic of)

In this work, magnesium oxide (MgO) thin films were grown via atomic layer deposition (ALD) as a buffer layer on titanium nitride (TiN) bottom electrode using bis(cyclopentadienyl) magnesium as the Mg precursor. Subsequently, beryllium oxide (BeO) and hafnium oxide (HfO₂) films were deposited by ALD on top of the MgO buffer layer using diethyl beryllium, tetrakis(ethylmethylamino) hafnium as the Be and Hf precursors, respectively. O₃ was used as the oxygen source for each ALD process. Such stacked films (MgO/BeO, MgO/HfO₂) were used as insulator layers for metal-insulator-metal (MIM) devices with TiN as bottom and top electrodes. The leakage current density (J) levels of the MIMs were significantly suppressed when the MgO buffer layer with a thickness of only ~1 nm was adopted. As a result, the 1 nm MgO buffer layer enabled a smaller total equivalent oxide thickness (EOT) value (defined by $J < 1 \times 10^{-7}$ A cm⁻² at an applied voltage of + 0.8 V) for the application of dynamic random access memory capacitor. The electrical performance improvement might be caused by the structural change with the addition of the MgO buffer layer. Therefore, the possible templating effect of in-situ crystallization of ultra-thin (< ~3nm) BeO and HfO₂ films on the MgO buffer layer, which was improbable directly on TiN, was investigated through scanning/transmission electron microscopy (S/TEM). Moreover, the intermixing occurring during deposition and post-deposition annealing were discussed based on the depth profiles by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

1:45pm AA1-WeA-2 Comparison of TiO_xN_{1-x} Layer Formation at Ferroelectric-Hf_xZr_{1-x}O₂/TiN Interface by H₂O and O₂ Plasma Gases During Atomic Layer Deposition, Takashi Onaya, National Institute of Advanced Industrial Science and Technology/Research fellow of Japan Society for the Promotion of Science, Japan; T. Nabatame, T. Nagata, S. Ueda, National Institute for Materials Science, Japan; Y. Jung, H. Hernandez-Arriaga, J. Mohan, J. Kim, The University of Texas at Dallas; C. Nam, E. Tsai, Brookhaven National Laboratory; H. Ota, Y. Morita, National Institute of Advanced Industrial Science and Technology, Japan

The discovery of the ferroelectricity in HfO₂-based films offered the possibility for the integration and scalability of ferroelectric memory devices because of capability of atomic layer deposition (ALD) technique. In our previous study, we have reported that the Hf_xZr_{1-x}O₂ (HZO) films fabricated by plasma-enhanced ALD (PE-ALD) using O₂ plasma showed a higher remanent polarization (2P_r) and superior fatigue properties compared to those fabricated by thermal ALD (TH-ALD) using H₂O gas. [1] To clarify the cause of these differences in ferroelectricity, we focused on the interface between the HZO film and TiN bottom-electrode (BE-TiN). In this work, we studied the TiO_xN_{1-x} interfacial layer (IL) formation between BE-TiN and HZO film deposited by TH- and PE-ALD and the ferroelectricity of TiN/HZO/TiN capacitors.

TiN/HZO/TiN capacitors were fabricated as follows: A 10-nm-thick HZO film was deposited on BE-TiN by TH- and PE-ALD at 300°C using H₂O and O₂ plasma as oxidants, respectively, and a (Hf/Zr)[N(C₂H₅)CH₃]₄ (Hf:Zr = 1:1) cocktail precursor. The Hf/Zr ratios in TH- and PE-ALD films were 0.4/0.6. Next, post-deposition annealing (PDA) was performed at 400°C for 1 min in a N₂ atmosphere. Finally, TiN top-electrode was fabricated by DC sputtering. The crystallinity was analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the NSLS II, Brookhaven National Laboratory. A TiO_xN_{1-x} IL formation was evaluated by synchrotron hard X-ray photoelectron spectroscopy (HAXPES) at the BL15XU of Spring-8.

The PE-ALD film dominantly formed ferroelectric orthorhombic phase evaluated by GIWAXS, resulting in a higher 2P_r of 20 μC/cm² than that of the TH-ALD film (13 μC/cm²). Compared with the maximum 2P_r after wake-up field cycling, the PE-ALD film showed less 2P_r degradation (~33%) after 10⁶ cycles, while the 2P_r of TH-ALD film decreased by ~47%. These superior fatigue properties of the PE-ALD film were attributed to the formation of

TiO_xN_y IL between the HZO film and BE-TiN during the ALD process, which can prevent the formation of oxygen vacancies in the HZO film during the PDA process and field cycling, evaluated by HAXPES spectra for Ti 2p and N 1s. Based on these results, we found that the TiO_xN_y IL formation at the TiN/HZO interface using O₂ plasma during the ALD process plays an important role to stabilize the redox reaction and achieve superior fatigue properties.

This work was supported by JSPS KAKENHI (JP21J01667 and JP20H02189). The HAXPES measurements were performed under approval of the NIMS Synchrotron X-ray Station (2020A4602 and 2020A4651).

[1] T. Onaya et al., APL Mater. 9, 031111 (2021).

2:00pm AA1-WeA-3 Atomic Layer Deposition of Ternary Germanium-Sulfur-Selenium and Its Application for Ovonic Threshold Switching, Seungwon Park, M. Kim, T. Kim, S. Chung, H. Kim, School of Electrical & Electronic Engineering, Yonsei University, Korea (Republic of)

As a steep increase of memory capacity has been required, 2-terminal storage class memory (SCM) based on three-dimensional (3D) vertical cross-point (VXP) structure is receiving a lot of attention. With this regard, selector devices are an essential part of minimizing leakage current that can make failures of memory operation. Among them, ovonic threshold switching (OTS) materials consisting of chalcogenide materials (e.g., S, Se, and Te) has been regarded as a promising candidate for 3D X-point owing to its low leakage and high on current (I_{on}). Nevertheless, research on atomic layer deposition (ALD)-based OTS applications, which is crucial for sophisticated thickness control and conformality, is still in the beginning stage and especially sulfur-based ALD OTS material research is lacking despite its potential to possess superior OTS characteristics.[1]

Herein, we developed a thermal ALD Ge_{1-x}S_x (Ge-S) process using HGeCl₃ precursor and H₂S reactant. The growth characteristics and film properties of Ge-S film were investigated in detail. Besides, by incorporating thermal ALD Ge-Se designed by W.H Kim et al.[2] to our Ge-S, we fabricated ALD ternary germanium-sulfur-selenium (Ge-S-Se) alloy devices spanning a broad range of compositions by adjusting the ALD super-cycle ratio. The film characteristics and electrical parameters of Ge-S/Ge-Se/Ge-S-Se were evaluated and compared to verify the effect of its composition change. We successfully presented the foundation of the thermal ALD technique of Ge-S and opened the possibility to tune threshold voltage and to apply the Ge-S-Se of various composition ratios for desired purposes suitably.

Acknowledgements

This paper was a result of the research projected supported by SK Hynix Inc.

References

- [1] S.Jia et al. Nature Communications 11, 4636 (2020)
- [2] W.H Kim et al. Nanotechnology 29, 365202 (2018)

2:15pm AA1-WeA-4 Scaling Down to sub-5 nm Ferroelectric Hf_{0.5}Zr_{0.5}O₂ Thin Films with Anhydrous H₂O₂ ALD Oxidant, Yong Chan Jung, J. Kim, H. Hernandez-Arriaga, D. Le, S. Hwang, University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; T. Onaya, National Institute of Advanced Industrial Science and Technology (AIST), Japan; C. Nam, Y. Zhang, Brookhaven National Laboratory; S. Kim, Kangwon National University, Korea (Republic of); J. Kim, University of Texas at Dallas

The ferroelectricity of doped HfO₂ thin films have been extensively investigated in many applications such as ferroelectric field effect transistor (FeFET), ferroelectric tunneling junction (FTJ) device, and ferroelectric random-access memory (FeRAM) etc. Previous studies have demonstrated that high-quality ferroelectric doped HfO₂ thin films can be easily obtained with a thickness of 5 nm or more.^{1,2} However, it is difficult to achieve good ferroelectric property as the thickness of the ferroelectric layers decreased to sub-5 nm. In addition, the crystallization temperature increases significantly with a down-scaling of the ferroelectric film thickness due to the increase of the surface-area-to-volume ratio.² Therefore, we intensively investigated atomic layer deposition (ALD) process and post annealing conditions to obtain stable ferroelectric property at the Hf_{0.5}Zr_{0.5}O₂ (HZO) thickness of sub-5 nm.

In this study, HZO films were deposited using anhydrous H₂O₂ as an ALD oxygen source with the variation of deposition temperature at 250 °C to 350 °C. In addition, annealing temperature was varied from 400 °C to 500 °C. To confirm robust ferroelectric property, we fabricated TiN/HZO/TiN capacitors and characterized electrically (PE hysteresis, Pulse, CV and IV analysis). The crystallinity of HZO films were also analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the

Wednesday Afternoon, June 29, 2022

Brookhaven National Laboratory. In addition, the half-cycle study using *in-situ* reflection absorption infrared spectroscopy (RAIRS) has revealed that anhydrous H₂O₂ forms high surface saturation. It is suspected that this chemical densification gives the advantages of scaling and low thermal budget of ferroelectric HZO film. The detailed results will be presented.

This work was supported by the Technology Innovation Program (20010806) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also partially supported by GRC-LMD program (#3001.001) of SRC, and the National Research Foundation of Korea (NRF) grant funded by MSIT (NRF-2019R1F1A1059972).

¹ Y. C. Jung et al., *Phys. status Solidi-RRL* **15**, 2100053 (2021).

² S. J. Kim et al., *Appl. Phys. Lett.* **112**, 172902 (2018).

2:30pm AA1-WeA-5 Engineering the Ferroelectric Properties in Hafnium Oxide by Co-Doping during Atomic Layer Deposition, Kati Kühnel, M. Lederer, A. Pourjafar, K. Mertens, F. Schöne, M. Neuber, L. Roy, T. Kämpfe, K. Seidel, M. Czernohorsky, Fraunhofer IPMS, Center Nanoelectronic Technologies, Germany

The presence of ferroelectricity in hafnium oxide thin films can be controlled via doping. Since those layers are usually deposited via atomic layer deposition, the doping element (like Zr, Al, Si, La) is supplied via monolayers. This way, the metastable ferroelectric phase can be stabilized. However, often wake-up effects and asymmetries like imprints are present in the produced films, impairing optimal device performance in e.g. embedded non-volatile memory devices like ferroelectric field effect transistors. These imperfections will also affect the device behavior in piezo- and pyroelectric sensors and actuators.

We report on a novel method to control the phase and the switching behavior in hafnium oxide thin films by atomic layer deposition on 300 mm wafers. By utilizing two different doping elements with strong differences in their ionic properties, especially in their ionic radius and charge with respect to Hf, the here presented co-doping process enables to tune local stresses or electric fields. This is implemented by varying the doping concentration homogeneously in the layer and implementing concentration differences within the layer. For the hafnium oxide deposition two different precursors are explored, namely hafniumtetrachloride (HfCl₄) and tetrakis(ethylmethylamino)hafnium(IV) (TEMAHf). Water and ozone are used as oxidizers, respectively. For the electrical characterization, the ferroelectric films are implemented in MIM stacks with TiN as electrode material. These MIM stacks are annealed at different temperatures between 650 and 1050 °C to achieve the improved ferroelectric properties.

Depending on the used processing method, alternating or block wise dopant deposition, the phase stabilization of the ferroelectric orthorhombic Pca2₁ phase can be influenced, as indicated by the grazing incident X-ray diffraction results.

The polarization-voltage hysteresis shape can be modified by defining favored polarization axis orientations or influencing the domain wall movement. Moreover, effects like imprint can be counteracted. This is reflected in the displacement current by the current peak position, amplitude, shape and width. Consequently, this will affect the mechanical displacement and the pyroelectric properties as well, since they are dependent on the polarization behavior.

2:45pm AA1-WeA-6 Magnetic and Electric Properties of Atomic Layer Deposited HfO₂-Fe₂O₃ Thin Films, Kristjan Kalam, M. Otsus, R. Rammula, University of Tartu, Estonia; J. Link, National Institute of chemical physics and biophysics, Estonia; R. Stern, National Institute of Chemical Physics and Biophysics, Estonia; G. Vinuesa, S. Duenas, H. Castan, University of Valladolid, Spain; K. Kukli, A. Tamm, University of Tartu, Estonia
Kristjan Kalam¹, Markus Otsus¹, Raul Rammula¹, Joosep Link², Raivo Stern², Guillermo Vinuesa³, Salvador Dueñas³, Helena Castán³, Kaupo Kukli¹, Aile Tamm¹

¹ Institute of Physics, University of Tartu, W. Ostwald 1, 50411 Tartu, Estonia.

² National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia.

³ Department of Electronics, University of Valladolid. Paseo Belén, 15. 47011 Valladolid, Spain.

E-mail of presenting author: kristjan.kalam@ut.ee

Atomic layer deposited thin films have had a role in memory technology for quite some time, mostly as high-k dielectrics [1]. In recent years, however,

such thin films have become a subject of interest as having intrinsic memory properties themselves, such as ferromagnetism and resistive switching [2-3]. HfO₂ thin films have been found to exhibit resistive switching properties [2]. Fe₂O₃ thin films have exhibited ferromagnetic properties [3]. Therefore, it is of interest to investigate if HfO₂ coupled with Fe₂O₃ would exhibit both resistive switching and ferromagnetic hysteresis in the same material sample.

Precursors to the films were FeCp₂ and HfCl₄, whereby O₃ was the oxidizer. Film thickness, elemental composition and crystal structure were evaluated. Most films exhibited ferromagnetic and/or superparamagnetic properties. Even un-doped HfO₂ could be magnetized, provided that the cubic phase was stabilized and present in the sample. Some films exhibited an electrical nonvolatile memory effect, unipolar resistive switching, where the resistance of a film can be switched between two distinct values. For example, a layered structure HfO₂+ Fe₂O₃+ HfO₂+ Fe₂O₃ was found to have both ferromagnetic and resistive switching properties.

[1] Niinistö, Jaakko, et al. Atomic layer deposition of high-k oxides of the group 4 metals for memory applications. *Adv. Eng. Mater.* **11** (2009) 223-234.

[2] Lin, Kuan-Liang, et al. Electrode dependence of filament formation in HfO₂ resistive-switching memory. *J. Appl. Phys.* **109** (2011) 084104.

[3] Kalam, Kristjan et al. Atomic layer deposition and properties of ZrO₂/Fe₂O₃ thin films, *Beilstein J Nanotech.* **9** (2018) 119.

3:00pm AA1-WeA-7 Atomic Layer Deposition of Antiferroelectric Perovskite Lead Hafnate Using O₂-Gas-Only as the Oxygen Precursor, Nicholas Strnad, W. Sarney, Army Research Laboratory; G. Fox, Fox Materials Consulting, LLC; B. Hanrahan, Army Research Laboratory; B. Rayner, Kurt J. Lesker Company; R. Rudy, J. Pulskamp, Army Research Laboratory

ALD-grown ferroelectrics have garnered much attention over the past decade due in large part to the discovery of ferroelectric doped-hafnia which has renewed interest in scalable, non-volatile, and neuromorphic memory. Nanolaminates consisting of ferroelectric, dielectric, and antiferroelectric thin films may be engineered to exhibit neuromorphic-enabling multi-state read/write capabilities, however, there are comparably few ALD processes available for archetypal antiferroelectric thin films compared to their ferroelectric and dielectric counterparts. Here, we present an ALD process to grow perovskite, antiferroelectric lead hafnate (PbHfO₃, PHO) using the commonly-used amide hafnium precursor tetrakis dimethylamino hafnium (TDMAH), lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) (Pb(DMAMP)₂) and O₂ gas as the co-precursor for both metalorganic compounds. We show that the composition may be controlled using a super-cycle consisting of *n* PbO cycles and one HfO₂ cycle. The films were deposited in an initially amorphous state with an interspersed polycrystalline PbO phase and crystallized into the perovskite state upon either furnace or rapid thermal anneal in an oxygen atmosphere. We observed dose saturation of the O₂ gas co-precursor only for extremely large exposures in excess of 3x10⁹ L. The growth per cycle (GPC) of the PHO, averaged across the supercycle, is shown to be approximately 0.5 Å. We investigate the chemical distribution and phase of the ALD PHO films before and after annealing using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS). Quantitative electrical characterization was performed on fabricated capacitor structures using 60 nm-thick PHO on a platinumized substrate, which showed double-hysteresis polarization versus voltage loops with max/min polarization values of ±50 μC/cm² at ±16 V.

3:15pm AA1-WeA-8 In-situ Half-Cycle Study of High Purity H₂O₂-based HfO₂ Atomic Layer Deposition for Hf based Ferroelectric Devices Applications, Jinhyun Kim, Y. Jung, S. Hwang, D. Le, H. Hernandez-Arriaga, K. Tan, University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; S. Kim, Kangwon University; J. Kim, University of Texas at Dallas

Recently, we have reported the ALD characteristics and film properties of Hf_{0.5}Zr_{0.5}O₂ (HZO) using high purity H₂O₂ and O₃. H₂O₂-based HZO showed higher GPC, lower wet-etch rate (WER), and higher film density than O₃-based HZO.¹ In comparison to H₂O, high purity H₂O₂ delivers 50% higher GPC, improved WER, and denser film from H₂O (SFig.1). H₂O₂ has low oxygen dissociation energy and high oxidation power comparable to O₃ as well as hydroxyl groups for ligand exchange reactions like H₂O, making it an ideal candidate for the oxide ALD process. Thus, an extensive study of H₂O₂ surface reactions is necessary to further investigate the reasons behind observed improvements. The conventional H₂O₂ precursor is commonly dissolved in a high content H₂O. Therefore, identifying the effects of H₂O₂ as an oxidant of ALD process from those of H₂O is a significant challenge.²

Wednesday Afternoon, June 29, 2022

In this study, we have implemented high purity anhydrous H_2O_2 to better understand ALD growth mechanism, interface formation, and film properties attributed by H_2O_2 while prohibiting the effects of H_2O .

It is expected that different oxidants (H_2O_2 , H_2O , and O_3) can significantly impact the overall film growth and interfacial growth behaviors. ALD processes of HfO_2 using various oxidants are monitored to examine the surface pathways of H_2O_2 , H_2O , and O_3 . Comprehensive surface studies of ALD- HfO_2 , deposited using TDMA-Hf and oxidants on TiN substrate, are studied using an *in-situ* reflection absorption infrared spectroscopy (RAIRS) system.³ Half-cycle study with differential and accumulated FTIR spectra will be investigated to identify the growth mechanism of different oxidants. This will allow us to observe the TiN and oxide interface formation and ligand exchange reaction while ALD process. Moreover, the FTIR spectra of the oxide bonding region will provide a better understanding of bonding density and oxide growth. Initial *in-situ* RAIRS study indicates that the surface absorption rate of H_2O_2 is significantly faster than H_2O , providing additional reaction sites during subsequent TDMA-Hf exposure steps. Eventually, the additional Hf-O bonds may increase film density, which can potentially provide enhanced film properties. Furthermore, interface formation is expected to be also observable using *in-situ* spectra of full ALD cycles by comparing the initial and bulk cycles (SFig.2).

This work was supported by Tech. Innovation Program (20010806) funded by MOTIE and GRC-LMD program (task#3001.001) through SRC. We thank RASIRC Inc. for providing the H_2O_2 source.

¹ J. H Kim et al., AVS, ALD 2021.

² D. Alvarez Jr. et al., Proc. SPIE 11326, 113260S (2020).

³ S. M. Hwang et al., *ECS Trans.*, **92**, 265 (2019).

Author Index

Bold page numbers indicate presenter

- A —
Alvarez, D.: AA1-WeA-4, 1; AA1-WeA-8, 2
- B —
Byun, S.: AA1-WeA-1, 1
- C —
Castan, H.: AA1-WeA-6, 2
Chung, S.: AA1-WeA-3, 1
Czernohorsky, M.: AA1-WeA-5, 2
- D —
Duenas, S.: AA1-WeA-6, 2
- F —
Fox, G.: AA1-WeA-7, 2
- H —
Hanrahan, B.: AA1-WeA-7, 2
Hernandez-Arriaga, H.: AA1-WeA-2, 1; AA1-WeA-4, 1; AA1-WeA-8, 2
Hwang, C.: AA1-WeA-1, 1
Hwang, S.: AA1-WeA-4, 1; AA1-WeA-8, 2
- J —
Jung, Y.: AA1-WeA-2, 1; AA1-WeA-4, 1; AA1-WeA-8, 2
- K —
Kalam, K.: AA1-WeA-6, 2
Kämpfe, T.: AA1-WeA-5, 2
Kim, H.: AA1-WeA-3, 1
Kim, J.: AA1-WeA-2, 1; AA1-WeA-4, 1; AA1-WeA-8, 2
Kim, M.: AA1-WeA-3, 1
Kim, S.: AA1-WeA-4, 1; AA1-WeA-8, 2
Kim, T.: AA1-WeA-1, 1; AA1-WeA-3, 1
Kühnel, K.: AA1-WeA-5, 2
Kuklij, K.: AA1-WeA-6, 2
Kwon, D.: AA1-WeA-1, 1
- L —
Le, D.: AA1-WeA-4, 1; AA1-WeA-8, 2
Lederer, M.: AA1-WeA-5, 2
Lim, J.: AA1-WeA-1, 1
Link, J.: AA1-WeA-6, 2
- M —
Mertens, K.: AA1-WeA-5, 2
Mohan, J.: AA1-WeA-2, 1
Morita, Y.: AA1-WeA-2, 1
- N —
Nabatame, T.: AA1-WeA-2, 1
Nagata, T.: AA1-WeA-2, 1
Nam, C.: AA1-WeA-2, 1; AA1-WeA-4, 1
Neuber, M.: AA1-WeA-5, 2
- O —
Onaya, T.: AA1-WeA-2, 1; AA1-WeA-4, 1
Ota, H.: AA1-WeA-2, 1
Otsus, M.: AA1-WeA-6, 2
- P —
Paik, H.: AA1-WeA-1, 1
Park, S.: AA1-WeA-3, 1
Pourjafar, A.: AA1-WeA-5, 2
Pulskamp, J.: AA1-WeA-7, 2
- R —
Rammula, R.: AA1-WeA-6, 2
Rayner, B.: AA1-WeA-7, 2
Roy, L.: AA1-WeA-5, 2
Rudy, R.: AA1-WeA-7, 2
- S —
Sarney, W.: AA1-WeA-7, 2
Schöne, F.: AA1-WeA-5, 2
Seidel, K.: AA1-WeA-5, 2
Seo, H.: AA1-WeA-1, 1
Shin, J.: AA1-WeA-1, 1
Song, H.: AA1-WeA-1, 1
Spiegelman, J.: AA1-WeA-4, 1; AA1-WeA-8, 2
Stern, R.: AA1-WeA-6, 2
Strnad, N.: AA1-WeA-7, 2
- T —
Tamm, A.: AA1-WeA-6, 2
Tan, K.: AA1-WeA-8, 2
Tsai, E.: AA1-WeA-2, 1
- U —
Ueda, S.: AA1-WeA-2, 1
- V —
Vinuesa, G.: AA1-WeA-6, 2
- W —
Wang, B.: AA1-WeA-1, 1
- Z —
Zhang, Y.: AA1-WeA-4, 1