

ALD Applications

Room Grand Ballroom A-C - Session AA3-TuA

ALD for Memory Applications I

Moderators: Scott B. Clendenning, Intel Corp., Adrien LaVoie, Lam Research Corp.

4:00pm **AA3-TuA-11 Doped Hi-K ALD Films of HfO_x and ZrO_x for Advanced Ferroelectric and Anti-Ferroelectric Memory Device Applications;** *Niloy Mukherjee, J Mack, S Rathi, Eugenius, Inc.; Z Wang, A Gaskell, N Tasneem, A Khan, Georgia Institute of Technology; M Dopita, D Kriegner, Charles University*

INVITED

The discovery of ferroelectricity in doped hafnium oxide has generated excitement in the solid-state device community in recent years since hafnium oxide is a relatively simple oxide compared to traditional perovskite-based ferro-/anti-ferroelectric materials, and hafnium oxide is already used widely in the semiconductor industry. The discovery has inspired many researchers to study the system in further detail in the past few years. Recently, this group has discovered the ability to obtain anti-ferroelectric ZrO_x in as-deposited ALD films alone, without the need for capping metallic electrodes or any post-deposition/post-metallization annealing. Tunability of the anti-ferroelectric behavior of ZrO_x is also demonstrated using lanthanum doping and is co-related to changes in unit cell tetragonality with lanthanum doping. Process methods, including precursor delivery schemes and ALD deposition schemes, used to deposit doped HfO_x and ZrO_x-based ferroelectric and anti-ferroelectric films will be described in detail. Structural and electrical properties of such films will be described in detail and co-related.

[See figure in attachment]

4:30pm **AA3-TuA-13 ALD of La-Doped HfO₂ Films for Ferroelectric Applications,** *Tatiana Ivanova, P Sippola, M Givens, ASM, Finland; H Sprey, ASM, Belgium; T Büttner, P Polakowski, K Seidel, Fraunhofer IPMS-CNT, Germany*

Ferroelectric (FE) HfO₂ and its doped compounds [1] have received increasing interest for potential to harness these materials for non-volatile memory applications. ALD HfO₂-based ferroelectrics can provide smooth process integration to silicon based semiconductor technology in contrast to e.g., perovskite FE materials. Especially, La-doped HfO₂ films have been shown to exhibit superior ferroelectric responses with the so far highest reported remanent polarization for doped FE-HfO₂ [2]. Nevertheless, a comprehensive in depth study of this promising material system has not been done.

This research covers highlights of the growth and FE properties of La-doped HfO₂ ALD films. The 10 nm La-doped HfO₂ films were deposited on 300 mm Si wafers in an ASM Pulsar® 3000 ALD reactor over a temperature range of 200-300 ° C. The La-doped HfO₂ ALD process utilized HfCl₄ and a novel lanthanum precursor with co-reactant oxidants. Spectroscopic ellipsometer and x-ray photoemission spectroscopy were used to study the film growth and composition properties, respectively. In addition, La-doped HfO₂ crystallization kinetics were studied with in-situ x-ray diffractometry (IS-XRD). The FE properties were studied via fabrication and electrical characterization of planar metal-ferroelectric-metal capacitors (MFMCap).

Control of La-doped HfO₂ in the range of [La] ~ 1-10 % (based on 100*[La]/([La] + [Hf])) was studied by varying the ratio of LaO_x:HfO₂ subcycles during the ALD process. The La-doped HfO₂ growth rate and residual C and Cl impurity concentrations were studied as a function of LaO_x:HfO₂ subcycle ratio and temperature for as-deposited films. IS-XRD analysis during high temperature annealing revealed the presence of the desired high symmetry phase of FE hafnium oxide for low [La] (1-5 %) and lower temperature (200-250 ° C) deposited samples, while samples with higher [La] showed an even stronger stabilization of the film which showed electrically no FE behavior. Crystallization temperatures increased with increasing La content, while it decreased with increasing deposition temperature: e.g. [La]~2 % samples deposited at 200-300 ° C crystallized at 615-470 ° C, respectively. The MFMCap studies confirmed the presence of strong FE responses for the low La content films exhibiting maximum remanent polarization of 26.5 μC/cm² (post cycle conditioning) for [La]~2 % films deposited at 250 ° C.

[1] T. S. Böske, et al., Applied Physics Letters 99, 102903 (2011)

[2] J. Müller et al., IEEE International Electron Devices Meeting (2013)

4:45pm **AA3-TuA-14 Characterization of Multi-Domain Ferroelectric ZrO₂ Thin Films for Negative Capacitance and Inductive Responses,** *Yu-Tung Yin, P Cheng, Y Jiang, J Shieh, M Chen, National Taiwan University, Republic of China*

By using a specific plasma-enhanced atomic layer deposition (PEALD) process, an as-deposited nanoscale ferroelectric ZrO₂ (nano-*f*-ZrO₂) thin film has been prepared. A unique periodically arranged crystalline has been observed under nano-beam electron diffraction (EBED) and dark field TEM images, indicating the presence of multi-domain structure in nano-*f*-ZrO₂. From the large-signal RLC oscillations in time domain analysis, the existence of positive imaginary part of the impedance, enhancement of small-signal capacitance of the series-connected capacitances, and the sub-60mV/dec subthreshold swing in nanoscale transistors, the multi-domain nano-*f*-ZrO₂ has provided the experimental observation for the inductive behavior and negative capacitance induced by the net polarization switching. According to the theoretical calculation, the net polarization switching of multi-domain nano-*f*-ZrO₂ produces an effective electromotive force which is similar in behavior with Lenz's law, leading to the inductive responses and the negative capacitance effect. Since the as-deposited multi-domain nano-*f*-ZrO₂ thin film provides a significant inductance behavior compared to conventional inductors, the PEALD deposited nano-*f*-ZrO₂ would become a promising material in a variety of applications including nanoscale transistors, filters, oscillators, and radio-frequency integrated circuits.

5:00pm **AA3-TuA-15 Scaling Ferroelectric Hf_{0.5}Zr_{0.5}O₂ on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) Structures,** *Jaidah Mohan, H Hernandez-Arriaga, H Kim, A Khosravi, A Sahota, The University of Texas at Dallas; R Wallace, University of Texas at Dallas; J Kim, The University of Texas at Dallas*

Ferroelectricity in Hafnium Zirconate (HZO) has recently garnered interest due to the possibility of achieving sub-60mV/decade Subthreshold swing (SS) at room temperatures [1]. Such steep slope behavior could lead to various advantages like reducing static power dissipation and lowering operating voltages. "Negative Capacitance" is the currently proposed mechanism for such behavior but substantial claims and controversies are still being reported. Big mystery questions remain unsolved, (i) can hysteresis free switching continue to get steeper even at GHz frequencies? (ii) Can negative capacitance really be stabilized Nevertheless, various observations of sub-60 SS swing have been reported using a ferroelectric material as the gate dielectric [2][3]. In this work, we study scaling of HZO on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) structures which can further aid in reducing the operating voltages.

In this study, the ferroelectric properties of HZO was studied on MIM and MFIS structures, scaling down to 3nm. HZO was deposited using TDMA-hafnium (Hf[N(CH₃)₂]₄), TDMA-zirconium (Zr[N(CH₃)₂]₄), and O₃ as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. Blanket TiN (90 nm thick) electrodes were deposited after the HZO deposition as the stress given by the TiN electrode helps in crystallizing HZO into the ferroelectric phase. Then, rapid thermal annealing was done at 450°C in an N₂ atmosphere for 60s to crystallize the HZO films. A conventional photolithography/etching process was used to make capacitors of different diameters. Grazing Incidence X-ray Diffraction (GIXRD) confirms that the ferroelectric orthorhombic phase is stable for HZO deposited on top of HF treated Silicon. The ferroelectric HZO film was scaled up to 5nm on top of Silicon and showed significant ferroelectric properties while 4nm and 3nm HZO showed very high leakage properties. Effects or reannealing to increase the grain size and hence the ferroelectric behavior was also studied. It was also observed that as the ferroelectric thickness decreases or the SiO₂ thickness increases, there is an increase in the ferroelectric dipole relaxation, i.e. the ferroelectric domains are naturally tend to orient themselves in a particular direction.

REFERENCES:

[1] S. Salahuddin et al, *Nano Lett.*, vol. 8, no. 2, pp. 405–410, 2008.

[2] S. Dasgupta, et al, *IEEE J. Explor. Solid-State Comput. Devices Circuits*, vol. 1, pp. 43–48, 2015.

[3] A.I. Khan et al., *IEEE Electron Device Lett.*, vol. 37, no. 1, pp. 111–114, 2016.

5:15pm AA3-TuA-16 Interface Characteristics of MIM Capacitors using Vanadium Nitride Electrode and ALD-grown ZrO₂ High-k Dielectric Film, *Jae Hyoung Choi, Y Kim, H Lee, H Lim, K Hwang, S Nam, H Kang*, Samsung Electronics, Republic of Korea

One of the most critical challenges for DRAM (Dynamic Random Access Memory) downscaling is cell capacitor technology, and so far ZrO₂ and TiN film have been adopted as a high-k dielectric and an electrode material respectively, for the capacitor application [1]. ZrO₂ film has been spotlighted in TiN/Insulator/TiN (TIT) capacitor due to its high dielectric constant, wide band gap, and thermal stability [2].

A wide variety of DRAM capacitor electrodes are currently being evaluated as replacements for TiN including VN, HfN, and Ru. Ru-base electrode has advantage of high work function but also has cost and integration problem. Thermally robust HfN/HfO₂ gate stack structure was reported with scaling down of equivalent oxide thickness (Tox_{eq}) less than 10Å and several attempts to prepare HfN films by metal organic chemical vapor deposition (MOCVD) have been continued [3,4]. Even though Vanadium Nitride (VN) exhibits high melting point, chemical inertness, low resistivity, and high work function from 5.05 to 5.15eV, very little is known about its qualities as DRAM capacitor electrode [5].

In this study, we fabricated new MIM (Metal/Insulator/Metal) capacitor using VN electrode and ALD-ZrO₂ dielectric for DRAM capacitor. VN films (100~1,000Å) were deposited at different temperatures ranging from 25 to 500°C by reactive magnetron sputtering. ZrO₂ films were used as a dielectric by atomic layer deposition (ALD) method with Tetra-Ethyl-Methyl-Amino-Zirconium (TEMAZ) liquid precursor and O₃ reactant at the temperature of 250°C. ALD-ZrO₂ films were progressed to post deposition anneal (PDA) in N₂ atmosphere to crystallize the dielectric layer. Electrical properties of MIM capacitor with VN/ZrO₂ combination such as capacitance, leakage current density and dielectric constant were compared with TiN/ZrO₂ stack. Resistivity, composition, interfacial reaction, and crystalline structure of VN and ZrO₂ films were analyzed by 4-point probe, Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Furthermore, the VN/ZrO₂ interface effects on the electrical properties will be discussed in detail.

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2. C. W. Hill et al., *J. Electrochem. Soc.*, **152**(5), G386 (2005).
3. H.Y. Yu, et al., *IEEE Electron Device Lett.*, **25**, 70 (2004).
4. Y. Kim, et al., *Proc. 15th EUROCVCD, ECS* **9**, 762 (2005).
5. R. Fujii et al., *Vacuum*, **80**(7), 832 (2006).
6. K. Yoshimoto et al., *Jpn. J. Appl. Phys.* **45**(1A) 215 (2006).

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