ALD Applications
Room Plaza ABC - Session AA-MoA

Memory and MIM I (1:30-3:30 pm)/Memory and MIM II (4:00-5:30 pm)

Moderators: John Smythe, Micron Technology, John Conley, Oregon State University, Robert Clark, TEL Technology Center, America, LLC

1:30pm **AA-MoA-1 Atomic Layer Deposited Ta-doped ZrO_2 for DRAM Capacitors**, ***Bo-Eun Park***, *I Oh, J Park, S Seo, H Kim,* Yonsei University, Republic of Korea

With accelerated scaling down of integrated circuit, it is very challenged to employ DRAM capacitor with high capacitance density and low leakage current. Until now, ZrO_2 has been wide used as a high-*k* dielectric, but oxygen vacancies (V_o) in ZrO_2 have been considered as one of the significant reasons for high leakage current [1]. Doping of higher valent element than tetravalent Zr can be possible solution for reduction of V_o in ZrO_2 films since it introduces excessive O atoms and passivates the vacant position of V_o. Among various high valent element-based materials, Ta could be expected to be a good dopant in ZrO_2, since Ta_2O_5 is a well-known high-*k* material with high dielectric constant (22-60), good dielectric breakdown strength, and thermal and chemical stability [2]. However, previous studies on Ta-doped ZrO_2 films have shown conflicting results on their electrical properties. The reduction of V_o by Ta doping can transform the crystal structure of ZrO_2 from cubic to tetragonal and monoclinic due to atomic arrangement around V_o [3], and the dielectric constants of ZrO_2 significantly depend on the crystal structures [4]. Also, since Ta has limited solubility in ZrO_2, high Ta concentration form new orthorhombic phase of $Ta_2Zr_6O_{17}$ [4].

Therefore, proper control of Ta concentration in ZrO_2 is very important to reduce leakage current related to V_o with maintaining high dielectric constant. In this paper, we investigated Ta-doped ZrO_2 with various Ta concentration by supercycle process of atomic layer deposition (ALD). X-ray photoelectron spectroscopy analysis showed gradual increase of O/(Zr+Ta) with increase of Ta concentration, indicating reduction of V_o concentration in films. The decrease of V_o concentration transformed the crystal structure of ZrO_2 from cubic to tetragonal in X-ray diffraction pattern. The introduction of high dielectric constant of tetragonal ZrO_2 and Ta_2O_5 increase the dielectric constant from 16 up to 29 in C-V characteristics. Simultaneously, the reduction of V_o affects decrease of leakage current density of Ta-doped ZrO_2 from ~10^{-7} A/cm^2 to ~10^{-9} A/cm^2 in I-V characteristics (Table. 2). These results are very interesting because the dielectric constant and leakage current densities of conventional high-*k* dielectrics are usually inversely proportional.

Reference

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[2] Min-Kyu Kim et al., Thin Solid Films, 542 (2013) 71–75

[3] Stefano Fabris et al., Acta Materialia, 50 (2002) 5171–5178

[4] J. Ferrand et al., ECS Transactions, 58 (10) 223-233 (2013)

1:45pm **AA-MoA-2 High Capacitance 3D MIM Structures Achieved by ALD Deposited TiO_2 for Advanced DRAM Applications**, ***Ahmad Chaker***, *P Szkutnik, P Gonon, C Vallée, A Bsiesy,* Univ. Grenoble Alpes, CNRS, France

The increase of capacitance density in Dynamic Random Access Memory (DRAM) is major challenge for CMOS advanced technology nodes. Metal-insulator-metal (MIM) structures based on high dielectric oxides (high k) is used in DRAM to increase the capacitance density. Titanium dioxide (TiO_2) is very promising candidate thanks to its high permittivity constant, up to 170, in its rutile crystalline phase. Rutile structure is obtained at low temperature (250°C) by ALD deposition on RuO_2 bottom electrode thanks to the small lattice mismatch with TiO_2. Planar (2D) TiO_2 based MIM structures can achieve capacitance density in the range of 50 nF/mm^2 which falls rather below the ITRS 100 nF/mm^2 preconized density. A way to increase this density is to build 3D capacitor structures, but conformal MIM deposition has to be achieved that exhibits uniform TiO_2 thin (10-20 nm) layer. In this paper, we report a study achieved on tapered silicon 3D substrate used to achieve high-density MIM capacitors (> 100nf/mm^2) which retains excellent electrical properties, comparable to flat (2D) MIM devices.

This paper will also discuss the effect of TiO_2 multicrystalline grain size on the MIM structure electrical properties. Indeed, two rutile TiO_2 layers, grown by ALD in different conditions to exhibit different grain size show that higher dielectric constant along with reduced conductance are obtained when the average grain size is larger. This result will be discussed by analyzing the grain boundaries role in the current transport mechanism.

2:00pm **AA-MoA-3 Seed-layer Effects on the Crystallization and Electrical Characteristics of ALD-grown Ta_2O_5 Thin Films**, ***Jae Hyoung Choi***, Samsung Electronics, Korea, Republic of Korea; *S Kang, S Chung, C Cho, S Oh, Y Kim, K Yoon, H Lim, K Hwang, H Kang,* Samsung Electronics, Republic of Korea

As the design rule of DRAM devices shrinks rapidly, Toxeq. (Equivalent Oxide Thickness) scaling of the capacitor by the development of high-k dielectric materials with permittivity over 50 has been attracted much interest to compensate the significant area reduction and to satisfy the cell capacitance. High dielectric constant over 50 was reported in Ta_2O_5 films of hexagonal crystal structure which was formed by Atomic Layer Deposition (ALD) using Tantalum halide precursors and H_2O reactant, such as $TaCl_5$ and TaF_5 [1, 2]. However, Ta_2O_5 dielectric material has critical demerit of high crystallization temperature over 800℃ on non-noble metal electrode.

In this study, we developed interface engineering inserting seed-layer before Ta_2O_5 film formation for facilitating crystallization during Post Deposition Annealing (PDA). The specific seed-layer effect on the lowering of the crystallization temperature and the leakage current of the capacitor were evaluated as well.

Ta_2O_5 thin films were prepared on TiN metal electrodes by ALD using both amide-type liquid TBTEMT (Tert-Butylimido-Tris-Ethyl-Methyl-Tantalum) and halide-type solid $TaCl_5$ precursors, respectively. As a reactant, O_3 was compared with H_2O. The crystallinity and crystal structure were analyzed by X-ray diffraction (XRD) and transmission electron microscopy.

First, we evaluated the ALD window and decomposition behavior with temperature. Figure 1 shows the ALD behavior of Ta_2O_5 films using TBTEMT and O_3 on Si substrate. Because the temperature window of ALD was observed between 290℃ and 350℃, we chose the temperature of 320℃ for film growth.

XRD patterns of ALD grown Ta_2O_5 films on TiN electrode were shown in Fig. 2. No crystalline Ta_2O_5 phases were observed in the films up to PDA temperature of 700℃. By inserting a seed-layer, however, the crystallization temperature of ALD-Ta_2O_5 film to hexagonal structure was significantly reduced to 575℃.

Figure 3 shows the dependence of Toxeq. of TIT-Ta_2O_5 and RIS-Ta_2O_5 (Top-Ru/Bottom-poly Si electrode) capacitor with Ta_2O_5 thickness. The dielectric constants of Ta_2O_5 films on the seed-layers were approximately 62, 61, respectively, even at the low crystallization temperature of 600℃. This indicates the interfacial engineering using seed-layers is very effective to lower the crystallization temperature of the Ta_2O_5 film without using non-noble metal electrode. Including these results, it will be discussed on the feasibility of the low temperature crystallized Ta_2O_5 films for the candidate of next-generation DRAM dielectric material.

REFERENCES

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2. C. W. Hill et al., *J. Electrochem. Soc.*, **152**(5), G386 (2005)

2:15pm **AA-MoA-4 Electrode Induced Variation in Voltage Nonlinearity of ALD Al_2O_3 and HfO_2 Metal-Insulator-Metal Capacitors (MIMCAPs)**, ***Dustin Austin***, *K Holden, J Hinz, C Remple, J Conley,* Oregon State University

The nonlinearity of capacitance vs. voltage (C-V) in high-κ MIMCAPs presents a major challenge for analog and mixed signal applications. The curvature in C-V is characterized empirically by the quadratic voltage coefficient of capacitance (αV_{CC}). High-κ dielectrics typically exhibit a positive αV_{CC} (C increases with V). Although a few dielectrics such as SiO_2 and TiO_2 have negative αV_{CC}. The magnitude of αV_{CC} increases with κ and with decreasing thickness, imposing a significant hurdle to increasing capacitance density. In addition, metal electrodes exhibit a secondary influence on αV_{CC}. The influence of metal electrodes increases as thinner dielectric layers are used. By pairing up positive and negative αV_{CC} insulators and relying on the precise thickness control afforded by ALD, it is possible to use the cancelling effect to create highly linear MIIM capacitors. However as the physical mechanisms responsible for αV_{CC} are not fully understood, re-optimizing a device for a new metal or a change in metal thickness, much less meeting future ITRS goals, will require significant trial and effort, leading to extended development time. Despite this, there have only been a few studies on the impact of metal electrodes on αV_{CC}. In this work we investigate the impact of a variety of metal electrodes on αV_{CC} in ALD Al_2O_3 and HfO_2 MIMCAPs.

MIMCAPs were fabricated using TaN bottom electrodes. 10 nm Al_2O_3 and 11 nm HfO_2 was deposited via ALD at 250 °C using H_2O and either TMA or

TEMA-Hf in a Picosun R-200 or R-150, respectively. Ag, Au, Ni, Pd, and Pt were evaporated through a shadow mask to form the top gate.

Plots of normalized capacitance (C/C_0) vs. electric field (E^2) show a similar dependence of αE_{CC} (quadratic electric field coefficient of capacitance) on Ni, Au, and Ag (Fig. 1) for both Al_2O_3 and HfO_2. Most studies have concluded that interfacial oxides dominate the influence of metal electrodes on αV_{CC}. However this cannot fully explain variation between near zero enthalpy of formation metals as they are unlikely to form substantial oxides. The αV_{CC} variation between these metals is likely due to an interaction between the bulk dielectric mechanism and an interfacial effect. One possible bulk mechanism for positive αV_{CC} materials is a decrease in film thickness due to voltage induced compression (Fig. 2). The compressive stress within the dielectric is modulated by the induced tensile stress at the metal interfaces. We see that metals with larger lattice mismatch show increased αV_{CC}. The effect of lattice mismatch and additional results showing effect of dielectric and metal thickness will be presented at the meeting.

1. Austin et al., IEEE EDL 36 (2015).

2:30pm **AA-MoA-5 High-Voltage Nanolaminate Metal-Insulator-Insulator-Metal (MIIM) Tunnel Diodes using ALD Al_2O_3 and Ta_2O_5**, *D Austin, M Jenkins,* ***Konner Holden****, J Conley,* Oregon State University

ALD nanolaminate tunnel barriers have enabled enhancements of low voltage asymmetry ($\eta_{asym} = I^-/I^+$) and non-linearity (f_{NL}) in MIIM tunnel diodes for applications such as rectenna based energy harvesting.[1,2] In this work, we investigate ALD bi-layers of Al_2O_3 and Ta_2O_5 for use in high-voltage applications such as electrostatic discharge (ESD) protection and high-voltage logic.

Nanolaminate Al_2O_3/Ta_2O_5 stacks were deposited on TaN bottom electrodes via ALD. ALD was performed at 200°C in a Picosun R-150 without breaking vacuum using alternating pulses of H_2O and either TMA or tris(ethylmethylamido)(tert-butylimido)tantalum. Al_2O_3:Ta_2O_5 thickness ratios of 1:1, 1:2, 1:3, 1:5, and 1:9 were fabricated, where the Al_2O_3 thickness is fixed at 30 nm. Bias was applied to Al top electrodes (formed by evaporation through a shadow mask).

I-V behavior (Fig. 1) was found to be a strong function of the Al_2O_3:Ta_2O_5 thickness ratio. Under positive bias, the reverse diode current for all devices remains low until the reverse "breakdown" voltage at which current increases rapidly. The reverse "breakdown" voltage increases with the thickness of the Ta_2O_5 layer, from 15 V for 1:1 to 53 V for the 1:9 devices. For small magnitude negative bias, in the range of 0 to -15V, the diode forward current *is higher* for thicker Ta_2O_5 layers, a somewhat counter-intuitive result. Beyond -15 V, the forward current is lower for thicker Ta_2O_5 layers, in line with expectations. Plots of $\log|\eta_{asym}|$ vs. V are shown in Fig. 2. That maximum asymmetry and voltage at which it occurs increases from ~900 at ~19 V for 1:1 to ~10^5 at ~52V for the 1:9 devices.

Multiple changes in slope of the I-V curves at both positive and negative bias reveal a number of competing conduction mechanisms. Overall, conduction and asymmetry are dominated by Fowler-Nordheim tunneling through the Al_2O_3 barrier and defect based conduction through the Ta_2O_5. The trends in conduction and η_{asym} are well explained by the asymmetric barrier (inset Fig. 1) created by the pairing of Al_2O_3 (E_G = 8.7 eV, χ = 1.4 eV, κ = 8.7) and Ta_2O_5 (E_G = 4.5 eV, χ = 3.2 eV, κ ~26). The detailed explanation will be discussed at the meeting.

This work demonstrates that ALD bilayers may be used to effectively engineer the reverse breakdown voltage, maximum asymmetry, and operating range of high voltage MIM diodes. These diodes may be of interest for implementation in back end of the line as well as for large area electronics due to low temperature fabrication.

2:45pm **AA-MoA-6 Capacitance Maximization of Ultra-thin Si-capacitors by Atomic Layer Deposition of Anti-ferroelectric HfO_2 in High Aspect Ratio Structures**, ***Stefan Riedel****, W Weinreich, C Mart, J Müller,* Fraunhofer IPMS, Germany

The increasing number of independent, electrical devices operating in networks intensifies the need for distributed and autonomous power supplies. Therefore, short term storage and buffering of electrical energy for both complete systems as well as individual integrated circuits is required for a multitude of applications. Anti-ferroelectric (AFE) capacitors are an emerging solution for this field of application due to their high energy density, low loss and fast charge and discharge rates.

Perovskite based materials like lead-lanthanum-zirconium-titanate (PLZT) are well known for showing promising energy storage properties [1]. However their scaling potential in thin films especially for three dimensional structures is limited due to the lack of conformal deposition methods. Additionally these materials contain heavy metals raising environmental concerns.

On the other hand HfO_2 based systems have been demonstrated to show both ferroelectric and anti-ferroelectric phases [2] and can be deposited by atomic layer deposition using well established chemistry. Additional HfO_2 is compatible with semiconductor processing enabling both an integration of AFE capacitors directly into semiconductor circuits or as stand-alone silicon based capacitors.

To demonstrate this applicability of AFE HfO_2 we fabricated metal insulator metal capacitors on 3D structured Si substrates. $TiCl_4/NH_3$ based ALD and CVD processes where applied to create metallic TiN electrodes. Silicon doped HfO_2 (Si:HfO_2) was used as anti-ferroelectric. These films were deposited using TEMAHf and 3DMAS as metalorganic precursors and ozone as co-reactant.

The Si:HfO_2 thin films have been characterized by means of XPS, XRR and XRD and electrical properties of these capacitors have been investigated in dependence of the silicon content, deposition temperature and post deposition thermal treatments. A maximum stored energy of >100 µJ/cm² could be achieved, which is sufficient to integrate these capacitors as buffer for low power integrated circuits.

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[2] T. S. Böscke, J. Müller, D. Bräuhaus, et al., Appl. Phys. Lett. 99, 102903 (2011)

3:00pm **AA-MoA-7 Ferroelectricity in Ternary HfO_2-ZrO_2-La_2O_3 Mixed Oxide Grown by ALD**, ***Anna Chernikova****, M Kozodaev, A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

Recently discovered ferroelectric (FE) properties of HfO_2 based thin films attracted much attention. The novel FE material is considered as promising candidate to replace perovskites in new generation of high density non-volatile memory concepts: FeFET, FeRAM [1-3] and even more challenging FTJ [4]. Notable feature of FE HfO_2 is complete compatibility with semiconductor fabrication process. Particularly, ALD is successfully applied to its growth. According to the previous works, FE in such films is caused by the presence of orthorhombic ($Pca2_1$) polar phase. Although numerous factors (thickness, annealing temperature, electrodes materials, etc.) were previously shown to affect stabilization of $Pca2_1$ phase, there is still strong focus to essentially promote FE (i.e. remnant polarization value P_r) of HfO_2 by doping with other elements [5,6]. Particularly, La doping of HfO_2 was already applied to achieve high P_r and promising endurance behavior, while ALD (including plasma enhanced PEALD) could be successfully utilized to ensure the required low level of doping [7]. At the same time since La doping usually increases the crystallization temperature of HfO_2 its integration to the BEOL process of FeRAM could be challenging and some ways to avoid this rise of crystallization temperature have to be found.

In this work, the first attempt to obtain FE in ternary HfO_2-ZrO_2-La_2O_3 oxide was made**.** The strategy was to combine the advantages of La doping with lower crystallization temperature of $(HfO_2)_x(ZrO_2)_y$ system. For this purpose metal-insulator-metal (MIM) structures based on 10 nm thick $(La_2O_3)_x(HfO_2)_y$ as well as $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ were entirely grown by PEALD. TiN as a desired material in semiconductor industry and simultaneously well-known feasible electrode for HfO_2 based FE was utilized for MIM structures formation. As grown as well as annealed in wide temperature range stacks were investigated in terms of crystalline structure, FE response and endurance characteristics. Stabilization of $Pca2_1$ in $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ and robust FE response of fully PEALD grown TiN/$(La_2O_3)_x(HfO_2)_y(ZrO_2)z$/TiN stacks were confirmed after annealing at relatively low temperature and dependence of FE response on annealing temperature was elucidated in details.

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[3] Zarubin S. et al. Appl. Phys. Lett. 109, 2016, 192903

[4] Chernikova A. et al. ACS Appl. Mater. Interfaces 8, 2016, 7232

[5] M.H. Park et al, Adv. Funct.Mater. 27(11), 2015, 1811

[6] S. Starschich and U. Boettger. J. Mater. Chem. C 5, 2017, 333

[7] Chernikova A.G. et al. Appl. Phys. Lett. 108, 2016, 242905

3:15pm **AA-MoA-8 A Study on the Oxygen Source and Annealing Temperature Effects of Atomic Layer Deposited Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films**, ***Si Joon Kim***, *D Narayan, J Lee, J Mohan,* University of Texas at Dallas*; S Summerfelt,* Texas Instruments*; J Kim,* University of Texas at Dallas

Ferroelectric random access memory (FRAM) has several advantages such as fast read/write cycle time, non-volatile data retention, low voltage/power operation, and simplified process flow. Texas Instruments reported the use of 70-nm-thick $Pb(Zr,Ti)O_3$ (PZT) film to make FRAM devices using 1.5 V 130 nm CMOS technology [1]. This conventional PZT ferroelectric (FE) material has the primary problem which is the difficulty in scaling down. Recently, FE properties in very thin doped HfO_2 have been identified [2]. However, although most studies use an atomic layer deposition (ALD) process for doped HfO_2 film deposition, there is no report of the effect of oxygen sources on the FE properties.

In this study, FE properties of 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films deposited on the TiN bottom electrode by ALD (Cambridge Nanotech Savannah S100) using TDMA-Hf (Hf-precursor), TDMA-Zr (Zr-precursor), and ozone or water (oxygen sources) have been investigated. The wafer temperature was set to 250°C during the HZO deposition and annealing processes were performed for 60 s at 300-500°C in an N_2 atmosphere using rapid thermal annealing after TiN top electrode deposition. Then, a conventional photolithography/etching process was performed to form a precise area of capacitors (diameter of 50-100 μm). The polarization-electric field hysteresis curves of the ozone- and water-based HZO samples were measured at 20 kHz after wake-up field cycling. A pulse write/read test was also performed to extract the real FE switching polarization. The ozone-based HZO sample annealed at 400°C showed large remanent polarization ($2P_r$, 46 μC/cm^2), large switching polarization (P_{sw}, 45 μC/cm^2), and low FE saturation voltage (1.5 V) compared to those ($2P_r$ of 42 μC/cm^2, P_{sw} of 38 μC/cm^2, and FE saturation voltage of 2.0 V) of the water-based HZO sample annealed at 400°C. Furthermore, the effect of the annealing temperature on the FE polarization of the ozone- and water-based HZO samples was examined. Both HZO samples annealed at 500°C exhibited a relatively high FE saturation voltage and also have high leakage current properties compared to the 400°C annealed HZO samples. Our investigations showed that the annealing temperature and oxygen source have a significant influence on the FE properties of HZO films.

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4:00pm **AA-MoA-11 Thickness Dependence of Polarization Response in $(Hf,Zr)O_2$**, ***Sean Smith***, *M Rodriguez, D Henry, M Brumbach, J Ihlefeld,* Sandia National Laboratories

$(Hf,Zr)O_2$ is an exciting recently discovered ferroelectric that can be deposited as a thin film by atomic layer deposition and has sparked interest in $(Hf,Zr)O_2$ FRAM and other thin film ferroelectric devices. $(Hf,Zr)O_2$ is unusual because its ferroelectric response is due to a metastable phase most commonly seen as a thin film and its polarization response has been shown to increase with decreased thickness -- at size scales that are unusual for conventional ferroelectrics. Still, like more traditional ferroelectrics, properties are expected to degrade at some point, as the thickness approaches that of a single unit cell. The surface limited growth of atomic layer deposition is a natural fit for producing the very thin films needed to investigate this thickness regime. We observe an increase in remanent polarization with decreasing thickness, from 16 μC/cm^2 for 20 nm films up to 20 μC/cm^2 for 15 nm films before the ferroelectric response drastically falls off for thinner films, dropping to 7 μC/cm^2 for 10 nm films,. We will discuss these results in the context of developing highly scaled (<20 nm) $(Hf,Zr)O_2$ ferroelectric thin film memory devices. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15pm **AA-MoA-12 ALD as a Primary Contributor Towards Enabling Key Materials in the Memory Roadmap**, ***John Smythe***, Micron Technology **INVITED**

Atomic layer deposition methods for dielectrics and metals have been widely reviewed in the literature for over a decade. Though there are exceptions, cost and complexity have largely limited adoption in more than a few high volume applications. The transition from proof of concept to robust implementation can illuminate the need for alternative precursors, reactants and hardware in various combinations. Think of the following scene: Engineers stand at the white board and draw a sketch depicting the next amazing memory cell. After some reflection, a common phrase shortly thereafter is some version of, "How are we going to make the structure with the required materials characteristics?" This talk will explore a selection of cases to explore the nature of past, present and future transitions related to the memory space.

4:45pm **AA-MoA-14 Plasma-Enhanced Atomic Layer Deposition of Oxygen Deficient TaOx Thin Films for Resistive Switching Memory Applications**, ***Konstantin Egorov***, *D Kuzmichev, Y Lebedinskii,* Moscow Institute of Physics and Technology, Russian Federation*; C Hwang,* Seoul National University, Korea*; A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

The plasma-enhanced atomic layer deposition (PEALD) process using $Ta(OC_2H_5)_5$ as a Ta precursor and plasma-activated hydrogen as a reactant for the deposition of TaOx films with a controllable concentration of oxygen vacancies (VO) is reported herein. The VO concentration control was achieved by varying the hydrogen concentration of the hydrogen-argon mixture inthe plasma, allowing the control of the leakage current density in the tantalum oxide films within the range of five orders of magnitude compared with the TaO_5 film grown via thermal ALD using the identical Ta precursor and H_2O.

The detailed chemical analysis and AFM topography were given for different growth temperatures and amount of ALD cycles. The saturation of growth rate for Ta-precursor pulse and reactant gas (H_2O and H_2/Ar plasma with different H_2 concentration) pulse time was studied too. Temperature-dependent current-voltage measurements combined with Poole-Frenkel emission modelling demonstrated that the bulk trap depthdecreases with the increasing hydrogen concentration, which could be attributed to the increase of the VO concentration. The change of VO quantity in the PEALD TaOx films grown under different hydrogen concentrations was confirmed by the *in-situ* X-ray photoelectron spectroscopy (XPS) measurements of the Ta4*f* core and valence band spectra. The comparison of the XPS-measured non-stoichiometry and the secondary ion mass spectrometry analysis of the hydrogen content allowed this study to conclude that the non-stoichiometry is largely related tothe formation of Ta-VO sites rather than of Ta-H sites.

Such oxygen-deficient TaOx layers were studied for application as a VO reservoir layer in a resistance switching random access memory stack (Ta_2O_5/TaOx) where the actual switching occurred within the stoichiometric Ta_2O_5 layer.The bilayer memory stack showed reliable resistance switching up to ~10^6 switching cycles, whereas the single-layer Ta_2O_5 memory showed only several hundred switching cycles.

5:00pm **AA-MoA-15 Monitoring Resistive Switching Properties of ALD Grown Al_2O_3/HfO_2 Nanolaminate ReRAM Structures by *iin-situ* Reducing Plasma Treatments**, ***Marceline Bonvalot***, *B Eychenne, P Gonon,* LETI-LTM, France

Metal oxide resistive random access memories (RRAM) are considered as strong candidates in novel memory and logic device applications, thanks to low power consumption, fast switching speed and easy down scaling below 20 nm. It is widely accepted that this soft breakdown is induced by the formation or rupture of a conductive filament (CF) based on oxygen defect migration upon voltage application. However, other mechanisms such as electrochemical reactions or Joule heating may also play a role in the switching. From the technological point of view, HfO_2 is undoubtly one of the most mature dielectric oxides under investigation for this purpose. One major issue that needs to be addressed before HfO_2 RRAM devices can be successfully implemented concerns the adequate control of their performance, in terms of variability and reliability of the switching parameters. To address this issue, Al_2O_3 has been used as an intercalation layer material in the HfO_2 dielectric oxide. Indeed, Al_2O_3 has a large band gap and a strong oxygen affinity. It also favors higher thermal stability of amorphous HfO_2 and thus impedes HfO_2 recrystallization potentially induced upon cycling, providing improved endurance.

Al_2O_3-HfO_2 bilayer structures have been deposited by ALD on Si/Ti/TiN bottom electrodes and capped with patterned Pt top electrodes using a shadow mask and a PVD process. Thickness values of each layer have been adjusted so as to maintain a 10 nm overall dielectric thickness.

We have observed that as deposited Al_2O_3-HfO_2 structures do not exhibit any memory effect. This is attributed to the defect free ALD Al_2O_3 layer which can sustain high electric fields without any breakdown. Subsequent reducing plasma treatments have then been applied in situ during the ALD Al_2O_3 growth in order to tune up a significant amount of oxygen vacancies

which have been quantified by XPS analyses for several durations to plasma exposure (between 60 and 200 seconds). These treatments have proven to be necessary to trigger reversible switching in Al_2O_3-HfO_2 RRAM structures. Our results suggest that the formation energy of oxygen defects to a threshold concentration is too large to allow the CF formation. However, when preexisting in the insulating material, these oxygen vacancies can easily migrate along the applied electric field without significantly damaging the insulating matrix. Our results also indicate that both SET voltage (V_{SET}) and RESET voltage dispersion (ΔV_{RESET}) can be significantly reduced by appropriate plasma exposure durations. All these results will be presented and discussed in the light of current knowledge on conductive filament propagation in the dielectric material.

5:15pm **AA-MoA-16 Properties of ALD Ferroelectric Si-doped HfO_2 Characterized with Noncontact Corona-Kelvin Metrology**, ***Dmitriy Marinskiy***, Semilab SDI*; P Polakowski,* Fraunhofer IPMS, Germany*; A Findlay, P Edelman, M Wilson, J Lagowski,* Semilab SDI*; J Metzger, R Binder,* GLOBALFOUNDRIES, Germany*; J Müller,* Fraunhofer IPMS, Germany

The recent discovery of ferroelectricity in Si-doped HfO_2 thin films opens an attractive possibility for new ferroelectric FET's based on HfO_2 already integrated in IC technology [1].

We report a pioneering application of rapid feedback noncontact corona-Kelvin metrology for characterization of the ferroelectric (FE) behavior of Si-doped HfO_2. The 10nm films with Si mol% of 3.5, 4.6, and 11.3 were deposited using a halide based ALD process on 300mm Si wafers. Based on previous studies, which showed enhanced ferroelectric behavior for capped layers, the films were covered with 10nm PVD-TiN and spike annealed at 800°C . For corona-Kelvin measurements, the top TiN was removed by SC1 etching. On sister wafers MIM capacitors were prepared for standard measurement.

In the corona-Kelvin method, corona deposits charge-bias pulses (ΔQ_C) on the dielectric. The induced change of surface voltage (ΔV) is measured with a Kelvin probe and capacitance is obtained as $C=\Delta Q_C/\Delta V$. Present results demonstrate that large charge bias provides a means for poling of the ferroelectric films similar to voltage biasing of MIM capacitors. Sequential small charge pulses are used for acquiring the Q-V and C-V characteristics that monitor the ferroelectric property again in good agreement with standard MIM polarization characteristics and permittivity derived from C-V.

Distinctly different properties are revealed in films with small and large Si doping. Based on structural analysis, the sample with 11.3% Si stayed amorphous after the anneal, while the samples with lower amount of silicon showed a distinct amount of orthorhombic, ferroelectric phase of HfO_2. The 11.3% Si film was found to be non-ferroelectric as demonstrated by linear Q-V and lack of hysteresis. For the two low Si films, a large Q-V hysteresis loop was measured after large positive corona charge poling (Q_C of 30μC/cm^2). In the hysteresis loop the coercive positive and negative fields were identified at about ± 1.2MV/cm for the 3.5% film and 1.0MV/cm for the 4.6% Si film.

For large positive charging the Fowler-Nordheim electron tunneling from TiN to HfO_2 conduction band was measured, showing a large effect of Si-doping manifested by the linear tunneling field decrease with %Si. This offers a possibility of %Si monitoring in HfO_2 with an estimated sensitivity of about 0.1mol%.

The corona-Kelvin technique facilitates whole wafer mapping of ALD film properties. Differences in maps that correlate with processing were observed showing promise for the technique as a fast, inline ALD and post deposition process monitor.

[1] J. Müller, P. Polakowski, S. Müller and T. Mikolajick, ECS J. Sol St. Sci. and Tech. 4, (2015): N30-N35

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