ALD Applications
Room Hall 3D - Session AA2-WeM

Memory Applications: RRAM & Neuromorphic, MIM Capacitors

Moderators: Uwe Schröder, Namlab, Seung-Yeol Yang, Samsung

10:45am **AA2-WeM-12 Towards Neuromorphic Computing Using ALD Grown HfO_2 Based Memristive Devices***, **Christian Wenger,*** IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany **INVITED**

Due to its advantages of massive parallelism, high energy efficiency, and cognitive functions, brain-inspired neuromorphic computing is attracting immense interest. As the basic unit cell for learning algorithms, the implementation of synaptic behavior into memristive devices is the key step toward neuromorphic computing.

Recent advances in the performance of resistive random access memory (RRAM) acting as memristive devices have led to a significant interest in neuromorphic applications. Although RRAM based memory arrays demonstrated excellent performance parameters, the variability is still a critical issue. Controlling this intrinsic phenomenon requires employing program-verify schemes. In this talk, an optimized scheme to minimize resistance state dispersion and to achieve reliable multi-bit operation is evaluated.

However, statistical variations can be tolerated in computing applications like neuromorphic networks. The synaptic behavior memristive devices can be evaluated by applying successive algorithms consisting of set or reset pulses. These algorithms can be used to study the synaptic functionality of memristive arrays.

Nevertheless, there is still a huge gap between the physical implementation and the verification of circuits and systems proposed for memristive devices. The first step, required to fill the gap, is the development of analog simulation tools, which are the base for the successful implementation of digital CMOS circuits with memristive elements. New designs and concepts need to be supported up by physical implementation and verification to be reliable. That means, new simulation tools for memristive devices have to address the following issues: device variability, cycling variability, data endurance, data retention as well as device switching speed. Meaning that memristive device models still have a long way to be completed.

11:15am **AA2-WeM-14 Novel Carbon-Doped HfO_x Memristor with Born-ON Characteristics Synthesized via ALD/MLD Combined Technique***, **Minjong Lee**, Y. Hong, J. Kim, D. Le, D. Kim,* University of Texas at Dallas*; R. Choi,* Inha university, Republic of Korea*; J. Rohan, G. Yeric,* Cerfe Labs*; J. Kim,* University of Texas at Dallas

Transition metal-oxide (TMO) materials are recognized as the most promising for memristive devices. The majority of TMO memristors require a one-time initialization step, during which a relatively large voltage induces filamentary switching. This forming process introduces challenges, including large overshoot currents under high voltage conditions [1]. Beyond typical memristive operations, including the initial forming process, the novel concept of a born-ON memristor generates universal non-polar switching in carbon-doped TMO films deposited by spin-on fabrication [2]. The introduction of additional defects to the pristine TMO film results in born-ON characteristics accompanied by excellent device yield and reliability. However, spin-on fabrication has a significant limitation as it is not compatible with CMOS process. In our previous presentation at the ALD/ALE 2023 conference, we demonstrated feasible born-ON characteristics by using a carbon-composited oxidant during the ALD process [3].

Herein, we extend the technical feasibility of previous work to demonstrate a super-cycle approach generating controllable HfOx film density and carbon concentration. Beyond typical HfOx film deposition using TDMA-Hf and H2O, we used ethylene glycol (EG) as an additional reactant for carbon doping. Within the super-cycle framework, we varied the 'm' cycles of the ALD process (TDMA-Hf/H2O) and the 'n' cycles of the MLD process (TDMA-Hf/EG). Notably, adjusting the ratio between the ALD and MLD processes resulted in HfOx film densities ranging from 4.5 to 9.4 g/cm3 (Fig. 1a). Furthermore, leveraging this super-cycle approach of ALD and MLD cycles provides control over the carbon rate, evident from the XPS profiles (Fig. 1b). The electrical characteristics of HfOx memristors were comprehensively investigated across various carbon concentrations (Fig. 2a). With an increase in carbon concentration to 10%, the set voltage decreases, and the initial leakage current closely aligns with OFF current, indicating a forming-free memristor. In devices with 15% carbon, we achieved born-ON memristive behavior. This device ensures reliable non-volatile memory operation with excellent endurance and retention properties (Fig. 2b). Our work marks a significant advance towards the development of novel forming-free TMO memristors within this controllable film density paradigm using super-cycle approach of ALD and MLD processes.

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[1] E. Ambrosi et al., IEEE IEDM, 443–446 (2022).
[2] C. A. Paz de Araujo et al., APL Mater. 10, 040904 (2022).
[3] M. Lee et al., ALD/ALE 2023 (2023).

11:30am **AA2-WeM-15 Evolution of Structural Order in Doped Hafnia Thin Films by Atomic Layer Deposition for Emerging Device Applications***, **Mohammad Hassan Sultani**, F. Cüppers,* Forschungszentrum Juelich GmbH, Germany*; A. Dippel, O. Gutowski,* Deutsches Elektronen Synchrotron DESY, Germany*; A. Besmehn, D. Müller, S. Hoffmann-Eifert,* Forschungszentrum Juelich GmbH, Germany

HfO_2-based thin films by atomic layer deposition (ALD) are widely used in emerging electronic devices. Monoclinic and tetragonal structures serve as high-k dielectric in field effect transistors (FET). Films with ferroelectric orthorhombic structures, often achieved by doping, enable ferroelectric FETs. Further, thin films of HfO_2 form the switching layer in resistive random-access memories (ReRAM) for new neuromorphic computing architectures. Due to limitation of the thermal budget in back-end-of-line to about 450°C, an amorphous state of the HfO_2 layer after full chip fabrication is essential for high device-to-device reproducibility. For a deeper understanding of the optimum design of emerging devices based on ALD HfO_2 films, it is crucial to describe the nature of the amorphous material and to control the crystallization process and the resulting phase by heterovalent and homovalent doping.

The present study investigates the structural properties of thin films from HfO_2 doped with Al, Si, and Ti. The films at a total thickness of 30 nm were grown in a FlexAL™ system at 250°C heater temperature using oxygen plasma as the counter reactant. Tetrakis(ethylmethylamido)hafnium, trimethylaluminium, Bis(tertiary-butylamino)silane, and tetrakis(dimethylamino)titanium served as metal precursors. Effective dopant concentrations between 2 and 10 at% were realized by the growth of nanolaminates of n-times (x cycles HfO_2 - y cycles MO_x – x cycles HfO_2)(with M=Al, Si, Ti). The laminate structures after growth and crystallization were characterized by X-ray reflectivity and by time-of-flight secondary ion mass spectroscopy. The local structure of the amorphous layers was probed by high-energy X-ray scattering at grazing incidence and pair distribution function analysis. Further, in-situ thermal treatment in vacuum allowed to study the crystallization process of the different films in detail. Crystallized films were analyzed by high-resolution grazing-incidence X-ray diffraction. The measurements were performed at PETRA-III storage ring at DESY

The results will be discussed with special emphasis on the effects of the dopant element, the laminate sequences, the effective doping concentration on the local structure of as-grown films, on the crystallization behavior, and on the crystalline phase obtained after annealing. Results of this study can enhance the understanding of the thin films' local structure and the crystallization process and thereby can support the optimization of material's and process' design for the various applications of HfO_2 thin films in emerging devices for energy-efficient next-era computing applications.

11:45am **AA2-WeM-16 ALD HfZrO2 Films from Ferroelectric to High-k Applications***, **Alessandra Leonhardt**,* ASM, Finland*; R. Ramachandran,* ASM, Belgium*; M. Surman,* ASM, Finland*; R. John, F. Tang, M. Balseanu,* ASM*; A. Illiberi,* ASM, Belgium

HfO2 based ferroelectric (FE) materials have gained tremendous attention as a potential candidate for memory applications such as FeFET and FeRAM. Since its first demonstration as a FE material [1], immense research has been done to circumvent the challenges such as scalability, increasing the remnant polarization (Pr), and improving endurance. Among others, Zr-doped HfO2, $HfZrO_2$ is being intensively studied due to its compatibility with complementary metal oxide semiconductor (CMOS) processing and excellent scalability. ALD has been the technique of choice for the deposition of those films, due to the high conformality, high film quality and simplicity of tuning the composition. $HfZrO_2$ has excelled in this field, with high polarization, high endurance and retention. Those properties were still further improved by the addition of dopants such as La, which resulted in the record high 2Pr for films fabricated by ASM and imec using metalorganic precursors [2].

In this presentation we take ALD $HfZrO_2$ one step forward, and describe how, with the addition of suitable dopants, the ferroelectricity can be modulated in a broad range, and how this can be incorporated in applications where high dielectric constants are desired. We discuss the use of Al dopants in $HfZrO_2$ and explore the relationship between film composition and electrical properties, discussing the physics of ferroelectricity and high dielectric constant. Thin Al:$HfZrO_2$ films show significant modifications in their dielectric properties with respect to pure $HfZrO_2$. Low Al doping levels initially boost the capacitance, while higher levels results in CV peak shifting which leads to a quasi-flat CV behavior at 5% Al doping. This is consistent with the model of dopants with small atomic radius promoting tetragonal phases inside the (initially orthorhombic) $HfZrO_2$ lattice [3]. This results in high dielectric constant at relevant operation voltages e.g. k>40 @ -1.2V for 6-7nm films, which is in line with future high-k applications.

References

1. T.S. Boscke et al, Appl. Phys. Lett. 99, 102903 (2011)
2. M. I. Popovici and J. Bizindavyi et al, IEDM 2022
3. Lee, Seung Won, et al. *Ceramics International* 49.11 (2023)

Author Index

Bold page numbers indicate presenter