ALD Applications
Room Van Rysselberghe - Session AA2-WeM2
ALD for Memory Applications I

Moderators: Robert Clark, TEL Technology Center, America, LLC, Charles Dezelah, ASM

10:45am **AA2-WeM2-1 Sub 10-nm Ferroelectric HfO_2 Capacitors Doped with Gd***, **Evgeniy Skopin**, N. Guillaume, L. Alrifai, A. Bsiesy,* LTM - MINATEC - CEA/LETI, France

Recent discoveries of the ferroelectric properties of doped HfO_2 opens the possibilities of its integration in Ferroelectric-based non-volatile Random-Access Memories (FeRAMs). Replacing memories based on perovskites materials by ferroelectric HfO_2 has many decisive advantages. Indeed, HfO_2 is readily used in CMOS back end of the line, and its use opens the possibility to grow thinner layers of around 10 nm *vs* 70-100 nm for the conventional ferroelectric perovskites. Thinner layers are mandatory for integration in advanced sub 100 nm CMOS technology nodes.

Plasma Enhanced Atomic Layer Deposition (PEALD) allows the synthesis of a different range of materials such as oxides and metals with low surface roughness and precise thickness control. TiN metal (M) layers and Gd doped HfO_2 insulator (I) layer were grown in the same PEALD chamber without contact with the air between depositions to synthesize ferroelectric MIM capacitors. Changing ratios between Hf and Gd PEALD cycles inside one supercycle allows choosing an appropriate Gd doping concentration. In its order, during annealing, Gd doping in HfO_2 (Gd:HfO_2) leads to a crystallization of HfO_2 in a metastable non-centrosymmetric orthorhombic phase, which induces the HfO_2 ferroelectric properties. A decrease of the ferroelectric oxide thickness can allow operating lower switching voltages for the low power circuits.

Continuing our previous work [SB], by using the growth of MIM capacitor by PEALD in one batch (*i.e*. without air break between metal, insulator, and metal layers), we recently demonstrated the ferroelectricity of sub-10 Gd:HfO_2 layers (8.8nm-, 6.6nm, and 4.4nm-thick layers) in TiN / Gd:HfO_2 / TiN stacks and studied the remnant polarization amplitude change with the Gd:HfO_2 layer thickness. Structural measurements (X-ray diffraction and reflectometry) confirmed a HfO_2 transformation to the orthorhombic (ferroelectric) phase. Electrical measurements showed that switching voltage can be decreased for the thinner Gd:HfO_2 layers (hysteresis loop measurements and Positive Up Negative Down measurements). Polarization switching cycling measurements demonstrate ferroelectric endurance of at least up to 10^8 cycles. This work opens the possibilities for the integration of sub-10nm Gd:HfO_2 in the memory device circuits thanks to the unique PEALD deposition capabilities.

References:

[SB] Applied Physics Letters 117.25 (2020): 252903.

11:00am **AA2-WeM2-2 Controlling Stochastic Resistive Switching in Organic-Inorganic Hybrid Memristor by Vapor-Phase Infiltration***, A. Subramanian,* Stony Brook University*; N. Tiwale, K. Kisslinger, **Chang-Yong Nam**,* Brookhaven National Laboratory

Resistive random-access memory (RRAM) is promising for next-generation data storage and non-von Neumann computing hardware. However, tuning device switching characteristics and, particularly, controlling their stochastic variation remain as critical challenges. Here, we report new organic-inorganic hybrid RRAM media whose bipolar switching characteristics and stochasticity can be controlled by vapor-phase infiltration (VPI), an ex-situ organic-inorganic hybridization technique derived from atomic layer deposition (ALD). Hybrid RRAMs based on AlO_x-infiltrated SU-8 doped with sliver perchlorate feature facile tunability of device switching voltages, off-state current, and on-off ratio by adjusting the amount of infiltrated AlO_x in the hybrid, wherein molecular network of AlO_x is homogenously distributed through the polymer free volume by the sequential infiltration of trimethylaluminum (TMA) and water vapor. Furthermore, a significant reduction in the stochastic, cycle-to-cycle variations of switching parameters, such as off-state current and set/reset voltages, was enabled by AlO_x infiltration, driven by the infiltration-induced changes in mechanical, dielectric, and chemical properties of the organic medium and their influence on the dimension and formation characteristics of a conductive silver filament. Finally, we demonstrate multi-level analog switching, potentially useful for neuromorphic applications, by controlling switching compliance current, as well as direct, one-step device patterning ability exploiting the negative-tone resist feature of SU-8. With the demonstrated control over switching characteristics and stochastic variation, combined with analog switching and one-step patterning capabilities, the results not only present a novel hybrid medium for RRAM applications but also showcase the utility of VPI for developing new, high-performance hybrid RRAM devices based on photoresist materials.

11:15am **AA2-WeM2-3 Atomic Layer Deposited Vanadium Oxide Thin Films for Thermocromic and Microelectronic Applications***, **Zsofia Baji**, J. Volk, L. Pósa, G. Molnár,* Centre for Energy Research, Hungary*; A. Surca, G. Drazic,* National Institute of Chemistry, Slovenia

Vanadium oxides are much-researched materials due to their wide range of applications from microelectronics, smart electrochromic and thermochromic windows, metamaterials, gas sensors, programmable critical thermal sensors to battery energy storage. V_2O_5 has been the most widely examined for energy storage and electrochromism, as the Li ions can easily be intercalated between its atomic layers. On the other hand, VO_2 undergoes a reversible transition at 68°C, where a change in light and electrical conductivity occurs, therefore, VO_2 is widely researched as a promising material for resistive switching and thermochromism. Resistive switching is presently at the core of emerging technologies, such as memristors and neuromorphic computing. By the switching between the insulating and metallic phase of VO_2, the switching of signals for nanoelectronical applications becomes possible. Alternative switching mechanisms are also widely researched, such as the field-induced transition. An advantage of the ALD method in the preparation of these films would be the control of the deposition parameters and an easy doping, which allows a better control of material properties (crystallinity, stoichiometry and defects), and, thus, the transition temperature.

The atomic layer deposition of vanadium oxides has been in the focus of much research effort. Several precursors and different reactions can be used for this purpose, but there are some substantial difficulties with all of them. Vanadium oxy-tri-isopropoxide, Tetrakis ethylmethyl-amino vanadium (TEMAV) or VCl_4 are all promising candidates for the process.

Most reports on the ALD of vanadium-oxides present the preparation of V_2O_5 which is the more stable phase and is easier to deposit. An advantage of the ALD method is that the oxidation state of the deposited films can be tuned by the selection of the reactant. More oxidising reagents (e.g. oxygen plasma) will result in films with higher oxidation states, while reactions with hydrogen or ammonia plasma yield lower oxidation states. In this way, by choosing the appropriate reactants and deposition parameters the preparation of VO_2 can be achieved.

The present work examined the ALD process of TEMAV and different oxidants (water, oxygen plasma) a number of annealing procedures in oxidising and reducing atmospheres. The films were annealed to improve the crystallinity and stoichiometry. Their properties were examined with Raman spectroscopy and transmission electron microscopy. The switching properties were analysed electrically and optically, and test structures were demonstrated.

11:30am **AA2-WeM2-4 Brain-Based Inspiration: Towards Neuromorphic Computing With ALD Based Memristive Devices***, E. Perez, M. Kalishettyhalli Mahadevaiah, E. Perez-Bosch Quesada,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany*; T. Rizzi,* IHP - Leibniz-Institut fuer innovative Mikroelektronik, Germany*; **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.

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