DF 12: High-k and Low-k Dielectrics II (Joint Session DS/DF)

Time: Wednesday 11:15-12:45

DF 12.1 Wed 11:15 H8

Electrical and structural characteristics of SrTaO/SrTiO based M-I-M capacitors — •CANAN BARISTIRAN KAYNAK¹, MIN-DAUGAS LUKOSIUS¹, BERND TILLACK¹, CHRISTIAN WENGER¹, GUEN-THER RUHL², and TOM BLOMBERG³ — ¹IHP Im Technologiepark 25, 15236 Frankfurt Oder, Germany — ²Infineon Technologies AG, Wernerwerkstr. 2, 93049 Regensburg, Germany — ³ASM Microchemistry Ltd., Väinö Auerin katu 12 A, 00560 Helsinki, Finland

In this work, on-chip M-I-M capacitors are realized using SrTiO /Sr-TaO dielectric stacks. The deposition of the SrTiO dielectric is done by ALD and to get a crystalline state correspondingly high k value, 550 $^{\circ}\mathrm{C}$ annealing temperature is applied. Moreover, SrTaO is considered as a part of barrier stack due to its amorphous characteristic at 550°C annealing temperatures. In this way, it is expected to improve the electrical characteristic of the devices. A set of M-I-M stacks such as Au/SrTiO/TaN/Si, Au/SrTaO/SrTiO/TaN/Si and Au/SrTiO/SrTaO/TaN/Si have been deposited and analyzed by means of electrical and analytical characterizations. The effect of thickness of SrTaO was also evaluated. From the C-V and J-V measurements, dielectric constant, corresponding capacitance densities and leakage current performance were extracted. For the investigation of interfaces between the stacks XPS and ToF-SIMS were utilized. The results mainly demonstrate that the use of SrTaO material in the barrier stack strongly improves the leakage current density of M-I-M capacitors due to its amorphous state which serves as a strong barrier between the dielectric and the electrode of the M-I-M capacitor.

DF 12.2 Wed 11:30 H8 Resistive switching in TiN/HfO₂/Ti/TiN MIM structures for future memory applications — •Christian Walczyk¹, Christian Wenger¹, Mindaugas Lukosius¹, Mirko Fraschke¹, Ioan Costina¹, Sebastian Schulze¹, Sebastian Thiess², Wolfgang Drube², and Thomas Schroeder¹ — ¹IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany. — ²Hasylab at DESY, Notkestrasse 85, 22607 Hamburg, Germany.

The electrically switchable resistance change phenomenon between a high (OFF-state) and a low (ON-state) resistive state of a metalinsulator-metal (MIM) diode structure has attracted considerable attention in recent years for future non-volatile memory applications (RRAM). Especially hafnium dioxide (HfO_2) as insulator is among the oxides particularly desirable due to the fact that it is nowadays considered as a BEOL Si CMOS compatible binary metal oxide system. Typical bipolar current-voltage characteristics of a $TiN/HfO_2/Ti/TiN$ stack with a HfO_2 thickness of 10 nm will be presented. The switching properties crucially depend on a) whether the additional Ti layer is integrated as top or bottom electrode and b) on the application of post-deposition annealings (PDA). To unveil the origin of these observations, a materials science study by TOF-SIMS, TEM and HA-XPS was carried out. It is possible to prove that this metallic Ti layer getters during the PDA treatments oxygen from HfO₂, resulting in the formation of non-stoichiometric HfO_x . Due to their significance in NVM technology, we will furthermore present the retention and cycling endurance characteristics.

DF 12.3 Wed 11:45 H8

Oxygen Engineering of HfO_{2-x} Thin Films grown by Reactive Molecular Beam Epitaxy — •ERWIN HILDEBRANDT¹, JOSE KURIAN¹, PETER ZAUMSEIL², THOMAS SCHRÖDER², and LAMBERT ALFF¹ — ¹Institut für Materialwissenschaft, TU-Darmstadt — ²IHP, Frankfurt, Oder

Reactive Molecular Beam Epitaxy (R-MBE) is an ideal tool for tailoring physical properties of thin films to specific needs. For the development of cutting-edge oxides for thin film applications a precise control of oxygen defects is crucial. R-MBE in combination with rf-activated oxygen allows reproducibly growing oxide thin films with precise oxidation conditions enabling oxygen engineering.

R-MBE was used to grow Hf and $\text{HfO}_{2\pm x}$ thin films with different oxidation conditions on sapphire single crystal substrates. Structural characterization was carried out using rotating anode x-ray diffraction revealing highly textured to epitaxial thin films on *c*-cut sapphire. Furthermore, switching of film orientation by varying the oxidation conditions was observed demonstrating the role of oxygen in the growth

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procedure. The investigation of electrical properties using a four probe measurement setup showed conductivities in the range of 1000 $\mu\Omega$ cm for oxygen deficient HfO_{2-x} thin films. Optical properties were investigated using a photospectrometer and additionally x-ray photoelectron spectroscopy was carried out to study the band gap and valence states. Both techniques were used to monitor the oxygen content in deficient HfO_{2-x} thin films. Our results demonstrate the importance of oxygen engineering even in the case of 'simple' oxides.

DF 12.4 Wed 12:00 H8 Band structure and electrical properties of MBE grown HfO₂ - based alkaline earth perovskites — •DUDEK PETER¹, LUPINA GRZEGORZ¹, KOZŁOWSKI GRZEGORZ¹, DABROWSKI JAREK¹, LIPPERT GUNTHER¹, MÜSSIG HANS-JOACHIM¹, SCHMEISSER DIETER², and SCHROEDER THOMAS¹ — ¹IHP-Microelectronics, Im Technologiepark 25, D-15236 Frankfurt (Oder) — ²BTU Cottbus, Konrad-Wachsmann-Allee 17, D-03046 Cottbus, Germany

Ultra thin dielectric films (<20 nm) deposited on TiN electrodes are interesting for MIM capacitor application. High capacitance density and dielectric permittivity must be accompanied by extremely low leakage currents (10^{-8} A/cm^2) at bias 0.5 V. To achieve such low leakage currents, high band gap and proper band alignment is required. Occupied electronic states can be probed with standard laboratory photoemission methods. Probing of unoccupied states is more challenging. Synchrotron based PES in combination with XAS forms a powerful method to study the band alignment. ASAM end station located at the U 49/2 PGM 2 beamline of BESSY II (Berlin) offers excellent conditions for performing such measurements. We investigated HfO₂ based alkaline earth perovskite - $BaHfO_3$ with subsequent admixture of TiO₂, resulting in formation of BaHf_{0.5}Ti_{0.5}O₃ compound. The analysis of data indicates that band gap for HfO₂ is similar to BaHfO₃ and amounts 5.8 eV; for BaHf_{0.5}Ti_{0.5}O₃ it decreases to 3.8 eV. We conclude that the addition of TiO₂ to BaHfO₃ increases significantly the dielectric permittivity but also impacts the band gap alignment. The conduction band offset shrinks, influencing the leakage current behavior.

DF 12.5 Wed 12:15 H8

In-situ EELS and UPS measurements on HfO₂ **ALD layers** — •MARCEL MICHLING, MASSIMO TALLARIDA, KRZYSZTOF KOLANEK, and DIETER SCHMEISSER — Brandenburgische Technische Universität Cottbus, Angewandte Physik/Sensorik, K.-Wachsmann-Allee 1, 03046 Cottbus

In this contribution we report on our in-situ cycle-by-cycle (up to 10 cycles) investigations of the HfO_2 ALD process using the methods of EELS and UPS.

We used TDMA-Hf as a precursor and p-type Si wafer with natural oxide as the substrate. The EELS measurements were done with a primary energy of 52,5 eV and the UPS measurements with He I (21,218 eV).

The change in the onset of the loss function is readily observed. Already after two cycles the value approach to the bulk value of HfO_2 . Upon ALD growth there is a remarkable decrease in the intensity of states within the gap. They are rather smooth and saturate after 10 cycles. With UPS we follow the variation of the VB onset and changes in the secondary electron onset. We summarize our data in a band diagram not based on bulk values but on cycle dependent quantities. With these cycle-by-cycle experiments we study the initial growth of HfO_2 especially in the very first cycles.

DF 12.6 Wed 12:30 H8

Determination of interfacial layers in high - k ALD nanolaminate materials by ARXPS and SRXPS measurements.

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— ²GLOBALFOUNDRIES, Dresden, Germany

The interfacial layers of high dielectric constant (high - k) nanolaminate films are here explored. Problems concerning ALD nanolaminate layers deals mainly with lack of accurate methods to determine in depth

profile of few nm thick stacks. Modified angle resolved XPS(ARXPS) and synchrotron radiation XPS(SRXPS) are proposed as methods suitable in layer profiling. Studied stacks containing ZrO/HfO or AlO/ZrO, were prepared on Si substrates by atomic layer deposition (ALD). Two sets of experiments were covered. First dealt with initial growth (up to 20 cycles, with thickness d < 2nm) of AlO/ZrO and included layer by layer *insitu* investigation by SRXPS. Second experiment refer to industrial grown ZrO/HfO films (d ~ 3nm) processed

with various parameters resulting in both, layer by layer and homogenous depositions. For those samples *exsitu* XPS, with angle dependent variation of probing depth, measurements were covered. By comparing obtained intensity ratios for different angles with computational developed stack model it was found that no simple layer by layer but some intermixing growth occurred including interaction with silicon substrate.