Electronic Materials and Processing
Room: 210E - Session EM-WeM

Beyond CMOS: Resistive Switching Devices
Moderator: Christopher Hinkle, University of Texas at Dallas

8:00am **EM-WeM1 Tantalum Oxide Resistive Memory Devices by IAD**, ***Ronald Goeke***, *M. Marinella, D.R. Hughart*, Sandia National Laboratories

Resistive random access memory (ReRAM), or memristors, may be capable of significantly improving the efficiency of neuromorphic computing, when used as a central component of an analog hardware accelerator. However, the current fabrication methods for these nano-ionic resistive memory devices suffer from significant electrical variation within a single device and between devices. This variation degrades the maximum efficiency and accuracy, which can be achieved by a ReRAM-based neuromorphic accelerator.

The switchable resistive thin film at the heart of these memristor devices has been fabricated from sub-stoichiometric tantalum pentoxide using Ion Assisted Deposition (IAD). These devices fabricated with IAD have shown a significant improvement in yield and a big reduction in device performance variability. This success has been repeated many times now. The devices are fabricated from a sub-stoichiometric tantalum pentoxide using IAD to control the oxygen to tantalum ratio. The IAD deposition approach involves e-beam evaporation of tantalum metal with a reactive beam of oxygen and argon ions impinging upon the growing film. Using this technique, the oxide formation occurs at the substrate resulting in good control over film stoichiometry. IAD is a popular technique for the deposition of oxide thin films in the optical coating industry, but has now been demonstrated as a valuable method for growth of oxide electronics. The electrical and optical characterization of these films will be presented.

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8:20am **EM-WeM2 Capacitance and Resistance Switching in HfO_2 RRAM**, ***Christophe Vallee***, *P. Gonon, C. Mannequin, T. Wakrim, M. Saadi*, LTM, Univ. Grenoble Alpes, CEA-LETI, France, *A. Sylvestre*, G2elab, Univ. Grenoble Alpes, France

This work addresses a new class of electrical devices that could be named "memory impedance", or "MEM-Z" devices. These structures are based on the capability of HfO_2 MIM (Metal – Insulator –Metal) to switch both their resistance and capacitance with a memory effect. Recently, during works led on HfO_2 OxRAM [1], we found that for a specific design, upon voltage biasing, not only does the resistance changes but the capacitance also varies from positive to negative values. In other words, *both the real and imaginary part of the impedance can be controlled by the voltage bias*. If the impedance state can be non-volatile (memory function), then a new class of devices (MEM-Z) can be defined. MEM-Z devices (mem-capacitors and mem-inductors) were recently theorized and their potential applications reviewed [2]: like memristors, they can be used as non-volatile memories, for fuzzy logic (non-binary computing based on continuous variables), and as self-learning devices (neuro-inspired systems, adaptive filters…). They can also be used in tunable electronic circuits such as reconfigurable impedance matching network, reconfigurable amplifiers, programmable filters and oscillators.

In the present work we investigate both resistance and capacitance switching of HfO_2-based MIM device. By comparison to HfO_2 OxRAM, the device has been modified in order to avoid any breakdown during the capacitance switch. Therefore a bi-layer structure is used to obtain a self-compliance MEM-Z device. With this structure a bipolar capacitance cycle has been obtained with decreasing values of capacitance in the ON state. Negative values of capacitance near SET and RESET voltages are also observed. Memory effect for both positive and negative values of capacitance is also demonstrated. At present, the physical origin of capacitance variation is an open question. One hypothesis is that conduction paths, which lead to resistance switching, are the same which lead to capacitance decrease (through the inductive behavior of conduction paths, hopping conduction). This will be discussed in this presentation from the frequency dependence study of the capacitance switch.

[1] P. Gonon, M. Mougenot, C. Vallée, C. Jorel, V. Jousseaume, H. Grampeix, F. El Kamel, "Resistance switching in HfO_2 metal-insulator-metal devices", *Journal of Applied Physics*, vol.107, p.074507 (2010)

[2] Y.V. Pershin, M. Di Ventra, "Memory effects in complex materials and nanoscale systems", *Advances in Physics*, vol. 60, p.145 (2011)

8:40am **EM-WeM3 Density Functional Theory Molecular Dynamics Simulations and Experimental Characterization of high-k/SiGe(110) and SiGe(001) Interfaces**, *A.C. Kummel, E. Chagarov*, University of California at San Diego, *B. Sahu*, Globalfoundries, *S. Oktyabrsky, S. Madisetti*, College of Nanoscale Science and Engineering, Albany-SUNY, ***Tobin Kaufman-Osborn***, University of California at San Diego

Density-Functional Theory (DFT) Molecular Dynamics (MD) simulations were employed to investigate formation at finite temperature of direct interfaces between a-Al_2O_3 oxide and $Si_{0.50}Ge_{0.50}$ substrate with Si- and Ge-terminations. The simulated interfaces revealed mixed bonding between the semiconductor substrate atoms and both O and Al oxide atoms. The oxide/SiGe band gaps were unpinned and close to the SiGe bulk band gap value. The interfaces had SiGe dangling bonds but they were nearly filled and therefore did not produce mid-gap states and could not be passivated by atomic H. The Si terminated surface had a better electronic structure after bonding to oxide compared to the Ge terminated surface since the dangling bonds on the Si atoms tend to be more filled since the Si terminated interface is a better charge acceptor. C-V spectroscopy combined with angle-resolved X-ray photoelectron spectroscopy (AR-XPS) experimentally confirmed formation of interfaces with low interface trap density via direct bonding between a-Al_2O_3 and SiGe.

9:00am **EM-WeM4 Density-Functional Theory Molecular Dynamics Simulations of a-HfO_2/Ge(100)(2x1) and a-ZrO_2/Ge(100)(2x1) Interface Passivation**, ***Evgueni Chagarov***, University of California at San Diego, *L.M. Porter*, Carnegie Mellon University, *A.C. Kummel*, University of California at San Diego

: The structural properties of a-HfO_2/Ge(2x1)-(001) and a-ZrO_2/Ge(2x1)-(001) interfaces were investigated with and without a GeOx interface interlayer using density-functional theory (DFT) molecular dynamics (MD) simulations. Realistic amorphous a-HfO_2 and a-ZrO_2 samples were generated using a hybrid classical-DFT MD "melt-and-quench" approach and tested against experimental properties. The oxide/Ge stacks were annealed at 800K, cooled to 0K, and relaxed providing system with enough freedom to form realistic interfaces. For each high-K/Ge stack type, two systems with single and double interfaces were investigated. All stacks were free of midgap states; however, stacks with an GeOx interlayer had band-edge states which decreased the band gaps by 0-30 %. These band-edge states were mainly produced by under-coordinated Ge atoms in GeOx layer or its vicinity due to deformation, intermixing, and bond-breaking. The DFT-MD simulations show that electronically passive interfaces can be formed either directly between high-K dielectrics and Ge or with a monolayer of GeO_2 if the processing does not create or properly passivates under-coordinated Ge atoms and Ge's with significantly distorted bonding angles. Comparison to the charge states of the interfacial atoms from DFT to experimental XPS results show that while most studies of gate oxide on Ge(001) have a GeO_x interfacial layer, it is possible to form a oxide/Ge interface without a GeO_x interfacial layer. Comparison to experiments is consistent with the dangling bonds in the suboxide being responsible for midgap state formation.

9:20am **EM-WeM5 Role of Active and Inert Electrodes in Filament Formation in Resistive Switching Devices (RRAM)**, ***Gargi Ghosh***, Virginia Tech, *S.W. King*, Intel Corporation, *M.K. Orlowski*, Virginia Tech

Reliable filamentary resistive switching (RS) depends largely on the electrochemical properties of the active and inert electrodes. A resistive switching memory cell in a RRAM is generally built as a capacitor-like MIM Cu/TaOx/Pt structure, comprised of an insulating or resistive material sandwiched between two electron conductors. Cu electrode produces via a redox reaction (Cu -> Cu^++e^-) highly mobile Cu^+ cations that drift in TaO_x and discharge at the inert Pt electrode forming a conductive filament (CF) of the ON state. To assess the role of active and inert electrodes, we report manufacturing and characterization of 4 derivative devices: Cu/TaO_x/Ta, Cu/TaO_x/Ti, Ta/TaO_x/Pt, Ti/TaO_x/Pt. For a possible integration of RRAM in CMOS back-end, two new metals Ta and Ti used in CMOS metalization are selected. In all four derivative cells a CF formation could be observed at voltages 2V-5V, comparable with Cu/TaO_x/Pt. However, Cu/TaO_x/Ti could not be reset, being permanently damaged. Cu/TaO_x/Ta could be reset but only a few times displaying noisy reset behavior. Ta/TaO_x/Pt device shows resistive switching with a low forming voltage of 2V. The best resistive switching behavior was shown by Ti/Ta_2O_5/Pt device. Main conclusions of

the study: 1) In Cu/TaO_x/Ti Cu CFs are formed with a weak base at the Ti electrode due to Cu dissolution in Ti. Cu CF has low resistance and cylindrical shape being difficult to rupture. 2) Cu/TaO_x/Ta device shows better switching properties than Cu/TaOx/Ti, because Ta is better diffusion barrier for Cu than Ti. 3) Ta/TaO_x/Pt is a potential candidate for RS but suffers from: i) the redox reaction Ta -> Ta^++e^- is much weaker than for Cu, ii) the diffusion of Ta in TaO_x is faster than of Cu in TaO_x. The result of these two competing mechanisms are fragile CFs with no resistive constrictions. Hence, the RS is observed but its operation is unreliable. 4) Ti/TaO_x/Pt displays if noisy RS. This is due to Ti being known as a getter for oxygen. The Ti CF is therefore fragile as Ti is easily and permanently incorporated in the oxide matrix forming a $Ta_xTi_yO_z$ compounds. The overall conclusion from this comparative study is a better understanding of conditions for reliable RS: a metallic filament has to be formed with a resistive constriction, e.g. in the form of truncated cone with a sharp apex. Cylindrical CFs are hard to rupture and hence undesirable for RS. Cone-like CFs for reliable RS require: a) copious supply of metal ions, b) high metal ion diffusivity in the dielectric, c) high ion stopping power of the counter electrode, and d) moderate compliance currents to be applied during the set operation to assure cone-like shape of the CFs.

9:40am **EM-WeM6 Neutron Induced Effects on HfO_x-Based Resistive Random Access Memory**, ***Karen Hsu***, *T. Chang*, University of Wisconsin-Madison, *L. Zhao*, Stanford University, *R. Agasie*, University of Wisconsin-Madison, *Y. Nishi*, Stanford University, *Z. Ma*, *J.L. Shohet*, University of Wisconsin-Madison

As the size of devices decreases and the complexity of electronic chips increases, cosmic-ray-induced crashes are becoming a severe threat to electronic circuits and devices. Resistive Random Access Memory (RRAM) [1], which is considered as a very promising memory technology for embedded systems, has undergone intense research in both industry and academia in the last ten years. As RRAM technology matures and electronic devices using RRAM are likely to be built soon, malfunctions of RRAM will become an important problem in industry since the size of these devices will continue to decrease. Neutrons that come from earth bound or from cosmic ray sources are likely one to produce significant effects on the RRAM [2] based on their fluxes at terrestrial altitudes and their interaction cross sections. In this work, neutrons from the University of Wisconsin Max Carbon Radiation Science Center were used as the radiation source The neutron-induced effects on HfO_X RRAM include single-event-upset (SEU), modification to forming voltage, resistance of both the high-resistance (HRS) and low-resistance states (LRS) and shifts in set/reset voltage.

Some RRAM cells can actually be formed during neutron irradiation and then switch from the HRS to the LRS after additional neutron irradiation. The SEU rate increases linearly as neutron fluence increases. For those neutron-irradiated RRAM cells that did not switch from the HRS to the LRS under irradiation, a smaller forming voltage was required after irradiation. In addition, an increase in the HRS resistance and better switching behavior was observed in those RRAM cells formed entirely by neutron irradiation.

Shifts in the set/reset voltage were also observed after neutron radiation. X-ray diffraction was used on HfO_2 films to investigate the physical mechanism, which is attributed to atomic-structure changes in HfOx caused by neutron irradiation.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359, by the National Science Foundation under Grant No. CBET-1066231.

References:

1. H.-S. Philip Wong, H-Y Lee, S. Yu, Y. S. Chen, Y. Wu, P-S Chen, B. Lee, F. T. Chen, and M-J Tsai, "Metal–oxide RRAM," *Proceedings of the IEEE***100** 1951 (2012).

11:00am **EM-WeM10 Relation of Low-k Interconnect Si-based Dielectric Breakdown to Resistive Switching Behavior**, ***Marius Orlowski***, *G. Ghosh*, *P. Kassalen*, *R. Gupta*, Virginia Tech, *S.W. King*, Intel Corporation

The relation between resistive switching (RS) and breakdown and reliability mechanisms are studied for metal-insulator-metal (MIM) structures with low-k dielectrics (SiOC:H, SiCOH, SiNC:H, SiCN:H, SiC:H, SiON:H, SiN:H) all 25 nm thick, with Ti, and Cu as electrode materials that are commonly used in the CMOS back-end process. The TDDB time is correlated with defect generation and related to mechanisms responsible for RS. Defect generation depends exponentially on E_a-bxE_{el}, where E_a is the activation energy, b is the bond polarization factor being proportional to the molecular dipole moment p_o, b=(2+k)/3p_o, and E_{el} is the electric field across the dielectric. The breakdown field E_{bd} is determined by E_a-bxE_{bd}=0, i.e. at high enough electric fields there is effectively no barrier impeding creation of defects. From this condition, the breakdown field E_{bd}=E_a/b is determined. We obtain, for SiC:H E_a=0.28 eV and p_o=10e-A, for SiCN:H E_a=0.26 eV and b=4e-A, for SiN:H, E_a=0.17 eV and p_o=1.2eA, for SiON:H p_o=1.5e-A. for SiOC:H we obtain E_a=1.67eV and p_o=15e-A. We find that E_a values of low-k dielectrics are very low compared with those for high-k dielectrics, e.g. E_a=4.4 eV for HfO_2 with k=21. On the other hand, the strength of the molecular dipole for low-k dielectrics is comparable to that for high-k dielectrics (e.g. p_o=11e-A for HfO_2). In terms of RS properties under a linear voltage sweep the low-k materials display varied behavior: SiNC:H does not exhibit resistive switching, i.e. under linear voltage stress it shows gradual decrease of resistance but the on-state is volatile, i.e. it evanesces when the cell is unpowered. A similar behavior is observed for SiCN:H, i.e. soft volatile breakdown with a volatile on-state. SiOC:H shows a sharp resistive switching that cannot be reversed - the cell is on permanently. The set voltage is high V_{set}=11.8V and it decreases significantly with increasing temperature. SiON:H shows comparable behavior as SiOC:H with slightly lower set voltages. SiC:H shows sharp resistive switching behavior at a moderate set voltage V_{set}=6.5V @ 300K. SiN:H displays also a sharp resistive switching but at much higher voltage, V_{set}=11.5V @300K. The high set voltages for SiC:H and SiN:H correlate well with high densities of those dielectrics, both at 2.5 g/cm^3 and similar dielectric constant of k=7.2 and 6.5, respectively. The on-state is attributed to the formation of a Cu conductive filaments. The conductive filaments are cylindrical and difficult to rupture. The paper discusses correlation, differences, and commonalities between data obtained for dielectric breakdown and resistive switching mechanisms in terms of the film properties.

11:20am **EM-WeM11 Thin Film Carbon Nanofuses for Permanent Data Storage**, ***Kevin Laughlin***, *S. Jamieson*, *H. Wang*, *J. Bagley*, *T. Pearson*, *R.C. Davis*, *M.R. Linford*, *B.M. Lunt*, Brigham Young University

As memory elements shrink, the reliable life span of digital data is decreasing. Today we all have more data, in less stable formats. For hard drives, DVDs, and flash memory, the reliable life of the data is less than 10 years. Rewriting data extends life, but at high maintenance costs. A potential solution to this challenge is write once read many storage media where writing the data results in a permanent, irreversible change. We have been developing thin film carbon nanofuses for use as a permanent data storage medium. Carbon shows particular promise as an electronic storage medium due to its high localized bond strength resulting in high surface stability and reasonable electrical conductivity. I will present the fabrication and characterization of nanoscale fuses with feature sizes down to ~50nm. The low resistance sp^2 carbon is arc deposited and then patterned using electron beam lithography and plasma etching. The electron beam resist used, HSQ, results in a glass etch mask for pattern transfer into the carbon film with an O_2 plasma. The fuses were written and detected electrically, and excellent stability was observed.

11:40am **EM-WeM12 Low-k/Cu Resistive 2-Level PROM Memory Collocated with CMOS Back-End Metallization**, ***Anshuman Verma***, *G. Ghosh*, Virginia Tech, *S.W. King*, Intel Corporation, *M.K. Orlowski*, Virginia Tech

Building nonvolatile memory directly into a CMOS low-k/Cu interconnects would reduce latency in connectivity constrained computational devices and reduce chip's footprint by stacking memory on top of logic. NVM memory includes two flavors: i) random-access memory, and ii) programmable read-only memory (PROM). The paper investigates suitable choice of materials for an integration of PROM compatible with manufacturing of CMOS back-end. Three capacitor-like MIM structures Al/Ti/I/Cu, with dielectrics I=SiOC:H, SiC:H, SiCN:H, all 25 nm thick, have been selected among samples manufactured by Intel Inc and investigated for resistive switching properties. The samples have been subjected to set and reset operations applied customarily to resistive switching devices with TiAl electrode being grounded and a positive bias applied to Cu electrode. For SiOC:H devices, a sharp transition from R_{OFF}=200MΩ to $R_{ON}(1)$=120kΩ at threshold $V_{set}(1)$= 0.9V - 1.2 V is observed. When the set device is subsequently subjected to a linear voltage ramp, a secondary sharp set transition from $R_{ON}(1)$=120kOhm to $R_{ON}(2)$=2-10Ω is observed at $|V_{set}(2)|$=1.0-1.3V and high compliance currents I_{cc}≈100mA, independent of the bias polarity. $R_{ON}(2)$ can be controlled by the level of I_{cc} (@I_{cc}≈10mA $R_{ON}(2)$=34Ω). Both transitions are irreversible and the low resistance states are stable. The 1st transition is likely to be caused by formation of a Cu conductive filament (CF). Because of the weak diffusion/migration stopping power of Ti for Cu, the resulting Cu CF is of a cylindrical form instead of a conical with the former being very difficult to rupture. The 2nd set transition leads to a dramatic decrease of R_{ON} by a factor 10^5. To ascertain the nature of the CF, we have measured the temperature coefficient of resistance α of the CF and obtain unusually high values, typically α=0.04K^{-1}, which is 10X larger than a for bulk Cu, α=0.0039K^{-1}, or for Cu CF in Cu/TaO_x/Pt, α=0.0033K^{-1}) and 40X higher than a for oxygen vacancy defects CF, α=0.001K^{-1}. The secondary set from $R_{ON}(1)$ to $R_{ON}(2)$ is attributed to some, presently unknown, dramatic phase transformation. Structures with SiC:H (same metal electrodes) show different behavior, but result in the same low resistivity state $R_{ON}(2)$. They

require high V_{set}= 3-4V and display volatile behavior at low I_{cc} values. At higher I_{cc} they set into a stable and very low R_{ON}≈5Ω, constituting thus only 1-level PROM. Similarly, devices with SiCN:H are setting permanently only at high I_{cc} currents (50-100mA) and display also very low final resistance of about 10Ω. The paper discusses the properties of the highly conductive, metallic CFs with the uncharacteristically high α.

12:00pm **EM-WeM13 Novel Contact Materials for Reliable Nanoelectromechanical Switches**, ***Frank Streller***, *G. Wabiszewski, D. Durham, R.W. Carpick*, University of Pennsylvania

Nanoelectromechanical (NEM) switches were identified by the roadmap of the semiconductor industry as a low-power "beyond CMOS" technology. However, the reliability of the contact interface currently limits the commercialization of NEM switches, as the electrical contact has to be able to physically open and close up to a quadrillion times without failing, which typically occurs due to adhesion (sticking shut) or contamination (reducing switch conductivity). These failure mechanisms are not well understood, and materials that exhibit the needed performance have not been demonstrated. Thus, commercially viable NEM switches demand the scientific development and characterization of novel contact materials, along with efficient methods to evaluate the interfacial performance of these materials.

We have developed novel contact material candidates that are highly conductive, minimally adhesive, chemically inert, mechanically robust, and amenable to CMOS fabrication processes.[1,2] One promising candidate is platinum silicide (Pt_xSi). The controlled diffusion of sequentially-deposited thin films of amorphous silicon and Pt allowed us to tune the chemical composition of Pt_xSi over a wide range ($1<x<3$). We measured the mechanical and electrical contact properties of Pt_xSi of multiple stoichiometries in comparison with pure Pt. These experiments showed that the Pt-rich silicide phase (Pt_3Si) may be an ideal contact material for NEM switches due to its desirable combination of mechanical robustness with metal-like conductivity. We also demonstrate that Pt_xSi can be used to release NEM switches with a self-formed gap caused by interfacial separation driven by shrinkage-induced tensile stress.

To assess contact material candidates under NEM switch-like conditions, we developed a novel, high-throughput electrical contact screening method based on atomic force microscopy that enables billions of contact cycles to be tested in laboratory timeframes. We compared the performance of self-mated and dissimilar single asperity Pt and Pt_xSi contacts under forces and environments representative of NEM switch operation, and cycled them up to two billion times. The contact resistance increased by up to six decades due to cycling-induced growth of insulating tribopolymer in the case of Pt-Pt contacts, while Pt_xSi exhibited better stability. Additionally, we found that the original conductivity can be largely recovered by sliding of the contact, which essentially leads to the displacement of the tribopolymer. This suggests a route for mitigating contamination-induced failure.

[1] Streller *et al.*, *Adv. Mater. Interfaces*, 1 (2014).

[2] Streller *et al.*, *IEEE Nanotech. Mag.*, 1 (2015).

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