

Wednesday Afternoon, November 2, 2011

Thin Film Division

Room: 109 - Session TF1+EM-WeA

Nonvolatile Memory

Moderator: T. Karabacak, University of Arkansas at Little Rock

2:00pm **TF1+EM-WeA1 Application of Amorphous Zinc Tin Oxide for Memristor Devices**, G.S. Herman, J.S. Rajachidambaram, S. Murali, J. Conley, Oregon State University, S.P. Sanghavi, P. Nachimuthu, V. Shutthanandan, T. Varga, S. Thevuthasan, Pacific Northwest National Laboratory

Amorphous zinc tin oxide semiconductor materials have been studied primarily as the active semiconducting material for thin film transistors with applications including transparent and flexible electronics. Due to the amorphous nature of these materials excellent uniformity can be obtained over a large area, while still having reasonably high electron mobilities ($>10 \text{ cm}^2/\text{Vs}$). Furthermore, considerable control over the electrical properties can be maintained, where insulating, semiconducting, and conductive properties can be obtained by varying the processing conditions. We have recently used sputter-deposited zinc tin oxide as a bipolar switching element in memristor devices. Memristors are a two-terminal nonvolatile data memory device that is very promising for the replacement of silicon-based Flash. A significant benefit is that memristors can be manufactured with high areal densities with potentially low manufacturing costs. A variety of oxide-based materials are being evaluated for memristors, however many of these are nanocrystalline which can lead to non-uniformity of devices. We have found that the switching properties of zinc tin oxide are closely related to the process conditions, the electrical test conditions, and the electrode materials. In this presentation we will discuss the physical and electrical characterization of the zinc tin oxide films and the switching mechanisms for these materials.

2:20pm **TF1+EM-WeA2 PE-MOCVD of GeTe Materials for Phase Change Memory Applications**, E. Despiou-Pujo, L. Dussault, C. Vallée, LTM/CNRS-UJF, France, E. Gourvest, ST Microelectronics, France, D. Jourde, S. Maitrejean, P. Michallon, CEA Leti Minatex Campus, France

Phase-Change Random Access Memories (PCRAM) are very promising candidates for next generation of non-volatile memories. Those devices store information using the high electrical contrast between the amorphous and crystalline phases of chalcogenide alloys such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (also called GST) which are mainly deposited by physical vapor deposition (PVD) [1]. However, two important drawbacks have to be overcome: a too short archival life for GST at high operating temperatures and a too high power consumption. The binary compound GeTe seems to be a promising candidate for high temperature applications since it has an estimated archival life up to ten years at 110°C . A pronounced increase in thermal stability of N- and C-doped GeTe was also demonstrated [2].

Concerning the power consumption, it was shown that a way to reduce the high operating currents is to confine the material. In this way, several groups try to develop a new deposition process to achieve the gap filling of the confined structure. Atomic Layer Deposition (ALD) of GST has shown very good step coverage but the deposition rate remains very low. Therefore, we proposed to study the deposition of GeTe in a shower-head type 200mm plasma-enhanced pulsed liquid injection CVD reactor (AltaCVD200). Ge and Te liquid precursors are introduced into the deposition chamber as vapours through a pulsed injection system and an evaporating furnace. A capacitively-coupled RF plasma is applied between the shower head and the substrate heater to decompose the precursors. Chamber walls are maintained at 70°C to avoid condensation of precursors vapours. The deposition chamber is mounted on a cluster tool which allows quasi *in situ* analysis of the deposited films by angle-resolved XPS while the plasma is analyzed by optical emission spectroscopy (OES).

In this paper, we investigate the optical emission spectra of high pressure (2-20 Torr) Ge- and Te-containing plasmas. Reference UV-visible emission spectra (200-800 nm) are recorded for various conditions of RF power, pressure, and flow rate. The role of electrons and H atoms in the decomposition of Ge and Te precursors is discussed by correlating the OES of the plasma with the chemico-physical properties of the deposited material. It is shown that H atoms induce a competitive effect between deposition (due to the decomposition of the precursors) and etching of Ge and Te atoms at the growing film surface. Role of C contamination in the phase change properties is also discussed and phase transitions of plasma deposited GeTe-C materials are compared with sputtered GeTe-C.

[1] G. W. Burr et al, J. Vac. Soc. Technol. B 2010, 28 (223)

[2] A. Fantini et al, IEDM 2010

2:40pm **TF1+EM-WeA3 Embedded HfO_2 based 1T1R Cells for Future RRAM Applications**, Ch. Wenger, T. Bertaud, Ch. Walczyk, D. Walczyk, M. Malgorzata, IHP, Germany **INVITED**

The integration of various functionality to (Bi)CMOS circuits is in the focus of the "More than Moore" approach. Here, we demonstrate the incorporation of nonvolatile memories (NVM) into the Back end of line (BEOL) of Bi(CMOS) circuits. The added functionalities open new technological possibilities for high value microelectronics systems.

Embedded nonvolatile memories (NVM) with high-density, high-speed, and low-power are attractive for a growing number of applications. One promising candidate for next-generation nonvolatile memories is based on the electrically switchable resistance change between a high (OFF-state) and a low (ON-state) resistive state of a metal-insulator-metal (MIM) structure. This approach is often termed resistance random access memory (RRAM) technologies. Due to the cost effectivity and BEOL compatibility with (Bi)CMOS technologies, this approach is highly attractive. By combining the MIM devices (R) with selection transistors (T), the 1T-1R cells offer good scalability, long retention time, and rapid read/write times. In this letter, the reliable bipolar resistive switching of $\text{TiN}/\text{HfO}_2/\text{Ti}/\text{TiN}$ devices embedded into 1T-1R cells is demonstrated.

The current-voltage (I-V) characteristics of the $\text{TiN}/\text{HfO}_2/\text{Ti}/\text{TiN}$ diodes and 1T-1R cells were studied by DC voltage sweep measurements. By applying a positive voltage at the top electrode, the resistance is reduced for $V > V_{\text{set}}$. The device can be switched back into the OFF-state when a negative voltage is applied beyond V_{reset} . In case of the 1T-1R cell, the forming and set processes can be controlled by changing the gate voltage (V_G) of the select transistor.

4:00pm **TF1+EM-WeA7 Synthesis and Characterization of Multiferroic Oxides by Radical Enhanced Atomic Layer Deposition**, C.D. Pham, J.H. Choi, J.P. Chang, University of California Los Angeles

Multiferroic materials exhibit two or more forms of ferroic order such as (anti)ferroelectricity, (anti)ferromagnetism, ferroelasticity, or ferrotoroidicity. Materials containing both ferroelectricity and ferromagnetism will exhibit some amount of magnetoelectric coupling which is a desirable aspect for the future of non-volatile memory, as these materials could potentially be used for devices that will be written magnetically and read electronically or vice versa, as well as the prospect of four-state memory devices. Materials which exhibit magnetoelectric coupling have been well studied, however, the synthesis methods may not easily translate into large scale integration.

One possible route for synthesis on a commercial scale, atomic layer deposition (ALD) is a thin-film processing technique which involves alternatively flowing non-self reacting precursor vapors or gases onto a substrate. As a result of the self limiting reaction, the precursors only form a single monolayer per cycle. The sequential and self-limiting nature of the deposition is used to deposit thin films with good compositional control, high conformity, high uniformity, and excellent thickness control.

To create multiferroic crystal structures, a 1:1 stoichiometric ratio between cations is desired with low contamination by organic ligands in order to form the crystal phases that permit multiferroicity. Therefore, in this work, multiferroic YMnO_3 and BiFeO_3 on various substrates are synthesized by radical enhanced atomic layer deposition (RE-ALD) using $\text{Y}(\text{tmhd})_3$ ($\text{tmhd} = 2,2,6,6\text{-tetramethylheptane-3,5 dione}$), $\text{Mn}(\text{tmhd})_3$, $\text{Fe}(\text{tmhd})_3$, and $\text{Bi}(\text{tmhd})_3$ as metal precursors and oxygen radicals as the oxidizer. By varying the cycle sequences, controlled composition is demonstrated and verified through XPS. Growth rates are shown on a thickness per cycle basis as a function of deposition temperature, precursor pulse times, and substrate. The crystal structure as well as atomic environment are examined by XRD and extended x-ray absorption fine structure spectroscopy (EXAFS) respectively and are accompanied by TEM micrographs. Finally, magnetic measurements made by a super conducting quantum interference device (SQUID) magnetometer, zero-field cooled and field cooled (ZFC-FC) M vs. T and M vs. H, are shown on 1:1 YMnO_3 stoichiometric films showing a Néel temperature $T_N = \sim 45 \text{ K}$ and a coercive magnetic field $H_C = 130 \text{ Oe}$ for Si(111) and $H_C = 300 \text{ Oe}$ for YSZ(111).

4:20pm **TF1+EM-WeA8 Perpendicular Magnetic Tunnel Junctions based on Thin CoFeB Free Layer and Co-based Multilayer SAF Pinned Layers**, A. Natarajathinam, S. Gupta, University of Alabama

We have previously reported on fully perpendicular Co/Pd multilayers (ML)-based CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJ's)1, 2.

However, Co/Pd ML-based MTJ's have rarely exhibited TMR ratios greater than about 10%. This has been attributed to the inability to pull a sufficiently thick CoFeB layer perpendicular on top of MgO, as well as the incomplete bcc templating of CoFeB from MgO owing to the adjacent fcc Co/Pd ML's³. Recent results³⁻⁷ have generated great interest in MTJ's with pinned perpendicular synthetic antiferromagnets (SAF), of the form AP1/Ru/AP2 where AP1 and AP2 are Co-based multilayers, for instance, Co/Ni or Co/Pd. We report on fully perpendicular MTJ's with a thin CoFeB free layer and a Co/Pd(Pt) ML-based SAF pinned layer. For Co/Pd ML SAF's, strong antiferromagnetic coupling was seen at tRu of 1.1nm, with a coupling strength of 0.017 mJ/m². For Co/Pt ML SAF's the optimum antiferromagnetic coupling was found at slightly higher Ru thickness of 1.3 nm, with a coupling strength of 0.013 mJ/m². Improved MTJ properties are expected from using a thin Ta-seeded CoFeB bottom free layer, along with a thin, amorphous Ta layer used to transition from bcc CoFeB to fcc Co/Pd(Pt) for the top pinned layer⁶. The full stack is of the form: bottom lead/Ta

(2)/CoFeB(1)/MgO(1.6)/CoFeB(0.8)/Ta(0.3)[{Co(0.3/Pd(1))5/Co(0.3) or {Co(0.5)/(Pt(2))5/Co(0.5)/Ru1.1 or 1.3/[Co(0.3/Pd(1) or Co(0.5)/(Pt(2))9/top lead. CIPT measurements indicated TMR values as high as 20% for as-deposited stacks. Magnetometry of blanket stacks showed a large separation in the switching fields of free and pinned layers, with free layer switching close to zero field and pinned layer switching at 0.8-1.8 kOe (Fig.1). This symmetric extended plateau of constant magnetization offers a large dynamic range over which the magnetic configuration remains stable⁷. The stacks were patterned into MTJ's, annealed at 240° C in an in-plane field of 0.5 T, and characterized magnetically and electrically.

Acknowledgements:

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References:

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3. K. Mizunuma et al., Appl. Phys. Lett. **95**, 232516 (2009).
4. H.He et al., IEEE Trans. Magn. **46**, 1327 (2010).
5. D. C. Worledge et al., _Proc. Int'l. Electron. Dev. Mtg. 10-296, (2010).
6. D. C. Worledge et al., Appl. Phys. Lett. **98**, 022501 (2011).
7. J. Sort et al. Appl. Phys. Lett. **83**, 1800 (2003).

4:40pm **TF1+EM-WeA9 Characterizing the Effects of Processing on Materials for Phase Change and Spin Torque based Non-Volatile Memory Technologies**, E.A. Joseph, R.M. Martin, J.S. Washington, D.W. Abraham, S. Raoux, J.L. Jordan-Sweet, IBM T.J. Watson Res. Ctr., D. Miller, IBM Almaden Res. Ctr., H.-Y. Cheng, Macronix International Co., Ltd, Taiwan, R.O.C., M.C. Gaidis, M. Gajek, M. Breitwisch, IBM T.J. Watson Res. Ctr., S.-C. Lai, Macronix International Co., Ltd, Taiwan, R.O.C., Y. Zhu, R. Dasaka, R. Sawant, D. Neumayer, IBM T.J. Watson Res. Ctr., R.M. Shelby, IBM Almaden Res. Ctr., H.-L. Lung, Macronix International Co., Ltd, Taiwan, R.O.C., C.H. Lam, N.C.M. Fuller, IBM T.J. Watson Res. Ctr. **INVITED**

Phase change memory (PCM) and spin-torque magnetic random access memory (ST-MRAM) have recently garnered significant interest for future non-volatile memory applications due to their promise for scalability beyond that of conventional DRAM and flash memory technologies. In addition, both PCM and ST-MRAM have potential to enable improvements in programming speed, low voltage operation and high endurance, as compared to current devices. However, the introduction of each technology not only brings with it new device challenges, but the fabrication process itself can also alter the properties of the materials, leading to performance degradation. In this work, we explore the effects of integration and processing on Ge₂Sb₂Te₅ (GST) and CoFeB for PCM and ST-MRAM devices respectively, with relevance towards scaling to the 14nm node and beyond. Using multiple analysis techniques including time resolved laser reflectivity and X-ray diffraction, we determine that exposure to various etch and ash plasma chemistries can cause a significant reduction in the (re)crystallization speed of GST, while concurrently increasing the transition temperature from the rocksalt to the hexagonal phase. Furthermore, by utilizing optical emission spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) we are able to link the changes in crystallization to etch-induced modification of the GST stoichiometry. For CoFeB materials, vibrating sample magnetometry is used to determine the effect that plasma exposure (as used for both patterning and encapsulation) has on the magnetic moment. We

find that even when relatively thick capping layers are present, magnetic moment can still be significantly degraded. The severity of this effect is heavily dependent on plasma chemistry. Further results of process-induced material modification and device degradation as a function of etch, encapsulation, and thermal processing will be presented, focusing primarily on the impact on scaling of these technologies. Finally, potential integration and processing solutions to circumvent these issues will also be discussed.

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