Thin Film
Room: Ruidoso - Session TF2-TuM

Nonvolatile Memory
Moderator: C. Vallee, Université Joseph Fourier, France

8:00am **TF2-TuM1 MRAM: A Practical Application of Spintronics**, ***D.W. Abraham***, IBM **INVITED**

Magnetic random access memory (MRAM) is a new class of solid state memory which is based on the spin of the electron (as opposed to its charge). This technology is a relative newcomer to the constellation of non-volatile memories, and offers a unique combination of non-volatility, density and speed. I will review the scientific discoveries that enabled the first MRAM chips, and then will discuss several distinct generations of the technology which have evolved in the last decade, including both field-switched and spin-torque-switched devices. Finally I will describe promising new structures which are currently under development which exploit the separation of spin and charge to allow more reliable and lower power operation.

8:40am **TF2-TuM3 Bipolar Resistive Switching Characteristics of HfO_x with Anode-Interface $HfAlO_x$ Layer**, *H.-C. Sohn,* ***J.G. Kim****, H.D. Na, K.-M. Lee, S.-H. Lee*, Yonsei University, Republic of Korea

In this work, we investigated the effect of anode-interface $HfAlO_x$ layer on the resistance switching characteristics of ALD HfO_x films. $HfAlO_x$ on TiN bottom electrode with the thickness and the cycle ratio of HfO_2 and Al_2O_3 was deposited and then HfO_2 thin film was grown by atomic layer deposition (ALD) process. The resistance switching behavior of the $Pt/HfO_2/HfAlO_x/TiN$ MIM stack was characterized in conjunction with physical property such as chemical bonding of HfO_x and $HfAlO_x$. $HfAlO_x$ layer with increasing the ratio of Al_2O_3 improved the endurance, the variance of V_{SET} and V_{RESET}, and the variance of R_{LRS} and R_{HRS}. Also, the resistances of LRS during first RESET processing were decreased with increasing the ratio of Al_2O_3 in $HfAlO_x$ films. X-ray photoemission spectroscopy showed that the cycle ratio of Al_2O_3 in $HfAlO_x$ layer caused an increase of metallic Hf (Hf^0) concentration. It was considered that an increase of metallic Hf (Hf^0) concentration is closely related to the migration of oxygen ions or vacancies at interface between transition metal oxide and TiN electrode, resulting in the enhanced endurance, the current level of LRS and HRS, and the narrowed distribution of $V_{SET\ \&\ RESET}$ and $R_{LRS}\&_{HRS}$.

9:00am **TF2-TuM4 Plasma Treatments of HfO2 Resitive RAM**, ***C. Vallée****, P. Gonon,* Ujf - Ltm, France*, C. Mannequin, T. Chevolleau,* Ltm - Umr 5129 Cnrs, France*, H. Grampeix, N. Rochat, C. Licitra, V. Jousseaume*, CEA-LETI-MINATEC, France

Resistive-switching Random Access Memories (RRAM) have attracted considerable attention in recent years for future non-volatile memory applications. This resistance switching can be based on a modification of the crystalline structure of a material (PCRAM, Phase Changed RAM). One can also exploits the resistive switching properties of some oxides (OxRRAM, Oxide Resistive RAM) which display a change in resistance upon application of a bias voltage. In this case, oxides materials are deposited in a metal-insulator-metal (MIM) structure. In the last years several different oxides have been studied such as metal oxides (NiO, TiO_2, ZrO_2, Cu_xO…) and perovskites ($BaTiO_3$, $SrTiO_3$…) [1]. Hafnium oxide (HfO_2) is among the oxides particularly desirable as far as integration and process compatibility are concerned since it has the advantage of being more mature from a technological point of view.

In this work, HfO_2 RRAM with different thicknesses of HfO_2 films (10 and 20 nm typically) are tested with and without plasma treatment. HfO_2 films are grown at 350°C by atomic layer deposition (ALD) using alternate cycles of H_2O and $HfCl_4$ precursors (1 Torr) on Pt and TiN electrode materials. It is known that oxygen vacancies are playing a critical role for resistive switching. Different solutions have been proposed to modify the oxygen vacancies concentration in the device: integration of a TiO_X/TiO_2 bilayer films [2], doping a ZrO_2 RRAM by metallic ions [3]. Here hydrogen-based plasma treatments are studied. Hence, several different hydrogen-based (NH_3) plasma annealing treatments of the HfO_2 dielectric are carried out in order to study the influence of the oxygen vacancies or defects on the subsequent switching behaviour before the deposition of the top electrode. The MIM structures are then electrically and physically characterized. I(V) curves are then recorded and switching parameters such the SET voltage are compared for MIM devices with and without plasma treatment. It is for example observed that a 1 min NH_3 plasma treatment of HfO_2 deposited on TiN improved the overall switching properties of the RRAM. The modifications of switching properties are correlated to chemical analysis results, mainly Angle-resolved X-ray Photoelectron Spectroscopy, Attenuated Total Reflexion (ATR) and Spectroscopic Ellipsometry (SE) up to 8 eV, with special attention devoted to metal/oxide interface investigations.

[1] A. Sawa, Materials Today **11** (6) (2008) 28

[2] J.J. Yang, et al, Nature Nanotech. **3** (2008) 429

[3] H. Zhang *et al*, Appl. Phys. Lett. **96** (2010) 123502

9:20am **TF2-TuM5 Growth of GeTe Films by MOCVD and PE-MOCVD for Phase Change Memory**, ***E. Gourvest***, STMicroelectronics, France*, C. Vallée,* UJF - LTM, France*, P. Michallon,* CEA-LETI-MINATEC, France*, J. Vitiello,* Altatech Semiconductor, France*, R. Blanc,* CNRS-LTM, France*, D. Jourde,* CEA-LETI-MINATEC, France*, S. Lhostis,* STMicroelectronics, France*, S. Maitrejean*, CEA-LETI-MINATEC, France

Phase-Change Memory (PCM) is one of the promising candidates for next-generation nonvolatile memory thanks to their low cost, low programming voltage and their excellent scalability to the nanoscale cell size [1]. This technology is based on fast and reversible phase change effect in the chalcogenide materials but suffers of the inherent lack of amorphous state stability which affects archival life of the memory cell. This proble is critical for embedded applications where a high retention time at high working temperature is required. In this case, binary compound GeTe material has been shown to be a good candidate since a phase transition temperature higher than the usual $Ge_2Sb_2Te_5$ material has been found and 10 years-fail time at 105°C has been estimated [2]. Moreover the reduction of the current pulse needed to change material from crystal phase to amorphous phase implies the confinement of phase change materials at dimensions below 100 nm [3]. In this case the growth of GeTe materials by chemical vapour deposition (CVD) or Plasma Enhanced CVD is required in order to fill confined structures.

For this purpose, this work investigates the deposition of GeTe materials by a pulsed liquid injection Metal Organic CVD system allowing storing the precursor at ambient temperature. The deposition is made in a 200 mm MOCVD tool that can be assisted by a Low Frequency as well as Radio Frequency plasma. The liquid precursors are injected into a heated evaporator where flash evaporation occurs. A sequential injection leads to a precise control of the deposited material stoichiometry. Furthermore deposition in amorphous or crystalline state is performed by setting the substrate temperature. This chamber is connected to a cluster tool which allows quasi in situ analysis of the deposited films crystalline state by Spectroscopic Ellipsometry (SE) and of the growth mechanisms by angle-resolved X-ray Photoelectron Spectroscopy (ARXPS). Impact of process parameters on the films properties are then evaluated in the MOCVD and PECVD mode. In the case of plasma assistance the impact of the Low to Radio Frequency ratio on the thin film deposition is also studied. Direct informations on Ge/Te ratio and carbon contamination are given by the plasma analysis thanks to optical emission spectrometry. In addition to the chemical and physical properties investigations, the phase change performances and the electrical properties of the deposited materials are evaluated.

[1] S. J. Hudgens, *J. Non-Crys. Solids*, **354**, 2748 (2008)

[2] L. Perniola *et al., IEEE Electron Device Lett.*, **31**, 5 (2010), pp. 488-490.

[3] S. L. Cho *et al*., *Symp. VLSI Tech. Dig.* (2005), p. 96

9:40am **TF2-TuM6 Effects of Halogenated Plasma Chemistries on Degradation of Magnetic Material Properties**, ***R.M. Martin****, D.W. Abraham, E.A. Joseph, Y. Zhang*, IBM T.J. Watson Research Center

Patterning of magnetic materials with plasma processes is an integral step in the fabrication of magnetic devices such as magnetic tunnel junctions (MTJs) for magnetoresistive random access memory (MRAM). Obtaining optimal device performance requires preservation of the magnetic material properties throughout the fabrication process, and thus places limitations on the process window (e.g. temperature, gas chemistry) for patterning devices. Due to this, the use of halogenated plasma chemistries, which are commonly used in reactive ion etching (RIE) processing, must be carefully employed when patterning MTJ devices, as they can significantly degrade magnetic properties during the etch. One method used to minimize magnetic degredation is the incorporation of metallic capping layers which potentially isolate the halogen etch chemistry from the critical magnetic layers. However, the optimal thickness and/or properties of these layers have yet to be fully explored. For example, when a Cl_2 based plasma is exposed to a 300 Å Ru capping layer, the magnetic moment/area of the underlying magnetic free layer is reduced 11% from 1.64 to 1.46×10^{-4}

emu/cm^2. Therefore in this work, the effects of the plasma etch chemistry on magnetic materials is explored using various halogenated chemistries and capping layer materials to understand the mechanisms by which patterning of magnetic devices can be achieved without degradation of magnetic properties.

10:40am **TF2-TuM9 Phase Change Materials for Random Access Memories: Deposition, Characterization and Performance**, ***C. Wiemer***, CNR-IMM, Italy **INVITED**

The optimization of phase change memory devices requires a compromise between reducing element sizes and maintaining data retention and reliability. The down-scaling of the memory cell size can be achieved only by a greater control of film deposition over non-planar structures than so far reached by physical vapor deposition techniques. A reduced cell size would allow lower programming currents, which lead to improved performances and lower costs. Metal organic chemical vapor deposition (MOCVD) is a very attractive method for growing layers because it enables the production of thin films with better conformality and composition control, including doping possibilities, and increased manufacturing throughput compared to sputtering techniques. Therefore, MOCVD is potentially attractive for the deposition of chalcogenide materials for phase change memory devices.

In this presentation recent advances in MOCVD of chalcogenide materials will be presented. Results will cover both the use of hot wire, liquid injection MOCVD and thermal, N2 based, MOCVD. The MOCVD growth is optimized both on flat SiO2/Si and patterned substrates. The deposition of Ge2Sb2Te5layers is achieved by thermal MOCVD thanks to the use of a thin seed layer of germanium. The obtained Ge-Sb-Te alloys exhibit up to 10 phase switching cycles upon laser irradiation. Better performances are achieved so far by hot wire MOCVD where the optical switching behavior is demonstrated to be comparable to the one of sputtered deposited Ge2Sb2Te5films of the same thickness. Moreover, prototype memory cells including Ge2Sb2Te5from hot wire MOCVD show promising performances.

Advances in material characterization will be also discussed. Since the switching of a memory device is driven by Joule heating, the exploration of new chalcogenide materials in terms of electrical performances cannot proceed without the knowledge of the thermal dependence of their fundamental properties, like thermal conductivity, electrical resistivity and crystallographic phase stability. The effect of reducing the cell size on the role played by the properties of the interfaces between the chalcogenide material and the other elements of the memory cell will be discussed. In particular, since most of the work performed in material characterization proceeds on flat, polycrystalline layers, special attention is devoted to the effects of size, preferential orientation and thin interfacial layers on the quantification of thermal and electrical properties as a function of temperature.

11:20am **TF2-TuM11 Bipolar Switching Behaviors in TiN/HfO_2/Pt Systems for Nonvolatile Resistive Memory Applications**, *D.-H. Ko,* ***D.S. Lee***, *Y.H. Sung*, Yonsei University, Republic of Korea

Resistive random access memory devices based on transition metal-oxides (TMO) have been considered as the most promising candidates for the next generation nonvolatile memories because of its simple structures and compositions, low voltage operation and process compatibility with CMOS.

In this presentation, stable bipolar resistive switching behaviors of TiN/HfO2/Pt structures will be discussed for the first time. . The HfO_2 films were grown by reactive stutter at room temperature using O_2 and Ar gas, and the subsequent heat treatment was performed in an ambient of O_2 at 300℃. TiN and Pt layers were used as the top and bottom electrode materials, respectively. For the characterization of stable bipolar resistive switching, current-voltage measurements were used in compliance with 1 mA. Excellent memory characteristics including low set/ reset voltages and long retention time were demonstrated without additional electroforming process. The bipolar resistive switching behavior can be explained by the formation of conductive path consisting of oxygen vacancies. We analyzed a composition and chemical bonding of HfO_2 by x-ray photoelectron spectroscopy. In addition, microstructures of the films were analyzed by transmission electron microscopy.

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