ALD Applications
Room On Demand - Session AA11

Memory Applications: Other Non-Volatile Memories (MRAM, FeRAM, Phase Change,...)

AA11-1 Fabrication of Vertical-Type Phase-Change Memory Leveraging Atomic Layer Deposition, ***Jeong Woo Jeon***, *C. Yoo, E. Park, W. Kim, W. Choi, B. Park,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

Storage Class Memory (SCM) is a new hybrid storage/memory tier to achieve high speed, low power computing using a nonvolatile and byte-accessible memory denser than DRAM and faster and more durable than flash memory.[1] Intel and Micron Technology recently commercialized the SCM using chalcogenide-based phase-change memory (PCM) that utilizes resistance contrast between the amorphous and crystalline states for data storage. It has stacked memory cell arrays that alternately share either wordlines or bitlines between the different memory layers. This structure inevitably requires lithography and patterning steps proportional to the number of layers, resulting in high production costs. For the commercial success of PCM-based SCMs, it is important to achieve high density and low cost per bit, which requires the development of a novel three-dimensional (3-D) architecture similar to the 3-D vertical-NAND device.

This report demonstrates the vertical-type PCM (V-PCM) enabled by atomic layer deposition (ALD) of $Ge_2Sb_2Te_5$ (GST-225), as shown in Fig. 1.[2] SiO_2 was used for interlayer dielectric (ILD) separating each memory layer, and TiN was used for the bottom electrode (BE). Fig. 1(b) shows an ALD GST-225 films conformally grown on vertically etched sidewalls, in which ILD and BE are alternately stacked. The switching region is defined by the patterned width and thickness of the BE, equivalent to the structure of a mushroom type cell vertically erected. In this work, the contact area was as high as 0.02 mm^2 due to the limited lithography capability of university scale research. The electrical characteristics of the fabricated device can be seen in Fig. 2. The SET and RESET characteristics of the V-PCM device are shown with a threshold voltage of 1.4 V and a RESET current of 4 mA, which corresponds to a RESET current density of 20 MA/cm^2. The cyclic endurance was more than 10^8 cycles, which is sufficiently high compared with the planar type PCM devices, showing the feasibility of the ultra-high density V-PCM.

References

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AA11-2 Effect of Ti Scavenging Layer on Ferroelectricity of $Hf_xZr_{1-x}O_2$ Thin Films Fabricated by Atomic Layer Deposition using Hf/Zr Cocktail Precursor, ***Takashi Onaya,*** Meiji University/National Institute for Materials Science/JSPS Research Fellow, Japan*; T. Nabatame,* National Institute for Materials Science, Japan*; N. Sawamoto,* Meiji Renewable Energy Laboratory, Japan*; A. Ohi, N. Ikeda, T. Nagata,* National Institute for Materials Science, Japan*; A. Ogura,* Meiji University/Meiji Renewable Energy Laboratory, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) films have attracted a lot of attention for ferroelectric field-effect transistor (FeFET) applications. Numerous papers have reported that an annealing process at > 300°C is required to obtain the ferroelectric orthorhombic (O) phase. [1] However, an interlayer such as SiO_x between an HZO film and a Si substrate was typically formed during the fabrication process of metal-ferroelectric-semiconductor (MFS) structures and an annealing process. To understand how the fabrication process affects the interlayer formation is important because the interlayer can cause reliability problem and reduction in remanent polarization ($2P_r$). We employed a Ti layer deposited on an HZO film because Ti can scavenge oxygen from a SiO_x interlayer. [2] In this work, we studied the effect of an annealing temperature on the interlayer formation and ferroelectricity of HZO-based MFS capacitors with a Ti layer.

A 10-nm-thick HZO film was deposited on a p^+-Si substrate by atomic layer deposition at 300°C using (Hf/Zr)$[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor and H_2O gas. Next, a 1-nm-thick Ti layer was deposited on an HZO film by DC sputtering. A 100-nm-thick TiN top-electrode was then fabricated by DC sputtering. Finally, a post-metallization annealing (PMA) was performed at 300 or 400°C for 1 min in N_2 ambient. TiN/HZO/p^+-Si capacitors were also fabricated as references.

For the MFS capacitor without a Ti layer, the SiO_x interlayer could be formed between an HZO film and a Si substrate after the PMA at 400°C while the formation of the interlayer was found to be negligible, evaluated by X-ray photoelectron spectroscopy. The 300°C-PMA-treated MFS capacitors showed almost the same capacitance (C) of 0.8 $\mu F/cm^2$ regardless of the presence of a Ti layer. After the PMA at 400°C, on the other hand, the higher C was obtained because HZO films were crystallized with the ferroelectric O phase. Moreover, the MFS capacitors with a Ti layer exhibited slightly higher C of 1.5 $\mu F/cm^2$ than that (1.3 $\mu F/cm^2$) without a Ti layer. This might be attributed to the reduction of the interfacial SiO_x layer due to the scavenging effect of a Ti layer. [2] Therefore, the higher $2P_r$ value (33 $\mu C/cm^2$) of the MFS capacitor with a Ti layer was achieved compared to that (26 $\mu C/cm^2$) without a Ti layer. Based on these results, inserting a Ti layer could be one of the pathways to improve ferroelectricity of HZO films in MFS structures.

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AA11-3 Atomic Layer Deposition of Antiferroelectric La-Doped $Hf_{0.5}Zr_{0.5}O_2$ Thin Film and Its Electrical Behaviors, ***Yong Chan Jung***, *J. Kim, S. Hwang, J. Mohan, H. Hernendez-Arriaga,* University of Texas at Dallas*; W. Maeng, K. Im,* SK hynix Inc, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

Recently, the ferroelectricity and antiferroelectricity of doped Hf-based fluorite-structured ferroelectric thin films have been extensively investigated. In particular, it has been reported that La-doping for $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films can be applied to stabilize the ferroelectric orthorhombic (O) phase ($Pca2_1$) if the low doping concentration is precisely controlled.[1] On the other hand, ferroelectric-antiferroelectric transition is shown when the amount of La doping is relatively large due to its amorphizing characteristic for HfO_2,i.e. increase of crystallization temperature.[2] For the antiferroelectricity of HZO, it is known as the nonpolar tetragonal ($P4_2/nmc$) is contributed, however, it is less clear than the ferroelectric O phase.

In this study, we investigated the doping effects of La on the antiferroelectric properties of the HZO film. The HZO film as a reference was deposited on the TiN bottom electrode by atomic layer deposition (ALD) using TDMA-Hf, TDMA-Zr, and O_3 as the precursors of Hf, Zr, and oxidant, respectively. To dope the HZO film with La, La(^{i}PrfAMD)$_3$ and O_3 were used as the La precursor and oxygen source, respectively. The 10-nm thick La-doped HZO film (LHZO) growth was proceeded with 6 super cycles consisting of 8 (Hf-purge-O_3-purge-Zr-purge-O_3-purge) and 1 (La(^{i}PrfAMD)$_3$-purge-O_3-purge). In Figure 1, the Hf, Zr, and La concentration of the LHZO film is 48, 48, and 4 at. % as confirmed by XPS depth profiling. After the TiN top electrode was deposited on HZO and LHZO films, rapid thermal annealing was done, and metal-insulator-metal capacitors were fabricated using a Pd/Au hard mask and wet etch process.

In Figure 2(a) and 2(b), the small-signal dielectric constant of LHZO film at 0 MV/cm was increased to 69 compared to 48 of HZO film and the leakage current density of LHZO film at 1 MV/cm was approximately 2 order magnitude lower than HZO film, respectively. We suspected that the higher dielectric constant and lower leakage current is caused by tetragonal phase in the LHZO film. In Figure 3(a), the ferroelectric-antiferroelectric transition of the LHZO film was proved by the polarization-electric field curves, the remnant polarization ($2P_r$) of HZO and LHZO devices is 56 and 5 $\mu C/cm^2$, respectively. As shown in Figure 3(b), interestingly, after 10^8 and 10^9 endurance cycling, the $2P_r$ of the LHZO film is recovered to 13 and 26 $\mu C/cm^2$, respectively. It is plausible to suggest that this phenomenon is occurred due to the field-induced ferroelectric phase transition[3] or the effect of domain unpinning after longer switching cycles with high electric field (2.5 MV/cm).

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AA11-4 Metal-insulator Transition in ALD VO_2 using VCl_4 and H_2O as Precursors, ***Jeya Prakash Ganesan***, *D. Dev, A. Krishnaprasad,* University of Central Florida*; D. Moser, R. Kanjolia,* EMD Electronics*; T. Roy,* Nanoscience Technology Center, University of Central Florida*; P. Banerjee,* University of Central Florida

Vanadium dioxide (VO_2) undergoes a reversible transition between the semiconducting (monoclinic) and metallic (tetragonal) state at 68 °C, thus making VO_2 a perfect candidate for electrical/optical switches, thermal

sensors, metamaterials, and oscillators. Atomic Layer Deposition (ALD) of VO_2 has been reported with different metalorganic and halide-based vanadium precursors. Out of these, the halide-based precursors have the advantage of a simpler chemistry, high vapor pressure and ease of delivery, little or no potential carbon residue and use of milder oxidants such as, H_2O.

In this talk, we demonstrate the ALD of VO_2 using VCl_4 and H_2O in a VEECO® FIJI Gen2 ALD system. The as-deposited films are amorphous and turn crystalline VO_2 only after a post-deposition anneal at 550 °C, 60-minute using forming gas. Raman spectroscopy is used to confirm the amorphous nature of the film pre-anneal, and its conversion to monoclinic VO_2 post-anneal. X-ray photoelectron spectroscopy suggests that the as-deposited film and the annealed film show vanadium oxides with mixed valence states on the surface and VO_2 in the bulk. Thus, despite using a V^{4+} precursor significant surface oxidation takes place during deposition to produce a multivalent oxygen-rich surface. The excess surface oxygen could result in an amorphous film. Temperature-dependent Raman spectroscopy and ellipsometric studies reveal the semiconducting to metallic transition (SMT) of annealed and crystallized VO_2 thin film. The transition temperature is recorded at 68 °C for a 30 nm film. Optical constants (*n, k*) from ellipsometry suggests that beyond 68 °C, significant free carrier absorption in the near infrared results in higher *k*. Electrical measurements performed on a fabricated device showed SMT behavior at 68 °C with a resistance high (semiconducting) : low (metallic) ratio of 66.

In conclusion, we have deposited 30 nm VO_2 via ALD using VCl_4 and H_2O at 350 °C. Contrary to a past report,[1] the VO_2 deposited in the current work is amorphous and must be annealed at 550 °C for 60 minutes in forming gas to obtain VO_2 films with SMT properties. Experimental investigations are currently underway to understand the synthesis-structure-property relationship in this promising ALD chemistry such that as-deposited, crystalline VO_2 films can be reliably obtained.

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