

Characterization of Silver Saturated-Ge₄₅Te₅₅ Solid Electrolyte Films Incorporated by Nitrogen for Programmable Metallization Cell Memory Device

Soo-Jin Lee and Soon-Gil Yoon^a

*Department of Nano information Systems Engineering, Chungnam National University,
220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea*

Sung-Min Yoon and Byoung-Gon Yu

*Basic Research Laboratory, Electronics & Telecommunications Research Institute(ETRI),
161 Gajeong-dong, Yuseong-gu, Daejeon 305-350, Korea*

^aE-mail : sgyoon@cnu.ac.kr

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The crystallization temperature in GeTe solid electrolyte films was improved by in situ-nitrogen doping by rf magnetron co-sputtering technique at room temperature. The crystallization temperature of 250 °C in electrolyte films without nitrogen doping increased by approximately 300 °C, 350 °C, and above 400 °C in films deposited with nitrogen/argon flow ratios of 10, 20, and 30 %, respectively. A PMC memory device with Ge₄₅Te₅₅ solid electrolytes deposited with nitrogen/argon flow ratios of 20 % shows reproducible memory switching characteristics based on resistive switching at threshold voltage of 1.2 V with high R_{off}/R_{on} ratios. Nitrogen doping into the silver saturated GeTe electrolyte films improves the crystallization temperature of electrolyte films and does not appear to have a negative impact on the switching characteristics of PMC memory devices.

Keywords : PMC-ReRAM, Chalcogenide, Solid electrolyte

1. INTRODUCTION

Many different emerging memory technologies such as ferroelectric random access memory(FeRAM), magnetic RAM(MRAM), and phase change RAM (PRAM) are investigated especially with respect to their inherent technical limits, such as scalability potential, switching power, non-volatility, and reliability concerns [1]. Programmable metallization cell(PMC) memory, which utilizes electrochemical control of nanoscale quantities of metal in thin films of solid electrolyte, shows great promise as a future solid state memory[2,3]. The introduction of silver into chalcogenide glasses causes substantial changes in the electrical properties of the material, decreasing the resistivity by many orders of magnitude[4]. PMC has also unique low-voltage and low-energy operational characteristics and could be compatible with CMOS(Complementary Metal-Oxide-Semiconductor) processes. The solid electrolyte for PMC memory, well known as chalcogenide materials, was mostly silver doped Ge-Se ternaries[5,6]. It has been known since the mid 1960s that silver can be

photodissolved in chalcogenide glasses to form materials with interesting technological properties[7]. The silver incorporation into the Ge-Se chalcogenide films[5,6] and Ge-S films[8,10] was performed using a photodiffusion. Alloying Ag with the Ge-Se glass leads to formation of a solid-state layer in which a significant portion of the silver ions are relatively mobile at room temperature. In this work, a saturation of silver in GeTe glasses was performed by an in situ deposition of silver films by an rf sputtering on GeTe layers. However, silver doped-GeTe solid electrolytes have a low crystallization temperature of about 250 °C[11]. For PMC applications, silver saturated-GeTe electrolytes should survive at temperatures above 350 °C because back-end-of line flow in semiconductor device processing is performed above 350 °C. The crystallization temperature above 350 °C in GeTe films is required for PMC device applications.

Incorporation of nitrogen into Ge-Te films was performed at the same time as the deposition of GeTe glasses at room temperature using a magnetron co-sputtering technique. The diffusion of silver into the Ge-

Te-N chalcogenide glasses was performed through the in-situ deposition of silver by rf sputtering on GeTeN alloys. The crystallization temperature of the GeTeN alloys as a function of nitrogen concentration was investigated using the relationship between resistance and temperature. The switching characteristics of PMC memory devices with a device diameter of 0.5 μm were also investigated as a function of nitrogen incorporation in Ag doped-GeTe electrolytes.

2. EXPERIMENTAL

The PMC structure is typically comprised of a bottom inert electrode of TiW, the solid electrolyte, a Ag anode, and a W top electrode. The electrodes are separated by dielectric and a through hole or via in this insulating layer defines the electrolyte area that contacts the bottom electrode. The schematic diagram of the PMCM devices used in this study was reported in an earlier study[12]. The device diameter, D , of 0.5 μm exhibits an active device area and the consequent resistance reduction will occur in the region of the electrolyte between the electrodes. The 200 nm thick-chalcogenide $\text{Ge}_{45}\text{Te}_{55}\text{N}$ films were deposited in 0.5 μm trench structure as a function of Ar/N_2 ratio at room temperature by rf magnetron co-sputtering with 2 inch diameter Ge and Te targets followed by the deposition of about a 300 nm thick-Ag anode. A 100 nm thick-W electrode was deposited on the silver layers. The composition of the chalcogenide films deposited on the planar SiO_2/Si substrates was investigated by means of an electron probe micro-analyser (EPMA) and nitrogen incorporation into Ge and Te films was identified by Auger electron spectroscopy (AES). An in situ diffusion of silver into Ge and Te films was investigated by secondary ion mass spectroscopy (SIMS). The complete crystallization of nitrated GeTe films as a function of annealing temperature was investigated by x-ray diffraction (XRD). The electrical properties of the devices were measured by connecting the electrodes, via tungsten probes held in micromanipulators in a vibration and electromagnetic interference-isolated probe station, to a semiconductor parameter analyzer (Agilent, HP 4145 B). Voltage double-sweeps were carried out starting at the maximum reverse bias (TiW bottom electrode: positive, W top electrode: negative), sweeping through zero to an appropriate forward voltage (TiW bottom electrode: negative, W top electrode: positive), and sweeping back again through zero to the reverse bias starting point. The relationship between sheet resistance and temperature in nitrated Ag-GeTe solid electrolytes was investigated with a Keithley 2400 electrometer using four-point probe method.

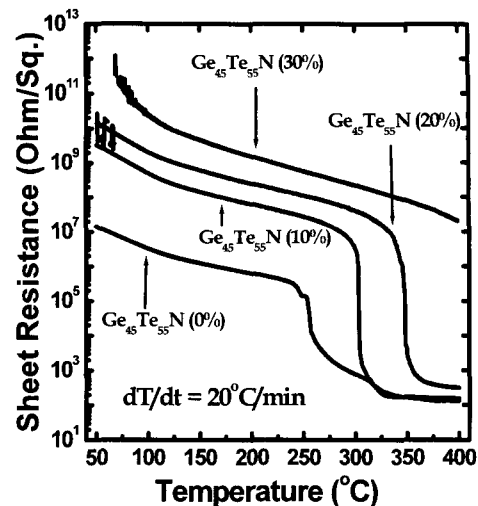


Fig. 1. A relationship between the sheet resistance and temperature in GeTe films deposited with various N_2/Ar ratios.

3. RESULTS AND DISCUSSION

Study for crystallization in GeTe electrolytes doped by nitrogen is important for survival of the PMC devices in back-end-of line flow at 350 $^{\circ}\text{C}$. The identification of the crystallization temperature in GeTe glasses doped with nitrogen was determined by measuring the variation in sheet resistance as a function of temperature. Figure 1 shows the relationship between the sheet resistance and temperature in GeTe films doped by various N_2/Ar ratios. The rate of change of temperature was approximately 20 $^{\circ}\text{C}/\text{min}$. As shown in Fig. 1, the temperature at which there is a drop in resistance in GeTe films increases with increasing nitrogen concentration in the films.

An abrupt variation of resistance at specific temperatures means a crystallization of the GeTe films. The GeTe films without nitrogen doping showed a crystallization temperature of about 250 $^{\circ}\text{C}$. On the other hand, an increase of nitrogen doping concentrations exhibits an increase of crystallization temperature in GeTe films. Films deposited at N_2/Ar ratios of 10 and 20 % exhibit a crystallization temperature of approximately 300 and 350 $^{\circ}\text{C}$, respectively. However, crystallization temperatures in films deposited with N_2/Ar ratios of 30 % were not confirmed because the equipment was limited up to ≤ 400 $^{\circ}\text{C}$. Crystallization of the films deposited with various N_2/Ar ratios was also identified by x-ray diffraction (XRD) measurement.

Figure 2 shows XRD patterns of GeTe films annealed at various temperatures without and with nitrogen doping concentrations of 10 %, 20 %, and 30 %. As shown in Fig. 2(a), samples without nitrogen doping showed weak GeTe peaks from 300 $^{\circ}\text{C}$ and the films doped at 10 % and 20 % clearly exhibit crystallization

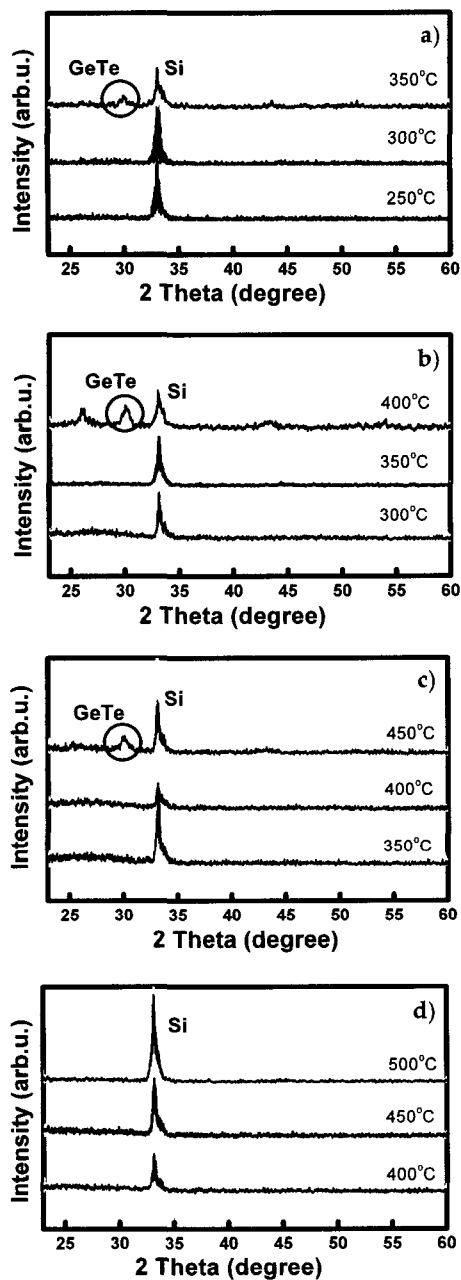


Fig. 2. G XRD patterns of GeTe solid electrolyte films annealed at various temperatures. (Films are deposited without (a) and with nitrogen/argon flow ratios of (b) 10 %, (c) 20 %, and (d) 30 %.

peaks at 400 °C and 450 °C, respectively. On the other hand, films doped by N₂/Ar ratios of 30 % did not show typical peaks exhibiting GeTe phases in samples annealed at 450 °C. This suggests that the films deposited by nitrogen/argon flow ratio above 20 % can survive at temperatures of back-end-of line flow in semiconductor device process.

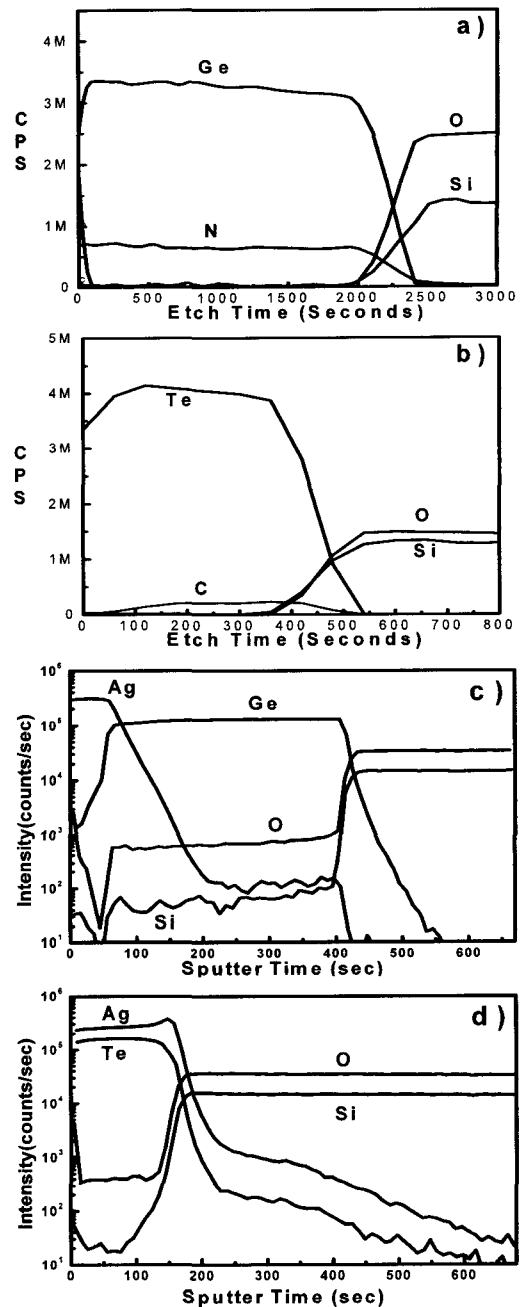


Fig. 3. Nitrogen depth-profiles in situ incorporated into (a) Ge and (b) Te films by Auger electron spectroscopy (AES) and Ag depth-profiles in situ incorporated into (c) Ge and (d) Te films by secondary ion mass spectroscopy (SIMS).

Figure 3 shows elemental depth-profiles by Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) exhibiting an in situ-incorporation of N and Ag into Ge and Te films. As shown in AES depth-profiles of Figs. 3(a) and 3(b), elemental nitrogen

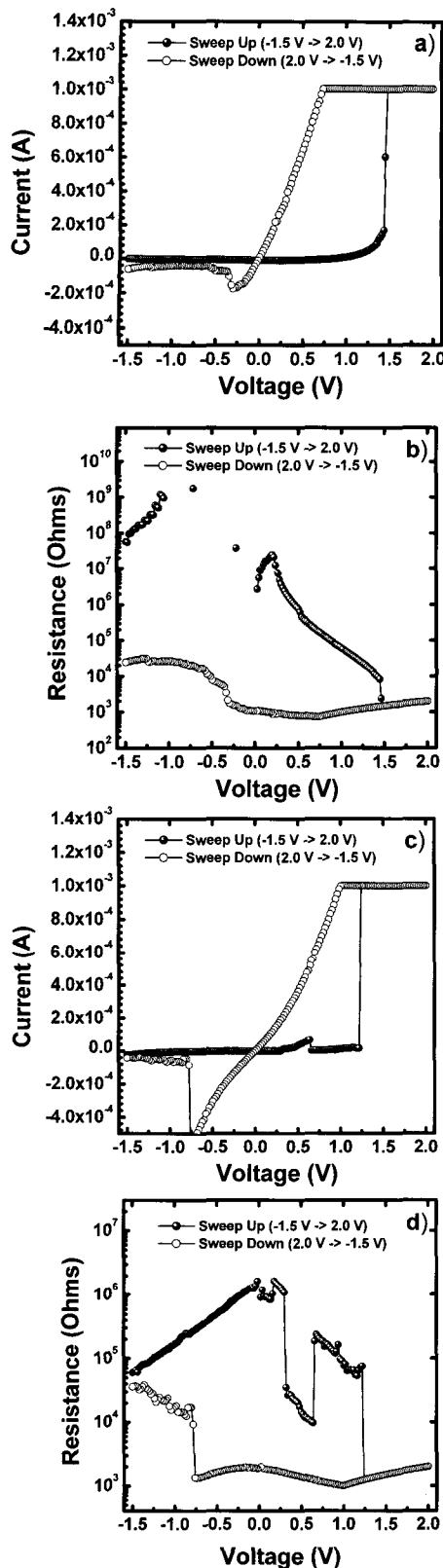


Fig. 4. Typical current-voltage and resistance-voltage plots for one cycle (a,b) and for 5 cycles (c,d) in a 0.5 μm diameter PMC device with a 200 nm thick-silver-rich $\text{Ge}_{45}\text{Te}_{55}$ solid electrolyte films deposited with nitrogen/argon flow ratios of 20 %.

is only incorporated into the Ge lattice and it was not found within the Te lattice. It is important to understand the origin that the nitrogen incorporated into the GeTe glasses increases the crystallization temperature of GeTe glasses. When GeTe transforms from amorphous to crystalline, the tetrahedral coordination of Ge for amorphous GeTe is changed to a rhombohedral (distorted rocksalt) structure for crystalline GeTe[13]. Upon crystallization, Ge atoms move from tetrahedral to octahedral sites. Nitrogen incorporated into GeTe amorphous phases can play a role of bottleneck for Ge movement because nitrogen is related with Ge lattice as shown in AES data. In the result, nitrogen incorporation into the GeTe glasses increases the crystallization temperature of silver-doped GeTe solid electrolytes. On the other hand, from the SIMS depth-profiles (see Figs. 3(c) and 3(d)) of elemental silver in Ge and Te layers, silver was completely incorporated into the Te lattice and it was not incorporated into the Ge lattice. From the results, silver and nitrogen were considered to be related with Te and Ge lattices, respectively, equally in case of GeTe alloy films. This result suggests that the nitrogen incorporated into the GeTe layers to increase the crystallization temperature of silver-doped GeTe electrolyte films does not play an important bottleneck for the movement of silver during switching of the PMC devices.

Figure 4 shows typical current-voltage plots for one cycle and for 5 cycles in a 0.5 μm diameter PMC device with a 200 nm thick-silver-rich $\text{Ge}_{45}\text{Te}_{55}$ electrolyte films without and with nitrogen doping by N_2/Ar ratios of 20 %. The programming current limit was 1mA and the voltage sweep in both one and 5 cycles was -1.5 V to +2.0 V to -1.5 V. As shown in Figs. 4(a) and 4(b) of devices without nitrogen doping, the device swept for one cycle shows a threshold voltage of about 1.0 V and after 5 cycles, a threshold voltage of device was decreased by 0.5 V. On the other hand, devices with nitrogen doping showed variation in threshold voltage from 1.5 V to 1.2 V.

The higher write threshold voltage in devices with nitrogen doping than the PMC devices without nitrogen doping was attributed to the higher bandgap of the electrolyte films with the introduction of the nitrogen. The reduction in threshold voltage with sweep number in PMC devices with and without nitrogen doping suggests that the electrolyte films could be becoming more saturated with Ag during cycling.

Figures 5(a) and 5(b) show the variation in the resistance in PMC devices including GeTe electrolyte films doped by 20 % nitrogen as a function of positive pulse and negative pulse voltage, respectively, under the condition of a pulse width of 1 μsec . As shown in Fig. 5(a), the resistance of the device abruptly changes from $\sim 10^7$ Ohm to $\sim 10^3$ Ohm at a pulse voltage of + 0.7 V. On the other hand, at a pulse voltage of -2.5 V, the resistance changes abruptly as shown in Fig. 5(b). This exhibits the conditions for the endurance testing of PMC

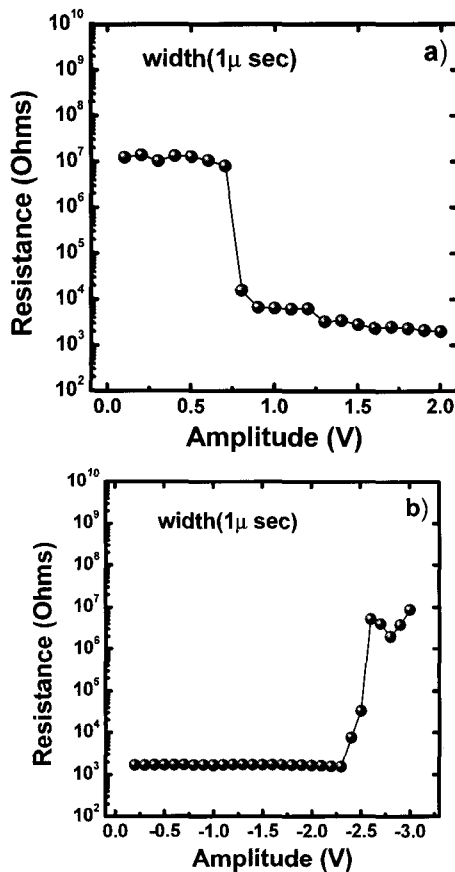


Fig. 5. The variation in the resistance in PMC devices including GeTe electrolyte films deposited by nitrogen/argon flow ratio of 20 % as a function of (a) positive pulse and (b) negative pulse voltage under the condition of a pulse width of 1 μ sec.

devices at room temperature. Conditions for switching in PMC devices are the application of a pulse voltage larger than the threshold voltage.

The pulse conditions for the switching test in PMC device with 20 % nitrogen doping are depicted in the inset of Fig. 6. Trains of positive (write) pulses of 1.5 V in magnitude and 1 μ sec duration is followed by -2.5 V negative (erase) pulses and 1 μ sec duration. The endurance characteristics of PMC device under this pulse condition are shown in Fig. 6. The relationship between resistance and switching cycles aids in maintaining good sweep characteristics up to 100 switching cycles. The endurance test was performed manually up to 100 cycles. This means that PMC devices with Ag saturated-GeTe electrolytes doped by 20 % nitrogen can reliably operate with good sweep characteristics. As a result, in this work, nitrogen doping into the silver saturated GeTe electrolyte films improves the crystallization temperature of electrolyte films and does not have a negative impact on the switching

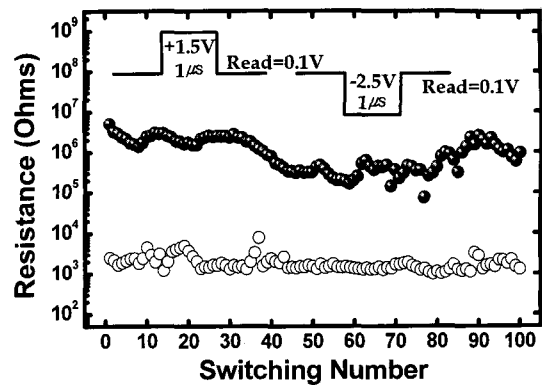


Fig. 6. The endurance characteristics of PMC devices including GeTe electrolyte films deposited by nitrogen/argon flow ratio of 20 % under pulse conditions. (Inset shows the pulse conditions for the switching test in PMC devices).

characteristics of PMC memory devices.

4. CONCLUSION

The crystallization temperature in GeTe solid electrolyte films was improved by an in situ-nitrogen doping by rf magnetron co-sputtering technique. The crystallization temperature of 250 $^{\circ}$ C in electrolyte films without nitrogen doping increases above 400 $^{\circ}$ C in films deposited with nitrogen/argon flow ratios of 30 %. A PMC memory device with Ge₄₅Te₅₅ solid electrolytes deposited with nitrogen/argon flow ratios of 20 % shows reproducible memory switching characteristics based on resistive switching at threshold voltage of 1.2 V with high R_{off}/R_{on} ratios. Nitrogen doping into the silver saturated GeTe electrolyte films improves the crystallization temperature of electrolyte films and maintains acceptable switching characteristics of PMC memory devices.

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