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GeSbTe deposition for the PRAM application

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Abstract

GeSbTe (GST) chalcogenide thin films for the phase-change random access memory (PRAM) were deposited by an atomic layer deposition (ALD) process. New precursors for GST thin films made with an ALD process were synthesized. Among the synthesized precursors, $Ge(N(CH_3)_2)_4$, $Sb(N(CH_3)_2)_4$, and $Te(i\text{-}Pr)_2$ (i-Pr = *iso*-propyl) were selected. Using the above precursors, GST thin films were deposited using an H_2 plasma-assisted ALD process. Film resistivity abruptly changed after an N_2 annealing process above a temperature of 350 °C. Cross-sectional scanning electron microscope (SEM) photographs of the GST films on the patterned substrate with aspect ratio of 7 shows that the step coverage is about 90%.

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1. Introduction

Phase-change memories are receiving much interest as next generation non-volatile memory technology, due to their high speed and easy integration process [1,2]. Memory operation depends on the ability of chalcogenide materials to modify their structure from amorphous to crystalline and vice versa, and on a high dependence of chalcogenide resistance on the phase state.

In particular, a high resistance state is achieved with a large current pulse, raising the chalcogenide temperature above the melting point. The melted chalcogenide quenches into a glass state along with the abrupt fall of the reset pulse. A low resistance state is recovered with a small current, heating the glass and activating the nucleation and growth of the crystalline phase. Reset currents in the range of 0.5–1.5 mA have been reported with set currents in the same order of magnitude.

To minimize the reset/set currents, the cell structure has to be optimized by accurate device engineering. The optimized cell structure must be three-dimensional structures [3], where the chalcogenide materials are filled into a hole-type structure (contact hole).

Since depositing particles in a conventional magnetron sputtering deposition has an isotropic directionality, the step coverage which is defined to be the thickness ratio of films at the bottom of the contact hole over those on the flat surface is decreased by increasing of the aspect ratio of the contact hole.

However, in an ALD process, excellent step coverage of 100% for both the side/bottom and side/top sections of the contact hole with a high aspect ratio of 10:1 can be confirmed due to the complete surface reaction limited mechanism, which limits the deposition rate in the ALD process. Therefore, to obtain the above structure, chalcogenide materials must be processed by an atomic layer deposition (ALD) where as chemical vapor deposition (CVD) or sputtering methods cannot be applied to a small hole that may be below 50 nm in diameter.

In this study GeSbTe (GST) films were deposited by an ALD method. In order to deposit GST thin films, Ge, Sb, and Te precursors were synthesized and the ALD process was also modified with H_2 plasma-assisted method. The phase transition properties of GST films were characterized by X-ray diffraction (XRD) methods. After deposition, scanning electron microscope (SEM), atomic force microscope (AFM) and transmission electron microscope (TEM) were used to obtain cross-sectional image and surface morphology of GST films, respectively.

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2. Experimental details

2.1. Precursor synthesis

Standard schlenk techniques [4], vacuum and nitrogen filled glove box system were used in handling the starting material and complexes. Toluene was dried over sodium and distilled immediately prior to use. Several precursors such as tetramethylgermanium, bis(isopropyl tellurium), and tri(dimethylamino)antimony [5] were commercially available. New germanium, antimony and tellurium organometallic sources were synthesized according to the method below. "^{1}H and ^{13}C" nuclear magnetic resonance (NMR) spectra were provided by a Bruker Instrument 400 MHz spectrometer. Pyrolysis-gas chromatography mass spectra (GCMS) were performed. The result of pyrolysis-GCMS was obtained using Aglient 6890/5973 with frontier lab VA-5 capillary column.

2.1.1. Tetra(dimethylamino)germanium $Ge(N(CH_3)_2)_4$

$GeCl_4$ was dissolved in dried ether and was slowly dropped in the cold solution. The mixture was refluxed and stirred for 20 h and then cooled. All the volatile components were removed in a vacuum below 5 °C. $Ge(NSi(CH_3)_2)_4$ was purified with vacuum distillation at room temperature. The yield was 59% based on $GeCl_4$. FW: 248.89, mp 14 °C, bp 92 °C/16 Torr, ^{1}H NMR (300 MHz, C_6D_6): 2.65 (s, $-CH_3$, 24H), ^{13}C NMR (300 MHz, C_6D_6): 40.40 ($-CH_3$).

2.1.2. Tri(dimethylamino)antimony $Sb(N(CH_3)_2)_3$

$SbCl_3$ was dissolved in dried toluene and dimethylamine in gas was slowly bubbled into the solution. The mixture was refluxed and stirred for 20 h and then cooled. All the volatile components were removed in a vacuum. $Sb(N(CH_3)_2)_3$ was purified with vacuum distillation. The yield was 60% based on $SbCl_3$. FW: 235.99, mp 10 °C, bp 60 °C/10^{-1} Torr, ^{1}H NMR (400 MHz, C_6D_6): 2.76 (s, 72H), ^{13}C NMR (400 MHz, C_6D_6): 8.41 (s, 4C).

2.1.3. Tetra(hexamethyldisilyamino)germanium $Ge(N(Si(CH_3)_3)_2)_4$

$GeCl_4$ was dissolved in dried toluene and lithium bis(trimethylsilyl)amide was slowly dropped into the solution. The mixture was refluxed for 20 h by stirring and cooling. Then the entire volatile components were removed in a vacuum. $Ge(N(Si(CH_3)_3)_2)_4$ was purified with vacuum distillation. The yield was 62% based on $GeCl_4$. FW: 714.17, white crystal and liquid, moisture sensitive, mp 30 °C, bp 60 °C/10^{-1} Torr, ^{1}H NMR (400 MHz, C_6D_6): 0.360 (s, 72H), ^{13}C NMR (400 MHz, C_6D_6): 4.315 (s, 24C).

2.1.4. Tri(hexamethyldisilyamino)antimony $Sb(N(Si(CH_3)_3)_2)_3$

$SbCl_3$ was dissolved in dried toluene and lithium bis(trimethylsilyl)amide was slowly dropped in the solution. The mixture was refluxed and stirred for 20 h and then cooled. All the volatile components were removed in vacuum. $Sb(N(Si(CH_3)_3)_2)_3$ was purified by vacuum distillation. The yield was 60% based on $SbCl_3$. FW: 602.92, bright yellow liquid, moisture sensitive, bp 80 °C/10^{-1} Torr, ^{1}H NMR (400 MHz, C_6D_6): 0.293 (s, 72H), ^{13}C NMR (400 MHz, C_6D_6): 6.183 (s, 24C).

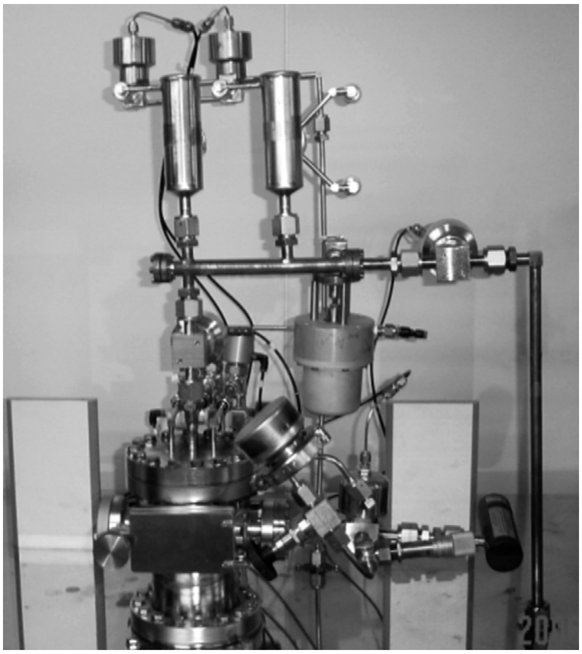

Fig. 1. The experimental plasma enhanced atomic layer deposition system.

2.2. Atomic layer deposition process

Because of both the different vaporization temperature of Ge, Sb, and Te precursors and the different process temperature windows for Ge, Sb, and Te precursors, we developed a nozzle-type vaporizer and a plasma-assisted atomic layer deposition process. GST thin films were deposited on 100 nm thick SiO_2/Si wafers at the deposition temperature of 200–350 °C. Newly synthesized precursors were used as GST precursors and liquid state Ge and Sb precursors were changed into a vapor state through a newly designed vaporizer at the vaporization temperature of 120 °C with a carrier gas flow rate of 300 sccm and the Te precursors were vaporized through a bubbling method at room temperature with a carrier gas flow rate of 100 sccm due to its high vapor pressure.

To prevent the condensation of vaporized precursors in the feeding line, the line was heated to 120 °C. Each precursor deposition cycle for the Ge, Sb, and Te process was composed of four consecutive pulses: (i) a pulse of precursor vapor, (ii) a purge pulse, (iii) a pulse for exposure to H_2 plasma, and (iv)

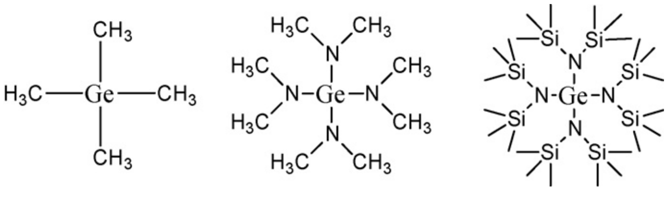

Fig. 2. Structure of Ge organometallic precursors.