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Atomic Layer Deposition of Germanium Antimony Telluride Thin Films

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ABSTRACT

This paper reviews the current status of our ongoing work on development of Atomic Layer Deposition (ALD) processes for $Ge_2Sb_2Te_5$ (GST) and related phase change materials. Identification of alkylsilyl tellurium compounds as efficient new ALD precursors made it possible to develop a well controlled ALD process for highly conformal GST films using germanium and antimony chlorides as the other precursors. High-temperature x-ray diffraction and laser based crystallization measurements were exploited for verifying phase change properties.

Key words: atomic layer deposition, phase change, germanium antimony telluride.

1. INTRODUCTION

Phase change random access memories (PCRAM) are considered as one of the most promising solutions for future non-volatile memories. $Ge_2Sb_2Te_5$ (GST), the most widely studied phase change material for PCRAMs is usually deposited by sputtering. However, lowering the reset current requires GST to be deposited into sublithographic holes where the confinement of GST both increases current density and improves thermal isolation. Filling such holes poses high demands for the conformality of the films and therefore sputtering needs to be replaced by chemical vapour phase deposition methods, most preferably with ALD because of its inherent excellent conformality [1-3]. ALD of metal tellurides has not been extensively studied, however, because of limited interest and, more importantly, because of a lack of precursors that would both be safe and exhibit high reactivity as required in ALD. Until recently, only plasma-assisted ALD processes have been attempted for GST but with limited success [4,5].

A breakthrough in ALD of GST, and also of other tellurides and selenides, was made recently when silyl compounds with a general formula $(R_3Si)_2M$ (M = Se, Te) were found to meet the key requirements of ALD precursors: volatility, thermal stability and high reactivity [6]. These compounds react efficiently with various metal halides forming the corresponding metal tellurides and selenides. Sb_2Te_3, GeTe and GST films were deposited by ALD at remarkably low temperature of 90 °C using $(Et_3Si)_2Te$, $SbCl_3$ and $GeCl_2{\cdot}C_4H_8O_2$ as precursors. GST films were highly conformal and were found to exhibit phase change properties similar to sputtered films [7]. This paper reviews the current state of the ongoing development in ALD of GST.

2. EXPERIMENTS

$(Et_3Si)_2Te$ was synthesized in good yields by reacting Li_2Te with Et_3SiCl following literature methods [6,8]. $SbCl_3$ and $GeCl_2{\cdot}C_4H_8O_2$ were of commercial origin. The films were grown in a flow type F120 ALD reactor (ASM Microchemistry) operated at a pressure of about 10 mbar. $SbCl_3$, $GeCl_2{\cdot}C_4H_8O_2$ and $(Et_3Si)_2Te$ were evaporated inside the reactor at 30, 70 and 40 °C, respectively, and were pulsed with inert gas valving. The GST films were deposited at a substrate temperature of 90 °C. The substrates were 5 x 5 cm^2 pieces of silicon with either native oxide, 30 nm SiO_x, 40 nm TiN on 30 nm SiO_x, or 40nm SiN_x.

Field emission scanning electron microscope images were acquired using a Hitachi S-4800 FESEM. Energy dispersive x–ray (EDX) spectra were measured using an INCA Energy 350 EDX spectrometer. Film compositions and thicknesses were determined from the k ratios by using a GMR electron probe thin film microanalysis program [9].

Thicknesses were also determined by x-ray reflectivity (XRR) measurements with a Bruker D8 Advance X-ray diffractometer. Film crystallinity was examined with a PANalytical X'Pert Pro MPD X-ray diffractometer. For in situ XRD measurements an Anton-Paar HTK1200N oven was used. To analyze light impurities, time-of-flight elastic recoil detection analysis (TOF-ERDA) was carried out using 43 MeV $^{79}Br^{8+}$ as a primary beam.

Crystallization times were measured using a static laser tester equipped with a 658 nm pulsed pump laser to crystallize or melt-quench the films, and 635 nm cw laser for measuring the reflectivity. Resistivity as a function of temperature was measured in a nitrogen atmosphere using a custom-made two-probe set-up. The heating rate was 1 K/s.

3. RESULTS & DISCUSSION

The Sb_2Te_3 process showed peculiar temperature dependency where the growth took place with a good rate of about 0.6 Å/cycle at as low temperature as 60 °C but at higher temperatures the growth rate dropped rapidly (Fig. 1). Reason for this behavior is currently unknown but seems to be related to antimony because zinc telluride could be grown at a high temperature 400 °C using the same tellurium precursor. The germanium precursor required a source temperature of 70 °C so GeTe and GST needed to be grown at 90 °C. Both binary processes showed the self-limiting behavior as expected in ALD, in other words the growth saturated when the precursor pulses were elongated [6,7].

GST was deposited by mixing the binary cycles. A growth rate of about 0.30 Å/cycle was obtained where the cycle refers to a sum of binary cycles of Ge-Te and Sb-Te. [6,7]

The control of the ternary composition of GST is much more challenging compared to the binaries which usually adopt automatically the correct composition. The common way for controlling the ternary composition in ALD is to vary the cycle ratio of the binary constituents. Ideally, the film would then adopt the corresponding stoichiometry when the exposure times of all precursors are long enough. However, because the GST materials are more alloy-like there is not any strong driving force towards a particular stoichiometry. Indeed, in the current process the antimony content increased and the germanium and tellurium contents decreased with increasing $SbCl_3$ exposure times without saturation. Anyhow, by adjusting the exposure times and ratio of the binary cycles Ge-Te and Sb-Te, the GST composition could be controlled close to the stoichiometric $Ge_2Sb_2Te_5$. If desired, the composition can be driven to other stoichiometries too, like $Ge_8Sb_2Te_{11}$ that is preferred in recent optical storage products such as the re-writable Blu-ray™ discs because of their larger optical contrast at blue wavelengths [10].

Considering the low deposition temperature, the GST films contained reasonably low impurity contents of about 2.4 at. % oxygen, 1.0 at. % hydrogen, 0.7 at. % carbon, and 0.6 at. % chlorine as measured by TOF-ERDA. The silicon content was more difficult to measure because the films were on silicon, but it appears to be below 1 at. %.

As characteristic to ALD, the films have shown excellent conformality in all test structures tested so far, and complete filling of the holes in actual device structures was verified too (Fig. 2). While the binaries Sb_2Te_3 and GeTe were polycrystalline, GST was usually amorphous in the as-deposited state. This is considered beneficial because extensive crystallization could complicate the hole filling. In some antimony-rich GST films a few isolated crystalline grains could be observed, though. High temperature XRD measurements under N_2 flow revealed a crystallization onset at around 130 °C. First the metastable rock salt (fcc) structure was formed but at around 250 – 300 °C the structure transformed to the stable hexagonal phase. The crystallization of the ALD GST films is similar to the sputtered GST [11].

The resistivity vs. temperature curve of the ALD GST has a similar shape as the sputtered reference film, but is shifted to slightly higher temperatures (Fig. 3). The drops in resistivity correlate with phase changes observed with high temperature XRD. More than five orders of magnitude change in resistivity occurs upon crystallization. Upon cooling the resistivity stays at low level verifying that the drop was caused by crystallization. Besides being shifted to higher temperature, the curve of the ALD GST is also shifted toward higher resistivities at each state of crystallization. The differences between the ALD and sputtered GST films are most likely due to impurities or the off stoichiometric composition of this particular sample. Especially oxygen impurities are known to increase the crystallization temperature of GST [12]. Actually, both shifts may turn out beneficial: the shifts toward higher temperature increase the stability of the amorphous phase against undesired crystallization, and the higher resistivities ensure more efficient

Joule heating in the SET and RESET processes. A potential concern related to the impurities is their effect on long term stability.

Detailed studies on crystallization kinetics were done by illumination with laser pulses (658 nm wavelength) of different energies and durations and measuring the changes in reflectivity (Fig. 4). Full crystallization of the as-deposited GST films occurred within 150 – 1000 ns depending on the underlayer, the fastest crystallization occurring on SiN_x. Recrystallization after melt-quenching areas in an annealed crystalline film occurred always faster than the crystallization of the original amorphous film. Also in this respect the ALD GST films behave similarly to their sputtered counterparts [13].

4. CONCLUSION

GST thin films were successfully deposited by ALD exploiting the novel alkylsilyl tellurium based process. The films showed excellent conformality and their phase change characteristics were similar to sputtered GST films. Some differences were observed too: in the ALD films the phase change temperatures and resistivities were somewhat higher than in the sputtered films. The small amounts of impurities, oxygen in particular, in the ALD GST films may explain these differences. Laser pulse experiments verified that the ALD GST films can be repeatedly switched between amorphous and crystalline states as required in PCRAM devices. Experiments on phase switching by electric current are currently waiting for the depositions on full wafers with actual device structures For these experiments the ALD GST process has already been scaled up to planar 200 mm wafers at ASM Microchemistry.

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Biographies

Mikko Ritala is a professor of inorganic materials chemistry at University of Helsinki (since 2003). He received his M.Sc. degree in 1991 from University of Turku, and Ph.D. degree in 1994 from University of Helsinki, both in inorganic chemistry. His research is largely centered on the atomic layer deposition method but involves also fabrication of nanomaterials.

Viljami Pore is a Ph.D. student at University of Helsinki. His thesis is focusing on thin film growth by atomic layer deposition.

Timo Hatanpää is a Ph.D. student at University of Helsinki. In his research he has synthesised a number of new precursor compounds that have enabled atomic layer deposition of several technologically important materials.

Mikko Heikkilä is a Ph.D. student at University of Helsinki. He is specialised on x-ray and electrochemical characterisation of thin films.

Markku Leskelä is a professor of inorganic chemistry in the Department of Chemistry at University of Helsinki, Finland (since 1990). His research activities are focused on thin films and other nanostructured materials made by various chemical methods (atomic layer deposition, electrodeposition and successive ionic layer adsorption and reaction). His other research area is coordination compound catalysts and related metalorganic synthesis. The third, more recent research area comprises nanomaterials in preparation of which the thin film deposition and metalorganic synthesis techniques are combined. He has earlier worked as associate professor in University of Oulu (1979-1986) and as professor in University of Turku (1986-1990). During 2004-2009 he acts as Academy Professor. He has worked as a visiting scientist or professor in University of Utrecht (1983), University of Florida (1987-88) and University of Paris VI (1999).

Alejandro Schrott has been a Research Staff Member at the IBM T.J.Watson Research Center since 1986. He has worked on surface and interface properties of materials, aiming at fabrication of exploratory devices. Since 2004, Dr. Schrott has focused his attention to processing and integration of Phase Change Memory Devices.

Simone Raoux is a Research Staff Member at the IBM T. J. Watson Research Center. She received her MS degree in 1984 and Ph.D. degree in physics in 1988 both from Humboldt University, Berlin, Germany. From 1988 to 1991 she worked as a Staff Scientist at the Institute for Electron Physics in Berlin, Germany. From 1992 to 2000, she was a Staff Scientist at Lawrence Berkeley National Laboratory. Her current research interests include the physics and materials science of phase change materials.

Stephen M. Rossnagel is a Research Staff Member at the IBM Thomas J. Watson Research Center in Yorktown Heights, New York since 1983. His work centers on materials and process technology for interconnect and packaging applications, based mostly on PVD and ALD.

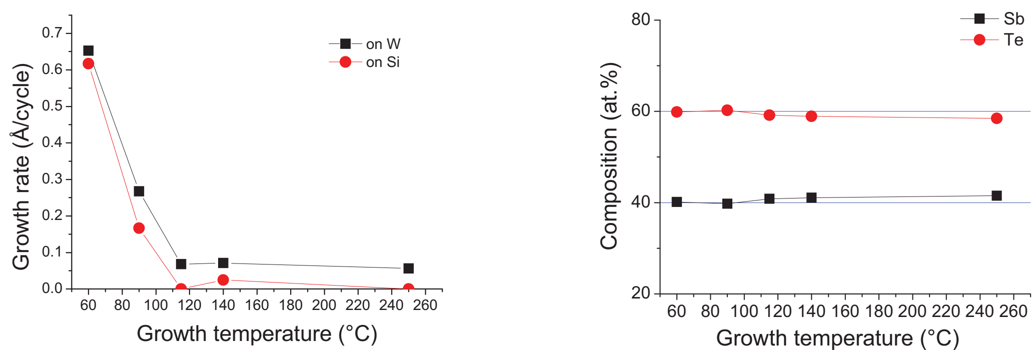

Figure 1. Temperature dependence of the Sb_2Te_3 growth rate and composition.

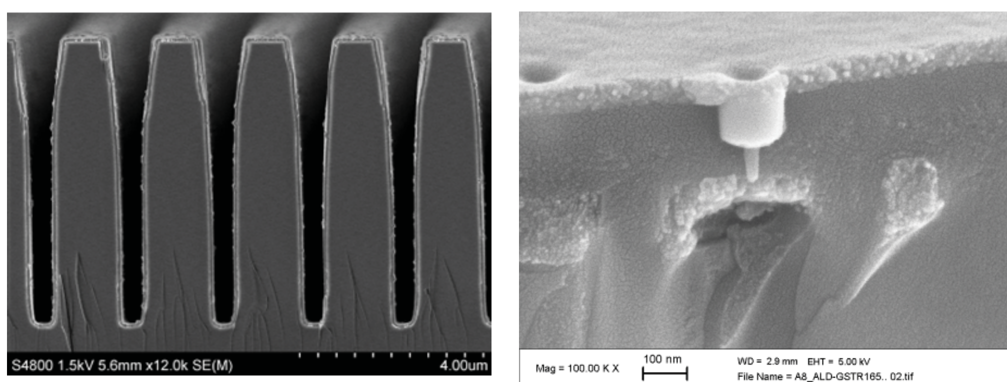

Figure 2. Examples of the conformality of the ALD GST films.

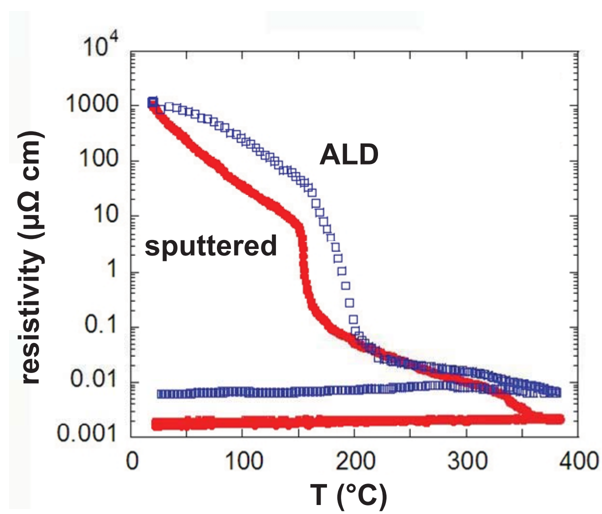

Figure 3. Resistivity vs. temperature curves of ALD and sputtered GST films.

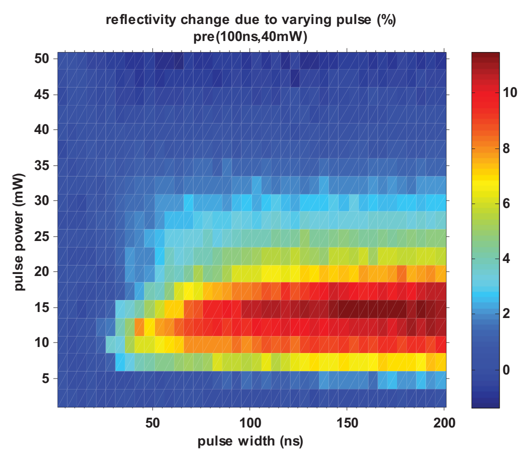

Figure 4. Laser crystallization experiment on ALD $Ge_2Sb_2Te_5$ film on SiO_x.