Atomic Layer Deposition of phase change materials

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ABSTRACT

Phase Change Random Access Memeory (PCRAM) memories with the highest integration densities and lowest power consumptions require scaling of the memory cells into nanometer scale 3D structures. This requires a highly conformal thin film deposition method for the phase change material. Atomic Layer Deposition (ALD) has in general become a method of choice for this kind of applications, but to apply ALD for phase change memories, proper chemistry needs to be developed. This paper reviews the current status of ALD of $Ge_2Sb_2Te_5$ (GST) and related phase change materials, mostly focusing on our own work based on alkylsilyl tellurium precursors but also referring to its further development by other groups.

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

1. INTRODUCTION

Reaching high integration densities together with low power consumption in phase change memories requires that memory cells are scaled into dimensions of a few nanometers only. The confinement of the phase change material into small areas and volumes is most efficiently done by depositing the material into tiny vias. This in turn requires excellent conformality from the thin film deposition method, thereby severely challenging the so far dominant sputtering methods. Atomic Layer Deposition (ALD) has become a preferred method in applications with extreme conformality requirements, such as Dynamic Random Access Memory (DRAM), and is of a high interest for PCRAMs, too.

ALD is a chemical vapor phase technique where the film growth occurs via alternating saturative surface reactions [1-3]. The precursor vapors are pulsed into the reactor one at a time, and the precursor pulses are separated by inert gas purges. Each precursor pulse saturates the surface by a monolayer of that precursor to react subsequently with the other precursor. Thus the film growth proceeds in a self-limiting manner (sub)monolayer by (sub)monolayer, and the film thickness can be accurately and simply controlled by the number of the deposition cycles repeated. Because of this self-limiting growth mechanism, the growth occurs the same everywhere in the ALD reaction chamber and therefore the resulting films have superior conformality, and their thicknesses and compositions are uniform also over large area substrates and large batches. ALD allows also straightforward control of ternary compositions by varying the cycling ratio of the binary constituents, and artificial materials such as nanolaminates can be prepared by combining materials into stacks of ultrathin films.

Adoption of ALD to new materials and applications is not always trivial. Proper precursors need to be found for controlled deposition of materials of interest. Precursors need to have sufficient volatility, and to ensure efficient self-limiting surface reactions, they must be highly reactive towards each other, yet thermally stable against self-decomposition. The common phase change material $Ge_2Sb_2Te_5$ (GST) consists of three elements that had not been studied much and had remained challenging in ALD until recently. In this paper, a review is made of development of ALD processes for GST and related materials.

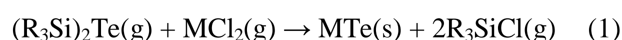
2. ALD PROCESSES FOR GST AND RELATED MATERIALS

From the chemistry point of view, the processes explored for ALD of GST can be divided into two groups. The first studies used precursors that have been commonly exploited in CVD of the same materials, namely organometallics and alkylamides, and a common precursor in all cases was $^{i}Pr_2Te$ [4-10]. These compounds appear to lack the desired

high reactivity towards each other, however, and therefore they have been explored mostly in plasma enhanced ALD. Even with plasma activation, no true self-limiting ALD growth seems to have been achieved, and the processes have involved significant CVD contributions. Another common feature to these studies is that the ternary deposition was attempted, at least conceptually, by combining deposition cycles of elementary films, whereas in the ALD processes using alkyl silyl tellurium precursor this has been done by combining binary processes as will be discussed below.

A breakthrough in ALD of GST and related materials, including selenides, was made when alkyl silyl compounds $(R_3Si)_2M$ (M = Te, Se) were found to meet the key requirements of ALD precursors: volatility, thermal stability and high reactivity [11]. The compounds with the smallest alkyl groups, e.g. $(Me_3Si)_2Te$ and $(Et_3Si)_2Te$ are liquids at room temperature whereas $(^tBuMe_2Si)_2Te$ is a low melting point (44 ºC) solid. 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, where $C_4H_8O_2$ is a neutral dioxane adduct ligand.

$(R_3Si)_2Te$ offers a straightforward exchange reaction route to the deposition of the metal telluride and efficient elimination of the chloride ligands of the metal precursor, the overall reaction being:



$$(R_3Si)_2Te(g) + MCl_2(g) \rightarrow MTe(s) + 2R_3SiCl(g) \quad (1)$$

In situ reaction mechanism studies with a quartz crystal microbalance and quadrupole mass spectrometer verified the dechlorosilylation reaction mechanism and showed that the ligand exchange and formation of R_3SiCl as a byproduct occur stepwise during both metal chloride and alkyl silyl tellurium pulses [12].

Both Sb_2Te_3 and GeTe binary processes showed the self-limiting behavior as expected in ALD, i.e. the growth rates saturated with long enough precursor pulses. Despite the low deposition temperatures the saturation level was reached with reasonably short pulse times of only 1 s. Temperature-wise the processes showed peculiar features compared to the ALD processes in general. The growth of Sb_2Te_3 occurred with a good rate of about 0.6 Å/cycle at as low temperature as 60 °C but above that the growth rate dropped rapidly (Fig. 1). Also with GeTe the highest rate was achieved at the lowest possible deposition temperature of 90 °C, the limitation coming from $GeCl_2{\cdot}C_4H_8O_2$ that needs a source temperature of 70 °C [11,13]. Above 90 °C the GeTe depositon rate decreased rapidly and dropped to zero already at 150 °C. Indeed, currently the largest concern related to these processes arises from the modest volatility of $GeCl_2{\cdot}C_4H_8O_2$ combined with the strong temperature dependence of the growth rate. Various alternatives have been looked for $GeCl_2{\cdot}C_4H_8O_2$ but no better precursor has been found yet. Reasons for these temperature dependences are still under discussion but they seem to be related to these specific film materials rather than this chemistry in general because zinc telluride could be grown at a high temperature of 400 °C using the same tellurium precursor and $ZnCl_2$ [81].

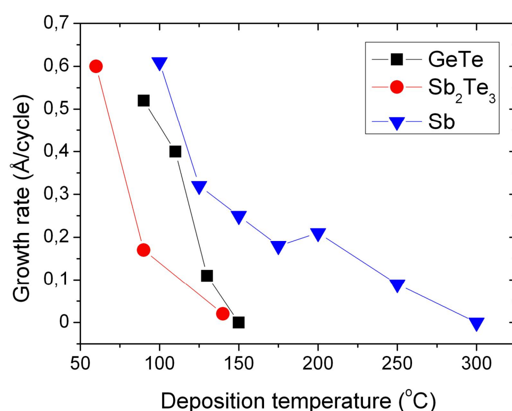


Figure 1. Temperature dependencies of ALD growth rates of various materials deposited with metal chlorides and alkyl silyl precursors of tellurium and antimony.

Ternary GST films were deposited by mixing the binary ALD cycles of GeTe and Sb_2Te_3. 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 [11, 14]. A common way for controlling the ternary composition in ALD is to vary the cycle ratio of the binary constituents. Ideally, the film should adopt the stoichiometry corresponding to the composition of the stable ternary compound but because GST and related ternary materials are more alloy-like and many stoichiometric compositions exist along the pseudo-binary line between GeTe and Sb_2Te_3 ($Ge_1Sb_2Te_4$, $Ge_2Sb_2Te_5$, $Ge_3Sb_2Te_6$, etc.) there is no strong driving force towards a particular stoichiometry. Indeed, in the ternary process the antimony content increased and the germanium and tellurium contents decreased with increasing $SbCl_3$ exposure times without approaching any specific composition. Anyhow, the GST composition could still be adjusted close to the stoichiometric $Ge_2Sb_2Te_5$ by tuning the ratio of the binary cycles Ge-Te and Sb-Te. On the other hand, if so desired, the composition can be adjusted to other stoichiometries on the GeTe – Sb_2Te_3 tie line as well by just changing the binary cycle ratio.

The dechlorosilylation reaction was later extended to also elemental antimony (Fig. 1) and various metal antimonides, also those of germanium [15]. Elemental Sb films were deposited from $SbCl_3$ and $(Et_3Si)_3Sb$, while $GeCl_2 \cdot C_4H_8O_2$ and $(Et_3Si)_3Sb$ deposited a germanium – antimony alloy with a germanium rich composition of 82 at. % Ge and 18 at. % Sb. The germanium rich composition points to a reaction mechanism more complicated than the simple ligand exchange, most likely some antimony to germanium substitution is involved, too. Contrary to the Ge-Sb-Te system, Ge-Sb has no stoichiometric compound and tends to elemental segregation. Anyhow, by mixing ALD cycles of elemental Sb with those of $Ge_{82}Sb_{18}$, the film composition could be tuned in between these two extremes. Furthermore, when also GeTe and/or Sb_2Te_3 ALD cycles were added, the ternary Ge-Sb-Te composition could be tuned over a wide range of compositions in the ternary phase diagram (Fig. 2).

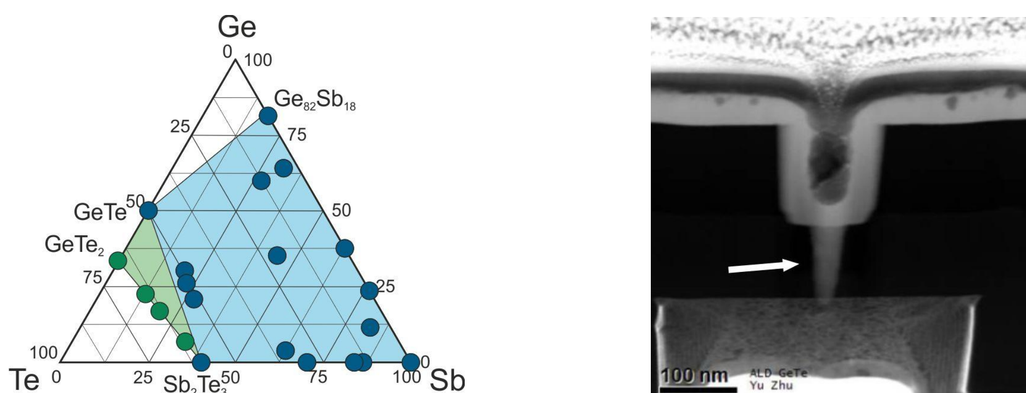


Figure 2. Left: Ge-Sb-Te phase diagram showing compositions reached so far with the alkyl silyl tellurium based processes. The blue area shows compositions obtained with germanium and antimony chlorides while the green area shows the extension achieved by alkoxides (see text). Right: Transmission electron microscopy image of a GeTe film filing a 31 × 84 nm via indicated by the arrow.

As typical for a good ALD process, the films showed excellent conformality in all structures tested so far. Complete filling of sub-100 nm holes in actual PCRAM device structures was also successfully demonstrated (Fig. 2).

Despite the low deposition temperature, the GST films deposited from the germanium and antimony chlorides 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 analysed by Time-of-Flight Energy Recoil Detection Analysis (TOF-ERDA) [11,14]. In elemental Sb films no chlorine could be detected with ERDA [15]. The silicon residues were more difficult to analyse because the films were on Si substrate, but the silicon content appeared to be below 1 at. %. Low levels of silicon and carbon in the GST films have also been verified with Secondary Ion Mass Spectrometry (SIMS) [16].

The binary Sb_2Te_3 and elemental Sb films were found to grow in polycrystalline form whereas with GeTe both amorphous and polycrystalline films have been obtained. The ternary GST has usually been amorphous in the as-

deposited state which can be considered as a fortunate consequence of the low deposition temperature because strong crystallization during the growth could prevent complete filling of the three-dimensional PCRAM memory cell structures.

Crystallization of the amorphous films has been studied with High Temperature X-Ray Diffraction (HTXRD) measurements under nitrogen. With GST the crystallization to the metastable rock salt (fcc) structure started at around 130 °C and the structure transformed to the stable hexagonal phase at 250 – 300 °C [14]. The GeTe films crystallized at 165 °C to the rhombohedral phase, which transformed further to the cubic phase [13]. These observations on the ALD GST and GeTe films are comparable to those on sputtered films, as is their resistivity vs. temperature behavior. More than five orders of magnitude change in resistivity occurred upon crystallization of GST. As compared to the sputtered film, the resistivity vs. temperature curve of the ALD GST is shifted to both higher temperature and toward higher resistivities, most likely due to the impurities. Especially oxygen is known to increase the crystallization temperature of GST. Fortunately, both shifts may be beneficial: the shifts toward higher temperatures increase the stability of the amorphous phase against unintentional crystallization, and the higher resistivities enable more efficient Joule heating in the set and reset processes. It still remains to be explored if the impurities affect long term stability of the PCRAM device.

Phase change properties of the ALD films have mostly been explored with laser techniques because they do not require preparation of complex devices. The main conclusion of these studies has been that both GST and GeTe films made by ALD behave similar to their sputtered counterparts. As the most recent result, Fig. 3 shows crystallisation of a thin film with a composition of $Ge_{11}Sb_{83}Te_6$, away from the pseudobinary tie line between GeTe and Sb_2Te_3. This composition was achieved by mixing binary GeTe cycles with elemental Sb cycles. The antimony-rich composition $Ge_{11}Sb_{83}Te_6$ shows an excellent recrystallization time of 30 ns which makes it the fastest ALD-grown film measured so far. In addition, the antimony-rich composition has increased the crystallization temperature up to 200 °C. To further explore the possible compositions in the areas of the phase diagram available to ALD, a germanium-rich composition of $Ge_{64}Sb_{31}Te_5$ was tested. This composition was obtained by mixing binary cycles of GeTe and Ge-Sb, the latter resulting in a composition of about of $Ge_{82}Sb_{18}$. This germanium-rich composition had an even faster crystallization speed of 20 ns and a crystallization temperature of 375 °C. There are still explorations to be done in the various regions of the Ge-Sb-Te phase diagram.

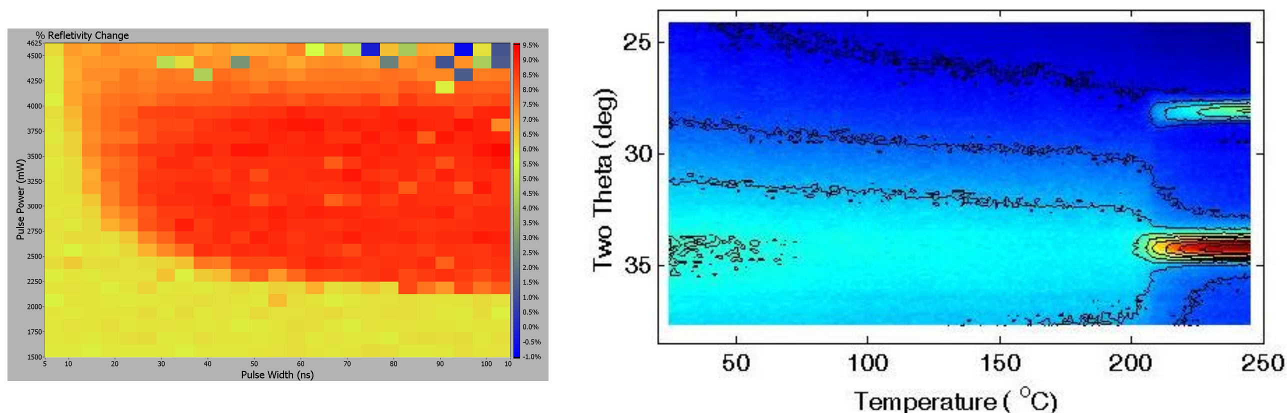


Figure 3. Laser crystallization and HTXRD results on ALD $Ge_{11}Sb_{83}Te_6$ film.

The most decisive test for the applicability of the ALD phase change material processes is the performance of the films in solid state devices where electric current rather than laser pulses are used to crystallize and amorphize the material. While the early research reviewed above was done on films made in small research scale reactor on 50 x 50 mm^2 substrates, later the GST ALD process was scaled up to 200 mm wafers with less than 3 % 1σ thickness nonuniformity, and integrated PCRAM devices were fabricated [16]. With these devices it was demonstrated that the memory cells could be switched between the low and high resistivity states up to 10^6 cycles with a very stable resistance for both states.

Recently Eom et al. [17] extended the alkyl silyl based ALD chemistry by using $(Me_3Si)_2Te$ and germanium and antimony alkoxides $Ge(OCH_3)_4$ and $Sb(OC_2H_5)_3$ for low temperature (70 °C) deposition of films with compositions lying on the $GeTe_2$–Sb_2Te_3 tie lines (Fig. 1). In the light of earlier work this was a happy surprise, because in our own experiments the alkyl silyl tellurium did not react with any alkoxide nor any Ge(IV) compound. Indeed, several peculiar features in the growth characteristics were observed and interpreted in terms of physisorption only, rather than the common reactive adsorption, of $Ge(OCH_3)_4$. Anyhow, the process was found quite robust and allowed highly conformal, smooth, and reproducible film growth over a contact hole structure with an extreme geometry. Also these films showed phase change properties comparable to sputtered GST films.

3. CONCLUSIONS

Because of its superior conformality, ALD is an attractive method for preparation of PCRAM memories with the highest integration densities and lowest power consumptions, achieved by scaling the memory cells into nanometer scale 3D structures. Lack of proper precursors for ALD of GST and related materials delayed the adoption of ALD into the PCRAM application but through the finding of alkyl silyl tellurium compounds as efficient ALD precursors when combined with germanium and antimony chlorides a major step toward this direction was made. After the first success in ALD of GeTe, Sb_2Te_3 and GST, the chemistry was extended to elemental antimony and Ge-Sb by using a similar alkyl silyl antimony precursor. A substantial coverage of the Ge-Sb-Te phase diagram has been obtained by combining the various metal chloride – alkyl silyl tellurium processes, and this has further been expanded by using the Ge(IV) alkoxide.

The films deposited by ALD have shown excellent conformality and phase change characteristics similar to sputtered GST films. Nevertheless, 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 likely explain these differences. Laser pulse experiments verified that the ALD GST films can be repeatedly switched between amorphous and crystalline states, and the first reports on solid state devices with ALD made phase change materials have been promising.

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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 ALD method but involves also fabrication of nanomaterials.

Tiina Sarnet is a Ph.D. student at University of Helsinki. Her thesis is focusing on thin film growth by ALD.

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.

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 ALD and various other chemical methods. 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 acted 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).

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.