

Atomic Layer Deposition of Metal Tellurides and Selenides Using Alkylsilyl Compounds of Tellurium and Selenium

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Compounds with a general formula $(R_3Si)_2Te$ and $(R_3Si)_2Se$ react efficiently with various metal halides to produce telluride and selenide materials. By using this chemistry in atomic layer deposition (ALD), various metal selenide and telluride thin films including the phase change material germanium antimony telluride (GST) can be deposited in a highly controlled manner.

Metal selenide and telluride thin films have been gaining continuously increasing interest. Two well-known examples are $CuInSe_2$ solar cell absorber and $Ge_2Sb_2Te_5$ phase change material. Phase-change random-access memory (PCRAM) is a promising technology for future nonvolatile data storage.¹ To be successful PCRAM must be scaled down to dimensions on the order of a few tens of nanometers or less, and the material has to be deposited conformally.^{1b,c,2} Therefore chemical deposition techniques, preferably ALD, are needed.

ALD is a unique modification of the chemical vapor deposition method for highly controlled deposition of thin films.³ Unique to ALD is that precursor vapors are brought onto the substrates alternately, one at a time, separated by purging periods with inert gas. The film grows via saturative surface reactions between the incoming precursor and the surface species left from the previous precursor. When all the reactions are saturative and no precursor decomposition takes place, the film growth is self-limiting providing a number of attractive features, such as easy and accurate film thickness control down to an atomic layer level, excellent large area uniformity, and unrivalled conformality on complex-shaped substrates.

The success of ALD depends strongly on appropriate precursor compounds. Reaching the self-limiting growth conditions places strict demands on the precursors.⁴ Besides volatile, they should be thermally stable against self-decomposition but at the same time also show high reactivity toward surface species formed by the other precursor. As decomposition cannot be exploited for the ligand elimination, the precursors must be chosen so that the ligands will be effectively eliminated by exchange reactions. Considering nonmetals, and the group 16 elements in particular, hydrides are often an ideal choice as they allow clean ligand elimination by protonation. However, hydrides of many nonmetals are highly toxic. In group 16 water of course is without this concern, and H_2S can be used with appropriate precautions because its odor threshold limit is much lower than the harmful level.⁵ By contrast, the hydrides of selenium and tellurium would require extensive safety systems and exhaust gas treatment. Alkyl compounds of selenium and tellurium have been quite widely used in CVD⁶ but it appears that in ALD they cannot provide efficient exchange reactions with the common metal precursors. Therefore ALD of metal selenides and tellurides has been scarce,⁷ and mostly limited to selenides and tellurides of zinc and cadmium because these are the rare cases where elements can be used as precursors for both constituents.^{7a–c} In addition, for GST, plasma enhanced ALD has been attempted but the outcome has been a combination of CVD and ALD growth

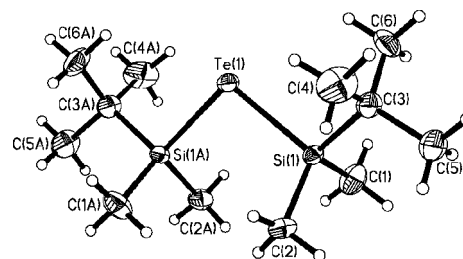


Figure 1. Molecular structure of $(BuMe_2Si)_2Te$ (thermal ellipsoids at 50%). Te to Si distances are 2.5141(13) Å and Si–Te–Si angle is 101.51(6)°.

at best.⁸ Thus there is an obvious need to develop efficient ALD processes for metal selenides and tellurides. In this paper we show a breakthrough in metal selenide and telluride ALD by exploiting alkylsilyl compounds $(R_3Si)_2Se$ and $(R_3Si)_2Te$ as precursors.

Compared to alkyls and alkylamides of Se and Te, $(R_3Si)_2Se$ and $(R_3Si)_2Te$ offer a much more straightforward reaction route for the elimination of ligands of the metal precursors. In $(R_3Si)_2Se$ and $(R_3Si)_2Te$ silicon, a hard Lewis acid is bonded to the heavy group 16 elements which are soft Lewis bases, thus forming an unfavorable hard–soft Lewis acid–base pair. Upon exchange reaction with metal chlorides, for example, silicon becomes bonded to the harder base:



Further, if the metal of the metal chloride is soft Lewis acid, the other product of the exchange reaction will form a favorable soft–soft Lewis acid–base combination ($M-Se$ or $M-Te$). Indeed, Groshens et al.⁹ reported that $(Me_3Si)_2Te$ together with $Sb(NMe_2)_3$ deposit stoichiometric Sb_2Te_3 in CVD at very low temperatures and that the growth occurs, quite untypical for CVD, through stoichiometric exchange reactions between the two precursors. These observations are very promising in what comes to the reactivity requirements of ALD precursors.^{3,4}

$(Et_3Si)_2Se$, $(Et_3Si)_2Te$, and $(BuMe_2Si)_2Te$ were synthesized in good yields by reacting Na_2Se^{10a} or Li_2Te^{10a} with Et_3SiCl or $BuMe_2SiCl$ following literature methods.^{10b} Chlorosilanes larger than Me_3SiCl were chosen to make less volatile tellurium/selenium compounds for safety reasons during the synthesis and use. $(Et_3Si)_2Se$ and $(Et_3Si)_2Te$ are liquids at room temperature while $(BuMe_2Si)_2Te$ is a low melting solid (mp 44 °C). The compounds prepared were analyzed with 1H NMR, ^{13}C NMR, MS, and TGA. Crystal structure of the only solid $(BuMe_2Si)_2Te$ (CCDC 708333) was solved using single crystal X-ray diffraction. Molecular structure of the strictly monomeric compound is shown in Figure 1. TGA (N_2 , normal pressure) revealed that all the compounds prepared evaporate completely. Thermal stability of the compounds was found to be remarkably high in ALD deposition tests conducted. The compounds prepared seem to be stable at least up to 400 °C.

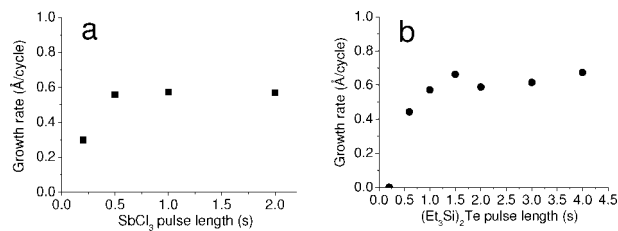


Figure 2. Growth rate as a function of (a) SbCl₃ and (b) (Et₃Si)₂Te pulse length for Sb₂Te₃ films deposited at 60 °C. The other precursor pulse lengths were kept at 1.0 s and all the purge lengths at 2.0 s.

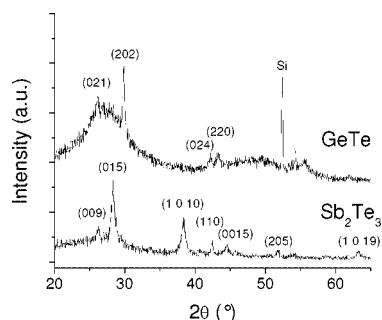


Figure 3. Grating incidence X-ray diffractograms of a Sb₂Te₃ film deposited at 60 °C and a GeTe film deposited at 90 °C.

ALD film growth experiments were performed in a flow type F120 ALD reactor (ASM Microchemistry) operated at a pressure of about 10 mbar. First binary antimony and germanium telluride processes were examined with SbCl₃ and GeCl₂·C₄H₈O₂ as precursors.

Both synthesized Te precursors were shown to result in Sb₂Te₃ film growth, but (Et₃Si)₂Te was chosen for further studies because of its easier handling (liquid). The saturative growth of Sb₂Te₃ from SbCl₃ and (Et₃Si)₂Te on native silicon oxide is demonstrated in Figure 2. As characteristic to ALD, the growth rate clearly saturates to around 0.6 Å/cycle when both pulse lengths are increased. An exceptionally low deposition temperature of 60 °C was possible because SbCl₃ and (Et₃Si)₂Te show high reactivity and evaporate sufficiently from open vessels inside the reactor at 30 and 40 °C, respectively. The composition of the films was very close to Sb₂Te₃ and no chlorine could be detected by EDX. The reaction thus appears to be very efficient at such a low temperature. When the deposition temperature was raised the growth rate started to decrease. With 1 s pulse times the growth rate dropped to 0.17 Å/cycle at 90 °C and further to only 0.02 Å/cycle at 140 °C. The films were crystalline showing the reflections of rhombohedral Sb₂Te₃ (ICDD-PDF-015-0874) (Figure 3).

Next, GeTe films were grown using (Et₃Si)₂Te and a germanium dichloride dioxane complex GeCl₂·C₄H₈O₂. The evaporation temperature for the Ge precursor was 70 °C which allowed the use of a low deposition temperature in this case also. A growth rate of 0.42 Å/cycle was obtained for the GeTe films at a deposition temperature of 90 °C. According to EDX the films were slightly Ge rich with a composition of 54% Ge and 46% Te. XRD indicated that the films were crystalline rhombohedral GeTe (ICDD-PDF-047-1079) with a noticeable fraction of amorphous phase (Figure 3).

In addition to SbCl₃ and GeCl₂·C₄H₈O₂, other antimony and germanium precursors that resulted in film growth with (Et₃Si)₂Te at a growth temperature of 140 °C were Sb(OEt)₃ and GeBr₂. Film growth was not observed with Sb(NMe₂)₃, Ge(N(SiMe₃)₂)₂, Ge(Oⁱ-Bu)₂, GeCl₄, or GeBr₄ at the same temperature but a wider range

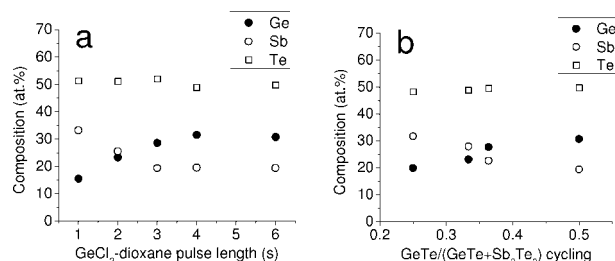


Figure 4. Composition of GST films as a function of (a) GeCl₂·C₄H₈O₂ pulse length and (b) GeTe/(GeTe+Sb₂Te₃) cycling ratio. SbCl₃ and (Et₃Si)₂Te pulse lengths were always 1.0 s and purges were 2.0 s.

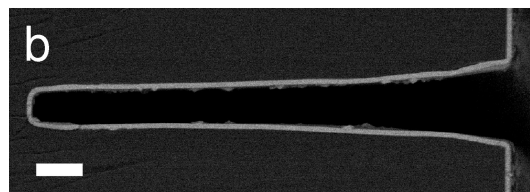
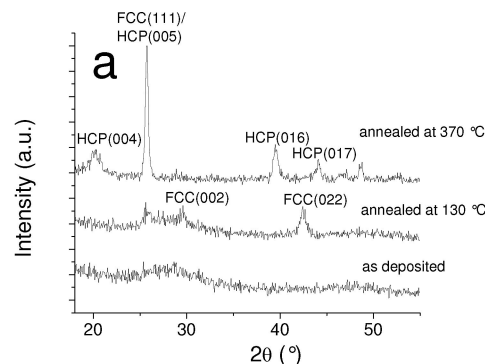


Figure 5. (a) Grating incidence X-ray diffractograms of as-deposited and N₂-annealed GST films. (b) Cross-section FESEM image of a GST film deposited on a high aspect-ratio trench pattern. Scale bar = 600 nm.

of deposition temperatures should of course be covered before these compounds can be completely excluded.

The Sb₂Te₃ and GeTe processes using SbCl₃, GeCl₂·C₄H₈O₂, and (Et₃Si)₂Te as precursors were combined in order to prepare the technologically important GST films. On the basis of the results obtained with the GeTe and Sb₂Te₃ binary processes the lowest possible deposition temperature, that is, 90 °C, was chosen for the experiments. Figure 4a depicts the composition of GST films as a function of the GeCl₂·C₄H₈O₂ pulse length when GeTe and Sb₂Te₃ cycles were applied in a 1:1 ratio. With increasing GeCl₂·C₄H₈O₂ pulse length the Ge content increases and then saturates with pulse lengths of 4 s and more. The growth rate in these films saturated to around 0.3 Å/cycle which is in line with the growth rates of the individual binary processes at 90 °C (0.17 Å/cycle for Sb₂Te₃ and 0.42 Å/cycle for GeTe).

Based on the saturative behavior of all the precursors, it appears possible to prepare Ge_xSb_yTe_z films of various compositions by ALD in a controlled manner just by adjusting the GeTe and Sb₂Te₃ cycling ratio. Figure 4b shows the variation of film composition when different GeTe/(GeTe+Sb₂Te₃) cycling ratios were used. The Ge/Sb ratio in the films increases linearly as the GeTe/(GeTe+Sb₂Te₃) cycling ratio is increased. To get equal amounts of Ge and Sb in the films, a GeTe/(GeTe+Sb₂Te₃) cycling ratio of ~0.35 is required.

A GST film with a composition of 23% Ge, 28% Sb, and 49% Te was subjected to high temperature XRD measurements where the sample is annealed under N₂ flow and measured with XRD in

Table 1. Process Parameters and Characteristics of Tellurides and Selenides Prepared by ALD Using (Et₃Si)₂Te and (Et₃Si)₂Se as Precursors^a

material	metal precursor/evaporation temperature	growth temperature (°C)	growth rate by EDX (Å/cycle)	composition by EDX
ZnTe	ZnCl ₂ /360 °C	400	0.61 ± 0.05	Zn 47%, Te 53%
Bi ₂ Te ₃	BiCl ₃ /140 °C	165	1.21 ± 0.08	Bi 40%, Te 60%
ZnSe	ZnCl ₂ /360 °C	400	0.55 ± 0.04	Zn 48%, Se 50%, Te 2% ^b
Bi ₂ Se ₃	BiCl ₃ /140 °C	165	0.97 ± 0.07	Bi 41%, Se 59%
In ₂ Se ₃	InCl ₃ /285 °C	295	0.55 ± 0.04	In 41%, Se 59%
CuSe	Cu(II) pivalate/155 °C	165	0.63 ± 0.06	Cu 50%, Se 50%
Cu _{2-x} Se	Cu(II) pivalate/165 °C	200	0.48 ± 0.05	Cu 61%, Se 39%
Cu ₃ Se	Cu(II) pivalate/165 °C	300	0.16 ± 0.03	Cu 69%, Se 31%
Cu ₂ Se	CuCl/350 °C	400		

^a Native silicon oxide and glass were used as the substrates. ^b Te contamination from previous runs.

situ at 15 °C intervals. The initially amorphous film started to crystallize at 130 °C showing reflections belonging to the metastable rock salt structure.¹¹ Further increase in temperature transformed the film gradually at around 250–300 °C to the stable hexagonal phase.¹¹ These observations are consistent with earlier studies on the crystallization of GST.¹² The cubic and hexagonal phases can be clearly distinguished in Figure 5a.

Many of the potential PCRAM structures call for deposition of GST films conformally in deep trenches and pores.^{1b,c,2} To study the conformality of the GST ALD process, a GeTe/(GeTe+Sb₂Te₃) cycling ratio of 0.33 was used to deposit a film on a high aspect-ratio trench pattern. The FESEM image in Figure 5b shows that the film thickness (~65 nm) is virtually the same in the different parts of the structure. It can be concluded that with this precursor combination GST films can be grown conformally on complex shaped substrates in a typical ALD fashion.

In addition to Sb₂Te₃, GeTe, and GST many other tellurides and selenides can be deposited by ALD using alkylsilanes of tellurium and selenium as precursors. Table 1 shows all the materials and precursor combinations that have so far been demonstrated. These include ZnTe, Bi₂Te₃, ZnSe, Bi₂Se₃, In₂Se₃, and Cu₃Se_y. Higher deposition temperatures were required for these materials to ensure sufficient evaporation of the metal precursors. It is noteworthy that the deposition of ZnTe and ZnSe at as high temperature as 400 °C was possible. The applicable temperature range for (Et₃Si)₂Te and (Et₃Si)₂Se is thus wide and the deposition of various metal tellurides and selenides is possible. The growth rate is also very good in many cases. The dramatic decrease in the growth rate of Sb₂Te₃ with increasing temperature (see above) thus seems to be related to the Sb precursor and not to the tellurium precursor. The range of materials in Table 1 represents successful single growth experiments and the saturative ALD growth behavior of these processes is still to be verified. The general appearance of the films was however quite good with relatively little variations apparent across the substrate. All films were crystalline as verified by XRD.

Metal chlorides seem to react very efficiently with (Et₃Si)₂Te and (Et₃Si)₂Se but also other precursors, such as carboxylates and alkoxides were shown to result in film growth. Growth experiments using copper(II) pivalate and (Et₃Si)₂Se seemed especially interesting because depending on the deposition temperature the stoichiometry could be controlled between CuSe and Cu₂Se. This process combined with In₂Se₃ could allow the ALD of CuInSe₂, a well-known solar cell absorber, and is currently under further study.

In summary, by using alkylsilyl compounds of tellurium and selenium as precursors the ALD of many tellurides and selenides

is possible, and it seems that a whole new class of ALD processes has been found.

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Supporting Information Available: Description of the precursor synthesis, film characterization, crystallographic data file (CIF) of (BuMe₂Si)₂Te and complete ref 2b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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