Department of Chemistry
Faculty of Science
University of Helsinki
Helsinki, Finland

Precursor Chemistry for Atomic Layer Deposition

Timo Hatanpää

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public examination in Auditorium A110 of the Department of Chemistry (Chemicum), A. I. Virtasen aukio 1, on August 30th, 2019, at 12 o'clock noon.

Helsinki 2019

Supervisors

Professor Mikko Ritala
Professor Markku Leskelä
Department of Chemistry
University of Helsinki
Helsinki, Finland

Reviewers

Professor Risto Laitinen
Environmental and Chemical Engineering
University of Oulu
Oulu, Finland

Professor Charles H. Winter
Department of Chemistry
Wayne State University
Detroit, Michigan, USA

Opponent

Docent Ari Lehtonen
Department of Chemistry
University of Turku
Turku, Finland

© Timo Hatanpää
ISBN 978-951-51-5328-9 (pbk.)
ISBN 978-951-51-5329-6 (PDF)
http://ethesis.helsinki.fi/

Unigrafia
Helsinki 2019

Abstract

Precursors have an essential role in making thin films using chemical vapor phase methods, including atomic layer deposition (ALD). In these methods, precursor molecules are transported through the gas phase to the substrate surface where thin films of solid material are formed as a result of chemical reactions on the surface or in the vicinity of the surface. While a right choice of the precursor or precursor combination is needed to make the film growth possible, the choice will also, together with growth parameters, affect the structure, morphology, purity, electrical, optical, mechanical, and other properties of the forming films. New precursors are needed for new materials and to make better processes for known materials, or to make known materials in a form that fulfills the requirements of a specific application.

Essential general requirements for ALD precursors are volatility, thermal stability, and sufficient reactivity. Because of the different properties of the elements, finding precursors fulfilling all the above requirements is easy for some elements and extremely difficult for some others. The required properties are pursued by molecular design, i.e., by choosing or tailoring the right kind of ligands and compounds. In this work, precursors for making different materials of interest by ALD were invented, synthesized, and characterized.

For magnesium a β-diketonate bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II), $Mg(thd)_2$, and its adducts were studied. It was found that the dimeric $Mg_2(thd)_4$ evaporated cleanly and was a suitable precursor in that sense. However, $Mg_2(thd)_4$ is lacking reactivity with water. Adducting led into monomeric compounds, but the volatility was not enhanced in perceptible degree.

For strontium and barium, different cyclopentadienyl compounds were prepared and characterized. It was found that due to high thermal stability, volatility and reactivity strontocenes and barocenes with polysubstituted large and sterically demanding cyclopentadienyl ligands like Me_5C_5, $^{i}Pr_3C_5H_2$ and especially $^{t}Bu_3C_5H_2$ are most suitable precursors for the preparation of strontium and barium containing oxide films by ALD. Adduct forming ligands and donor-functionalized cyclopentadienyl ligands were found not to give any significant advantages considering the usage in ALD. Introduction of the cyclopentadienyl compounds of strontium and barium to ALD allowed the deposition of their oxides in sufficiently pure form for the first time. Still, the cyclopentadienyl compounds are the state-of-the-art precursors for depositing strontium and barium containing oxide materials.

For bismuth oxide and bismuth-containing oxide materials, different compounds were studied as possible precursors. It was found that a silylamide $Bi(N(SiMe_3)_2)_3$ has volatility and thermal stability allowing its usage barely as a precursor for the deposition of ternary and quaternary bismuth-containing oxides while binary bismuth oxide deposition is difficult. The best precursor for depositing bismuth oxide was found to be $Bi(OCMe_2{}^{i}Pr)_3$, an alkoxide with sufficiently bulky ligands. Alkoxides with smaller or larger ligands were found to be thermally less stable. Properties making $Bi(OCMe_2{}^{i}Pr)_3$ an excellent precursor for making oxides are 1) reactivity with water, 2) low melting temperature making the precursor a liquid source, 3) large deposition temperature window that can be used, 4) ability to deposit pure films 5) higher growth rate (0.38 Å/cycle) than with any previous or later process achieved, and 6) sufficiently good long term stability at source temperature.

Typically, most of the silver compounds have low thermal stability. Adding an adduct forming ligand with strong π-acceptor properties was found essential for making silver compounds with good volatility and thermal stability. Among the compounds studied $Ag(fod)(PEt_3)$, a fluorinated β-diketonate adducted with triethylphosphine was found the most suitable precursor. In this compound good volatility is combined with sufficient thermal stability. Another synthesized and tested silver precursor was $Ag(O_2C^tBu)(PEt_3)$ – this compound was used in the first ALD process reported for silver.

For ALD of different chalcogenides and pnictides alkylsilyl compounds of As, Sb, Bi, Se, and Te were synthesized and identified to be excellent precursors when used together with metal chlorides. Introduction of the alkylsilyl compounds opened up a way to easily deposit many chalcogenide materials that were earlier not successfully deposited by ALD. The alkylsilyl compounds are volatile and thermally stable compounds that have sufficiently high reactivity against metal halides and also some other metal compounds.

Preface

The experimental work for this thesis was done during the years 1998-2013 in the Laboratory of Inorganic Chemistry, University of Helsinki. Somehow writing the thesis was delayed, and then the burden started to grow, making it mentally more difficult year by year. However, now it is done. Cheers to that. While this thesis includes results presented in ten papers and deals with ALD precursor compounds for 9 elements, that is of course not all that I have done here at the University of Helsinki during all the years. Alongside and after, among other things, a lot of ALD precursors not included in this thesis have been synthesized and studied. I calculated that over the years, I have synthesized or been involved in synthesizing precursor compounds for 47 elements. The number of individual compounds studied is calculated in hundreds.

I am most grateful to my supervisors Professor Markku Leskelä and Professor Mikko Ritala, for allowing me to work in the interesting field of ALD precursor chemistry and giving advice and guidance during the years. It took a long time – thanks for your patience. It has been a privilege to work in the group and learn from the best.

The official reviewers, professors Risto Laitinen and Charles H. Winter, are acknowledged for their valuable comments on my thesis.

I thank all my present and former co-workers in the former Laboratory of Inorganic Chemistry and in the present group of Materials Chemistry – Thin Films and Other Nanostructured Materials, for being good workmates and helping me with my Ph.D. work. Ph.Lic. Timo Hänninen, who was doing precursor chemistry with me in the beginning, is thanked for co-working, sharing the knowledge, and giving support. Dr. Jarkko Ihanus is thanked for the deposition experiments with the early β-diketonate precursors and the strontium and barium sulfide depositions. Dr. Marko Vehkamäki is thanked for the strontium, barium and bismuth oxide depositions. Dr. Jaakko Niinistö, Dr. Maarit Mäkelä, and Dr. Antti Niskanen are thanked for the silver depositions. Dr. Viljami Pore and Dr. Tiina Sarnet are thanked for the depositions with the alkylsilyl compounds of chalcogen and pnictogen elements. Dr. Ilpo Mutikainen, Dr. Jarno Kansikas, and Dr. Martin Nieger are thanked for teaching and helping me with the single crystal XRD. The contributions of Dr. Marianna Kemell, Dr. Kai Arstila, and Prof. Timo Sajavaara to the papers being part of my Ph.D. work are greatly appreciated.

Thanks to all my friends for a good time outside work. I thank my parents Sirkka and already two years ago departed father Raimo for their love and support. Thank you Arja, for being there for my support and giving understanding during these years.

Financial support from ASM Microchemistry Finland Oy is gratefully acknowledged as well as the support from the Academy of Finland and the former Finnish Funding Agency for Technology and Innovation.

Helsinki, July 2019

Timo Hatanpää

List of publications

This thesis is based on the following original publications, which are referred to in the text by the Roman numerals I – X. The author's contributions are described below each paper.

I T. Hatanpää, M. Ritala, M. Leskelä, Precursors as enablers of ALD technology: Contributions from University of Helsinki, *Coord. Chem. Rev.* **257** (2013) 3297–3322. (Excluding chapter 3. Group IV elements and chapter 6. Platinum group elements.)

The author compiled the literature mostly and wrote the article together with M. R. and M. L. The author did most of the work.

II T. Hatanpää, J. Ihanus, J. Kansikas, I. Mutikainen, M. Ritala, M. Leskelä, Properties of $[Mg_2(thd)_4]$ as a Precursor for Atomic Layer Deposition of MgO Thin Films and Crystal Structures of $[Mg_2(thd)_4)$ and $[Mg(thd)_2(EtOH)_2]$, *Chem. Mater.* **11** (1999) 1846–1852.

The author planned the study, did all the synthesis and analysis work except the single crystal XRD structure determination. The author wrote the first draft of the paper and finalized it with the co-authors.

III T. Hatanpää, J. Kansikas, I. Mutikainen, M. Leskelä, Ancillary Ligand Effect on the Properties of "$Mg(thd)_2$" and Crystal Structures of $[Mg(thd)_2(ethylenediamine)]_2$, $[Mg(thd)_2(tmeda)]$, and $[Mg(thd)_2(trien)]$, *Inorg. Chem.* **40** (2001) 788–794.

The author planned the study, did all the synthesis and analysis work except the single crystal XRD structure determination, which the author took only part. The author wrote the first draft of the paper and finalized it with the co-authors.

IV T. Hatanpää, M. Vehkamäki, J. Kansikas, I. Mutikainen, M. Ritala, M. Leskelä, Synthesis and characterisation of cyclopentadienyl complexes of barium: precursors for atomic layer deposition of $BaTiO_3$, *Dalton Trans.* (2004) 1181–1188.

The author did all the precursor synthesis work: Selected the compounds to study and did all the synthesis and analysis work except the single crystal XRD structure determination, which the author took part. Deposition work was done by M. V. The author wrote the first draft of the paper together with M.V. and finalized it with all the co-authors.

V T. Hatanpää, M. Ritala, M. Leskelä, Crystal structures and thermal properties of $Ba(1,2,4\text{-t-}Bu_3C_5H_2)_2$ and $Sr(1,2,4\text{-t-}Bu_3C_5H_2)_2$: precursors for atomic layer deposition, *J. Organomet. Chem.* **692** (2007) 5256–5262.

The author planned the study and did all the synthesis and analysis work. The author wrote the first draft of the paper and finalized it with the co-authors.

VI M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, Bismuth precursors for atomic layer deposition of bismuth-containing oxide films, *J. Mater. Chem.* **14** (2004) 3191–3197.

The author did all the precursor synthesis work: Selected the compounds to study, did all the synthesis and analysis work. Deposition work was done by M. V. The author wrote the first draft of the paper together with M. V. and finalized it with all the co-authors.

VII T. Hatanpää, M. Vehkamäki, M. Ritala, M. Leskelä, Study of bismuth alkoxides as possible precursors for ALD, *Dalton Trans.* **39** (2010) 3219–3226.

The author did all the precursor synthesis work: Selected the compounds to study, did all the synthesis and analysis work. Deposition work was done by M. V. The author wrote the first draft of the paper together with M. V. and finalized it with all the co-authors.

VIII A. Niskanen, T. Hatanpää, K. Arstila, M. Leskelä, M. Ritala, Radical-Enhanced Atomic Layer Deposition of Silver Thin Films Using Phosphine-Adducted Silver Carboxylates, *Chem. Vapor Depos.*, **13** (2007) 408–413.

The author did all the precursor synthesis work: Selected the compounds to study, did all the synthesis and analysis work. Deposition work was done by A. N. The author wrote the first draft of the paper together with A. N. and finalized it with all the co-authors.

IX M. Kariniemi, J. Niinistö, T. Hatanpää, M. Kemell, T. Sajavaara, M. Ritala, M. Leskelä, Plasma-Enhanced Atomic Layer Deposition of Silver Thin Films, *Chem. Mater.* **23** (2011) 2901–2907.

The author did all the precursor synthesis work: Selected the compounds to study, did all the synthesis and analysis work. Deposition work was done by M. K. The author wrote the first draft of the paper together with M. K. and J. N. and finalized it with all the co-authors.

X V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, Atomic Layer Deposition of Metal Tellurides and Selenides Using Alkylsilyl Compounds of Tellurium and Selenium, *J. Am. Chem. Soc.* **131** (2009) 3478–3480.

The author did all the precursor synthesis work: Selected the compounds to study, did all the synthesis and analysis work. Deposition work was done by V. P. The author wrote the first draft of the paper together with V. P. and finalized it with all the co-authors.

Other publications by the author

1. M. Vehkamäki, T. Hänninen, T. Hatanpää, M. Ritala, M. Leskelä, Growth of $SrTiO_3$ and $BaTiO_3$ Thin Films by Atomic Layer Deposition, *Electrochem. Solid-State Lett.* **2** (1999) 504.
2. M. Ritala, K. Kukli, M. Vehkamäki, T. Hänninen, T. Hatanpää, P. I. Räisanen, M. Leskelä, Atomic Layer Deposition of High-k Oxides, *Electrochem. Soc. Proc.* **2000-13** (2000) 597.
3. A. Niskanen, T. Hatanpää, M. Ritala, M. Leskelä, Thermogravimetric study of volatile precursors for chemical thin film deposition. Estimation of vapor pressures and source temperatures, *J. Therm. Anal. Cal.* **64** (2001) 955.
4. M. Lashdaf, T. Hatanpää, M. Tiitta, Volatile β-diketonato complexes of ruthenium, palladium and platinum. Preparation and thermal characterization, *J. Therm. Anal. Calorim.* **64** (2001) 1171.
5. J. Ihanus, T. Hänninen, T. Hatanpää, M. Ritala, M. Leskelä, Atomic Layer Deposition of SrS and BaS Tthin Films Using Cyclopentadienyl Precursors, *Chem. Mater.* **14** (2002) 1937.
6. T. Hatanpää, T. Hänninen, J. Ihanus, J. Kansikas, I. Mutikainen, M. Vehkamäki, M. Ritala, M. Leskelä, Alkaline Earth Cyclopentadienyl Compounds as Precursors for Atomic Layer Deposition, *Electrochem. Soc. Proc.* **2003-8** (2003) 516.
7. M. Lashdaf, T. Hatanpää, A. O. I. Krause, J. Lahtinen, M. Lindblad, M. Tiitta, Deposition of palladium and ruthenium β-diketonates on alumina and silica supports in gas and liquid phase, *Appl. Catal. A* **241** (2003) 51.
8. J. Ihanus, T. Hänninen, T. Hatanpää, M. Ritala, M. Leskelä, Electroluminescent SrS and BaS Thin Films Deposited by ALD Using Cyclopentadienyl Precursors, *J. Electrochem. Soc.* **151** (2004) H221.
9. J. Harjuoja, T. Hatanpää, M. Vehkamäki, S. Väyrynen, M. Putkonen, L. Niinistö, M. Ritala, M. Leskelä, E. Rauhala, New approach to the ALD of bismuth silicates: $Bi(CH_2SiMe_3)_3$ acting as a precursor for both bismuth and silicon, *Chem. Vapor Depos.* **11** (2005) 362.
10. O. Yu. Pankratova, R. A. Zvinchuk, A. V. Suvorov, T. Hatanpää, V. I. Kozlov, M. Leskelä, Thermal Decomposition of $Ti_5(Se,Te)_8$ in Argon and Nitrogen Atmospheres, *Russ. J. Gen. Chem.* **75** (2005) 1005.
11. O. Yu. Pankratova, J. S. Stepanova, R. A. Zvinchuk, A. V. Suvorov, T. Hatanpää, V. Kozlov, M. Leskelä, Thermal behaviour of titanium seleno-telluride Ti_5Ch_8 in Ar and N_2 atmospheres, *Thermochim. Acta* **428** (2005) 91.
12. R. Matero, A. Rahtu, S. Haukka, M. Tuominen, M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, Scale-up of the Barium Titanate Atomic Layer Deposition Process onto 200 mm Wafer, *ECS Transactions*, **1** (2006) 137.

13. T. Pilvi, T. Hatanpää, E. Puukilainen, K. M. Arstila, M. Bischoff, U. Kaiser, N. Kaiser, M. Leskelä, M. Ritala, Study of a novel ALD process for depositing MgF_2 thin films, *J. Mater. Chem.* **17** (2007) 5077.

14. M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, S. Väyrynen, E. Rauhala, Atomic layer deposition of $BaTiO_3$ thin films - Effect of barium hydroxide formation, *Chem. Vapor Depos.* **13** (2007) 239.

15. M. Vehkamäki, T. Hatanpää, M. Kemell, M. Ritala, M. Leskelä, Atomic Layer Deposition of Ferroelectric Bismuth Titanate $Bi_4Ti_3O_{12}$ Thin Films, *Chem. Mater.* **18** (2007) 3883.

16. K. Kukli, T. Hatanpää, M. Ritala, M. Leskelä, Atomic layer deposition of gadolinium oxide films, *Chem. Vapor Depos.* **13** (2007) 546.

17. S. Dueñas, H. Castán, H. Garcıá, L. Bailón, K. Kukli, T. Hatanpää, M. Ritala, M. Leskelä, Experimental observations of temperature-dependent flat band voltage transients on high-k dielectrics, *Microelectron. Reliab.* **47** (2007) 653.

18. S. Dueñas, H. Castán, H. García, A. Gómez, L. Bailón, K. Kukli, T. Hatanpää, J. Lu, M. Ritala, M. Leskelä, Electrical Properties of Atomic-Layer-Deposited Thin Gadolinium Oxide High-*k* Gate Dielectrics, *J. Electrochem. Soc.* **154** (2007) G207.

19. M. Tyunina, M. Plekh, J. Levoskaa, M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, Dielectric Properties of Atomic Layer Deposited Thin-Film Barium Strontium Titanate, *Integr. Ferrolectr.* **102** (2008) 29.

20. T. Hatanpää, V. Pore, M. Ritala, M. Leskelä, Alkylsilyl Compounds of Selenium and Tellurium: New Precursors for ALD, *ECS Transactions* **25** (2009) 609.

21. M. Leskelä, V. Pore, T. Hatanpää, M. Heikkilä, M. Ritala, A. Schrott, S. Raoux, S. M. Rossnagel, Atomic Layer Deposition of Materials for Phase-Change Memories, *ECS Transactions* **25** (2009) 399.

22. M. Ritala, V. Pore, T. Hatanpää, M. Heikkilä, M. Leskelä, K. Mizohata, A. Schrott, S. Raoux, S. M. Rossnagel, Atomic layer deposition of $Ge_2Sb_2Te_5$ thin films, *Microelectron. Eng.* **86** (2009) 1946.

23. H. Garcia, S. Duenas, H. Castan, A. Gomez, L. Bailon, K. Kukli, T. Hatanpää, J. Aarik, A. Aidla, M. Ritala, M. Leskelä, Electrical characterization of high-k based MIS capacitors using flat-band voltage transients, *in Proceedings of the 2009 Spanish conference on electron devices*, Edited by: A. G. Loureiro, N. S. Iglesias, M. A. A. Rodriguez, E. C. Figueroa (2009) Pages: 223.

24. J. Hämäläinen, T. Hatanpää, E. Puukilainen, L. Costelle, T. Pilvi, M. Ritala, M. Leskelä, (MeCp)Ir(CHD) and molecular oxygen as precursors in atomic layer deposition of iridium, *J. Mater. Chem.* **20** (2010) 7669.

25. K. Knapas, T. Hatanpää, M. Ritala, M. Leskelä, In Situ Reaction Mechanism Studies on Atomic Layer Deposition of Sb_2Te_3 and GeTe from $(Et_3Si)_2Te$ and Chlorides, *Chem. Mater.* **22** (2010) 1386.

26. J. Hämäläinen, T. Hatanpää, E. Puukilainen, T. Sajavaara, M. Ritala, M. Leskelä, Iridium metal and iridium oxide thin films grown by atomic layer deposition at low temperatures, *J. Mater. Chem.* **21** (2011) 16488.

27. J. D. Caldwell, O. J. Glembocki, F. J. Bezares, H. Qi, M. Kariniemi, S. Prokes, J. Niinistö, T. Hatanpää, M. Ritala, M. Leskelä, M. Mastro, Surface Enhanced Raman Scattering Enhancements from Silver Atomic Layer Deposition Coated Nanowire , *IEEE 2011 conference on lasers and electro-optics (CLEO) (2011).*

28. T. Sarnet, V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, A. Schrott, Y. Zhu, S. Raoux, H. Y. Cheng, Atomic Layer Deposition and Characterization of GeTe Thin Films, *J. Electrochem. Soc*. **158** (2011) D694.

29. J. D. Caldwell, O. J. Glembocki, F. J. Bezares, M. I. Kariniemi, J. T. Niinisto, T. T. Hatanpää, R. W. Rendell, M. Ukaegbu, M. K. Ritala, S. M. Prokes, C. M. Hosten, M. A. Leskelä, R. Kasica, Large-area plasmonic hot-spot arrays: sub-2 nm interparticle separations with plasma-enhanced atomic layer deposition of Ag on periodic arrays of Si nanopillars, *Opt. Express* **19** (2011) 26056.

30. T. Hatanpää, K. Kukli, M. Ritala, M. Leskelä, Crystal structures and thermal properties of some rare earth alkoxides with tertiary alcohols*, J. Therm. Anal. Calorim.* **105** (2011) 61.

31. V. P. Heljo, K. Jouppila, T. Hatanpää, A. M. Juppo, The Use of Disaccharides in Inhibiting Enzymatic Activity Loss and Secondary Structure Changes in Freeze-Dried beta-Galactosidase during Storage, *Pharm. Res.* **28** (2011) 540.

32. V. Pore, K. Knapas, T. Hatanpää, T. Sarnet, M. Kemell, M. Ritala, M. Leskelä, K. Mizohata, Atomic Layer Deposition of Antimony and its Compounds Using Dechlorosilylation Reactions of Tris(triethylsilyl)antimony, *Chem. Mater.* **23** (2011) 247.

33. M. F. Cervera, J. Heinämäki, N. de la Paz, O. Lopez, S. L. Maunu, T. Virtanen, T. Hatanpää, O. Antikainen, A. Nogueira, J. Fundora, J. Yliruusi, Effects of Spray Drying on Physicochemical Properties of Chitosan Acid Salts, *AAPS PharmSciTech* **12** (2011) 637.

34. J. Niinistö, T. Hatanpää, M. Mäntymäki, M. Kariniemi, L. Costelle, K. Mizohata, K. Kukli, M. Ritala, M. Leskelä, Cycloheptatrienyl-Cyclopentadienyl Heteroleptic Precursors for Atomic Layer Deposition of Group 4 Oxide Thin Films, *Chem. Mater.* **24** (2012) 2002.

35. J. Hämälainen, J. Holopainen, F. Munnik, T. Hatanpää, M. Heikkilä, M. Ritala, M. Leskelä, Lithium Phosphate Thin Films Grown by Atomic Layer Deposition, *J. Electrochem. Soc.* **159** (2012) A259.

36. J. Hämälainen, F. Munnik, T. Hatanpää, J. Holopainen, M. Ritala, M. Leskelä, Study of amorphous lithium silicate thin films grown by atomic layer deposition, *J. Vac. Sci. Technol. A* **30** (2012) 01A106.

37. I. M. Szilagyi, G. Teucher, E. Härkönen, E. Färm, T. Hatanpää, T. Nikitin, L. Khriachtchev, M. Räsänen, M. Ritala, M. Leskelä, Programming nanostructured soft biological surfaces by atomic layer deposition, *Nanotechnology* **24** (2013) 245701.

38. S. Vuorinen, M. Lahcini, T. Hatanpää, M. Sundberg, M. Leskelä, T. Repo, Bismuth(III) Alkoxide Catalysts for Ring-Opening Polymerization of Lactides and epsilon-Caprolactone, *Macromol. Chem. Physic.* **214** (2013) 707.

39. V. P. Heljo, H. Harju, T. Hatanpää, G. Yohannes, A. M. Juppo, The effect of freeze-drying parameters and formulation composition on IgG stability during drying, *Eur. J. Pharm. Biopharm. A* **85** (2013) 752.

40. P. Jalkanen, V. Tuboltsev, B. Marchand, A. Savin, M. Puttaswamy, M. Vehkamäki, K. Mizohata, M. Kemell, T. Hatanpää, V. Rogozin, J. Räisanen, M. Ritala, M. Leskelä, Magnetic Properties of Polycrystalline Bismuth Ferrite Thin Films Grown by Atomic Layer Deposition, *J. Phys. Chem. Lett.* **5** (2014) 4319.

41. T. Sarnet, T. Hatanpää, E. Puukilainen, M. Mattinen, M. Vehkamäki, K. Mizohata, M. Ritala, M. Leskelä, Atomic Layer Deposition and Characterization of Bi_2Te_3 Thin Films, *J. Phys. Chem. A* **119** (2015) 2298.

42. T. Sarnet, T. Hatanpää, M. Vehkamäki, T. Flyktman, J. Ahopelto, K. Mizohata, M. Ritala, M. Leskelä, $(Et_3Si)_2Se$ as a precursor for atomic layer deposition: growth analysis of thermoelectric Bi_2Se_3, *J. Mater. Chem. C* **3** (2015) 4820.

43. T. Sarnet, T. Hatanpää, M. Laitinen, T. Sajavaara, K. Mizohata, M. Ritala, M. Leskelä, Alkylsilyl compounds as enablers of atomic layer deposition: Analysis of $(Et_3Si)_3As$ through the GaAs process*, J. Mater. Chem. C* **4** (2016) 449.

44. M. Mäkelä, T. Hatanpää, K. Mizohata, K. Meinander, J. Niinistö, J. Räisänen, M. Ritala, M. Leskelä, Studies on Thermal Atomic Layer Deposition of Silver Thin Films, *Chem. Mater.* **29** (2016) 2040.

45. M. Mäkelä, T. Hatanpää, M. Ritala, M. Leskelä, K. Mizohata, K. Meinander, J. Räisänen, Potential Gold(I) precursors evaluated for atomic layer deposition, *J. Vac. Sci. Technol. A* **35** (2016) 01B112.

46. M. Puttaswamy, M. Vehkamäki, K. Kukli, M. C. Dimri, M. Kemell, T. Hatanpää, M. J. Heikkilä, K. Mizohata, R. Stern, M. Ritala, M. Leskelä, Bismuth iron oxide thin films using atomic layer deposition of alternating bismuth oxide and iron oxide layers, *Thin Solid Films* **611** (2016) 78.

47. B. Marchand, P. Jalkanen, V. Tuboltsev, M. Vehkamäki, M. Puttaswamy, M. Kemell, K. Mizohata, T. Hatanpää, A. Savin, J. Räisänen, M. Ritala, M. Leskelä, Electric and Magnetic Properties of ALD-Grown $BiFeO_3$ Films, *J. Phys. Chem. C* **120** (2016) 7313.

48. M. Mäkelä, T. Hatanpää, K. Mizohata, J. Räisänen, M. Ritala, M. Leskelä, Thermal Atomic Layer Deposition of Continuous and Highly Conducting Gold Thin Films, *Chem. Mater.* **29** (2017) 6130.

49. M. Mattinen, T. Hatanpää, T. Sarnet, K. Mizohata, K. Meinander, P. J. King, L. Khriachtchev, J. Räisänen, M. Ritala, M. Leskelä, Atomic Layer Deposition of Crystalline MoS_2 Thin Films: New Molybdenum Precursor for Low-Temperature Film Growth, *Adv. Mater. Interfaces* (2017) 1700123.

50. W. Zhang, D. Avdibegović, R. Koivula, T. Hatanpää, S. Hietala, M. Regadío, K. Binnemans, R. Harjula, Titanium alkylphosphate functionalised mesoporous silica for enhanced uptake of rare-earth ions, *J. Mater. Chem. A* **5** (2017) 23805.

51. J. Tupala, M. Kemell, M. Mattinen, K. Meinander, S. Seppalä, T. Hatanpää, J. Räisanen, M. Ritala, M. Leskelä, Atomic layer deposition of tin oxide thin films from bis[bis(trimethylsilyl)amino]tin(II) with ozone and water, *J. Vac. Sci. Technol. A* **35** (2017) 041506/1.

52. K. Väyrynen, T. Hatanpää, M. Mattinen, M. Heikkilä, K. Mizohata, K. Meinander, J. Räisanen, M. Ritala, M. Leskelä, Diamine Adduct of Cobalt(II) Chloride as a Precursor for Atomic Layer Deposition of Stoichiometric Cobalt(II) Oxide and Reduction Thereof to Cobalt Metal Thin Films, *Chem. Mater.* **30** (2018) 3499.

53. W. Zhang, S. Hietala, L. Khriachtchev, T. Hatanpää, B. Doshi, R. Koivula, Intralanthanide Separation on Layered Titanium(IV) Organophosphate Materials via a Selective Transmetalation Process, *ACS Appl. Mater. Interfaces* **10** (2018) 22083.

54. G. Popov, M. Mattinen, T. Hatanpää, M. Vehkamäki, M. Kemell, K. Mizohata, J. Räisänen, M. Ritala, M. Leskelä, Atomic Layer Deposition of PbI_2 Thin Films, *Chem. Mater.* **31** (2019) 1101.

55. K. Väyrynen, T. Hatanpää, M. Mattinen, K. Mizohata, K. Meinander, J. Räisänen, J. Link, R. Stern, M. Ritala, M. Leskelä: Atomic Layer Deposition of Intermetallic Co_3Sn_2 and Ni_3Sn_2 Thin Films, *Adv. Mater. Interfaces* (2018) 1801291.

56. T. Iivonen, M. Kaipio, T. Hatanpää, K. Mizohata, K. Meinander, J. Räisänen, M. Ritala, M. Leskelä, Atomic layer deposition of cobalt(II) oxide thin films from $Co(BTSA)_2(THF)$ and H_2O, *J. Vac. Sci. Technol. A* **37** (2019) 010908.

57. M. Mattinen, T. Hatanpää, P. J. King, K. Meinander, K. Mizohata, P. Jalkanen, J. Räisänen, M. Ritala, M. Leskelä, Crystalline tungsten sulfide thin films by atomic layer deposition and mild annealing, *J. Vac. Sci. Technol. A* **37** (2019) 020921.

58. K. Väyrynen, T. Hatanpää, M. Mattinen, M. J. Heikkilä, K. Mizohata, J. Räisänen, J. Link, R. Stern, M. Ritala, M. Leskelä, Atomic Layer Deposition of Nickel Nitride Thin Films using $NiCl_2$(TMPDA) and Tert-Butylhydrazine as Precursors, *Phys. Status Solidi A* **216** (2019) 1900058.

59. T. Tiainen, T. T. T. Myllymäki, T. Hatanpää, H. Tenhu, S. Hietala, Polyelectrolyte stabilized nanodiamond dispersions, *Diam. Relat. Mater.* **95** (2019) 185.

60. M. Vehkamäki, T. Hänninen, T. Hatanpää, A. Rahtu, R. Matero, Method for growing oxide thin films containing barium and strontium, *US Pat. Publ.* (2006) US7108747-B1.

61. A. Rahtu, R. Matero, T. Hatanpää, T. Hänninen, M. Vehkamäki, M. Ritala, M. Leskelä, Oxide films containing titanium, *US Pat. Publ.* (2006) US 7108747-B1.

62. M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, Bismuth-containing oxide thin film deposition used as ferroelectric or dielectric materials in integrated circuits involves contacting substrate with first metal reactant which is organic bismuth compound, *US Pat. Publ.* (2007) US7713584-B2.

63. M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, Process for producing oxide films, *US Pat. Publ.* (2009) US7618681-B2.

64. V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, Synthesis and use of precursors for atomic layer deposition of tellurium and selenium thin films, *Int. Pat. Appl. Publ.* (2009) WO2009132207-A2.

65. T. Hatanpää, M. Vehkamäki, M. Ritala, M. Leskelä, Process for producing oxide films, *US Pat. Publ.* (2010) US 7713584.

66. V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, Methods for forming thin films comprising tellurium using atomic layer deposition, *US Pat. Publ.* (2010) US8372483-B2.

67. V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, Synthesis and use of precursors for atomic layer deposition ALD of group va element containing thin films, *Int. Pat. Appl. Publ.* (2011) WO2011056519-A2.

68. T. Hatanpää, J. Niinistö, M. Ritala, M. Leskelä, S. Haukka, Precursors and methods for atomic layer deposition of transition metal oxide films using cycloheptatriene or cycloheptatrienyl-containing metalorganic compounds as precursors, *US Pat. Appl. Publ.* (2011) US2011293830-A1.

69. J. Hämälainen, J. Holopainen, T. Hatanpää, M. Ritala, M. Leskelä, Atomic layer deposition of metal phosphates and lithium silicates for lithium ion batteries, *US Pat. Appl. Publ.* (2012) US2012276305-A1.

70. O. J. Glembocki, S. M. Prokes, J. D. Caldwell, M. Ritala, M. Leskelä, J. Niinistö, E. Santala, T. Hatanpää, M. Kariniemi, Metamaterial thin films having mosaic-like nanostructure with gaps between mosaic elements, *US Pat. Appl. Publ.* (2013) US2013252016-A1.

71. M. Mäkelä, T. Hatanpää, M. Ritala, M. Leskelä, Vapor deposition of thin films comprising gold, *U.S. Pat. Appl. Publ.* (2018), US 20180209041-A1.

72. T. Hatanpää, M. Mattinen, M. Ritala, M. Leskelä, Synthesis and use of precursors for vapor deposition of tungsten containing thin films, *U.S. Pat. Appl. Publ.* (2018), US 20180099916-A1.

73. T. Sarnet, T. Hatanpää, M. Ritala, M. Leskelä, Synthesis and use of precursors for ALD of molybdenum or tungsten containing thin films, *PCT Int. Appl.* (2016), WO 2016191432-A1 .

List of abbreviations and acronyms

AACVD	aerosol assisted chemical vapor deposition
acac	acetylacetonato
ALD	atomic layer deposition
btsa	bis(trimethylsilyl)amido
CBE	chemical beam epitaxy
CIGS	copper indium gallium selenide
CN	coordination number
Cp	cyclopentadienide, cyclopentadienyl
COD	cyclooctadiene
CVD	chemical vapor deposition
deeda	N,N,N',N'-tetramethylethylenediamine
demamp	1-{[2-(dimethylamino)ethyl](methyl)amino}-2-methylpropan-2-oxy
dien	diethylenetriamine
diglyme	bis(2-methoxyethyl) ether, diethyleneglycolether
DME	monoglyme, 1,2-dimethoxyethane
dmeda	N,N'-dimethylethylenediamine
DRAM	dynamic random access memory
DSC	differential scanning calorimetry
DTA	differential thermal analysis;
E	chalcogen or pnictogen
EDS	energy dispersive X-ray spectroscopy
EGA	evolved gas analysis
en	ethylenediamine
fod	1,1,1,2,2,3,3-heptafluro-7,7-dimethyl-4,6-octanedionato
FRAM	ferroelectric random-access memory
GC	gas chromatography
GST	germanium antimony telluride
hfac	hexafluoroacetylacetonato
IC	integrated circuit
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IR	infra-red
LED	light emitting diode
LICVD	liquid injection chemical vapor deposition
MEthd,	1-(2-methoxyethoxy)-2,2,6,6,-tetramethylheptane-3,5-dionato
MLD	molecular layer deposition
mmp	1-methoxy-2-methyl-2-propanolato
MOCVD	metal-organic chemical vapor deposition
MOMBE	metal-organic molecular beam epitaxy
MOSFET	metal oxide semiconductor field effect transistor
MOVPE	metal-organic vapor phase epitaxy
MRAM	magnetoresistive random-access memory
MS	mass spectrometry

NHC	1,3-di-tertbutyl-imidazolin-2-ylidene
NMR	nuclear magnetic resonance
OMCVD	organometallic chemical vapor deposition
PCRAM	phase change random access memory
PEALD	plasma enhanced atomic layer deposition
PECVD	plasma enhanced chemical vapor deposition
Ph	phenyl
PVD	physical vapor deposition
py	pyridine
SDTA	single differential thermal analysis
SERS	surface enhanced Raman scattering or spectroscopy
SCXRD	single crystal X-ray diffraction
tfac	trifluoroacetylacetonato
TG	thermogravimetry
TGA	thermogravimetric analysis
TEM	transmission electron microscopy
THF	tetrahydrofuran
tdfnd	1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dionato
tetragylme	tetraethylene glycol dimethyl ether
thd	2,2,6,6-tetramethylheptane-3,5-dionato
tmeda	N,N,N',N'-tetramethylethylene-1,2-diamine
TMPO	trimethyl phosphate
TOF-ERDA	time-of-flight elastic recoil detection analysis
trien	triethylenetetraamine
triglyme	triethylene glycol dimethyl ether
tritox	tri(tert-butyl)methoxy

Table of Contents

Abstract i

Preface iii

List of publications iv

Other publications by the author vi

List of abbreviations and acronyms xii

Table of Contents 1

1 Introduction 3

2 General background 5

2.1 Chemical vapor deposition and atomic layer deposition 5

2.2 Requirements for ALD precursors 7

2.2.1 Volatility 7

2.2.2 Thermal stability 10

2.2.3 Reactivity 11

2.3 Precursor design and development 13

2.4 Precursors for ALD 16

2.4.1 Metal precursors 16

2.4.2 Non-metal precursors 18

2.4.3 Other precursors 18

3 Experimental 19

4 Results and discussion 20

4.1 Group II metals Mg, Ca, Sr and Ba 20

4.1.1 Precursors used in ALD and other volatile compounds 21

4.1.2 Bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II) and adducts[II,III] 23

4.1.2.1 About β-diketonates 23

4.1.2.2 Synthesis and properties of Bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II) and adducts 25

4.1.2.3 Conclusions 29
4.1.3 Cyclopentadienyl compounds of strontium and barium[I,IV,V] 30
4.1.3.1 About cyclopentadienyl compounds 30
4.1.3.2 Compounds studied: synthesis and properties 31
4.1.3.3 Conclusions 38
4.2 Bismuth 39
4.2.1 Precursors used in ALD and other volatile compounds 39
4.2.2 Precursors for bismuth[I,VI,VII] 40
4.2.2.1 Compounds studied: synthesis and properties 40
4.2.2.2 Conclusions 46
4.3 Silver 46
4.3.1 Precursors used in ALD and other volatile compounds 47
4.3.2 Precursors for silver[I,VIII,IX] 48
4.3.2.1 Compounds studied: synthesis and properties 48
4.3.2.2 Conclusions 51
4.4 Heavier Group 15 and 16 elements As, Sb, Se, and Te 52
4.4.1 Precursors used in ALD and other volatile compounds 53
4.4.2 Alkylsilyl compounds of As, Sb, Bi, Se and Te[I,X] 56
4.4.2.1 Compounds studied: synthesis and properties 56
4.4.2.2 Conclusions 63
5 Conclusions and Outlook 64
References 66

1 Introduction

Thin films are essential in a large variety of modern equipment and technologies. For example, microchips or integrated circuits (IC) are devices relying on thin films and thus without thin films, modern computers, cell phones, and other advanced electronics would not exist. Integrated circuits are typically manufactured layer by layer on semiconductor (n or p-type silicon) substrates. The materials, which are, for example, conducting, semiconducting, or insulating, are deposited and patterned to form different components and functional layers of the circuits. Other application areas of the thin films are also numerous. They are used in optoelectronics, optics, protective coatings, wear-resistant coatings, sensors and detectors, micromechanics, solar cells, all-solid-state lithium-ion batteries, and fuel cells. Therefore, thin films have an essential role in many of the current and future technologies that are around us everywhere.

Thin films are prepared in numerous ways. All the methods have their advantages and disadvantages on which the choice of the method for different applications rely. The methods may be divided into physical and chemical methods and also to liquid phase and gas phase methods. The most widely used method groups are physical vapor deposition (PVD) and chemical vapor deposition (CVD). The CVD methods have several advantages that make them suitable for many applications and especially for microelectronics. CVD methods 1) show good composition control, 2) are potential for large-area growth, 3) deposit highly uniform films, 4) show good doping control, and most importantly, 5) give excellent step coverage on non-planar device geometries.[1]

One unique method among the CVD methods is atomic layer deposition (ALD), which is known for its unique capability to deposit very thin films in a controlled manner. ALD can be used to deposit thin films with one atomic layer precision and superior conformality on extremely complex structures.[1–3] These capabilities are increasingly needed as the microelectronic components, and their features are continuously getting smaller and increasingly three-dimensional.

All the CVD methods, including ALD, rely on chemistry. Precursors are transported through the gas phase to the substrate surface where the films of solid material are formed as a result of chemical reactions on the surface. Thus, the success of chemical thin film deposition process depends largely on the choice of the precursors. Precursor properties together with other factors like growth parameters determine the structure, morphology, composition, and conformality of the deposited films, which in turn determine their various properties such as electrical, optical, and mechanical properties, and finally the performance of the films in different applications.

The need for new precursor compounds obviously raises from the need to deposit materials new for the CVD methods. Also, the existing CVD and ALD materials need new processes and precursors for many reasons such as 1) productivity issues, like lower cost, higher throughput and need to eliminate the usage of solid sources, 2) compatibility requirements, e.g., to solve nucleation problems on different substrates, 3) need for lower deposition temperatures, e.g. with, temperature-sensitive devices or plastic substrates or to prevent/limit island growth of metals, 4) need for higher deposition temperatures, e.g., to obtain crystalline films in the as-deposited state like in the case of $SrTiO_3$, or to minimize impurity contents.

In this work, precursors were synthesized to enable ALD of technologically interesting materials that had not been deposited before by ALD or lacked a decent ALD process. Alkaline earth metals Mg, Sr and Ba needed new precursors to enable deposition of MgO,[II] SrS,[4,5] $SrTiO_3$ [6,7] and other multi-component oxides of strontium, BaS,[5] $BaTiO_3$,[8,9] and $(Sr,Ba)TiO_3$ [9,10] used in various applications like electroluminescent displays and capacitors in future memory chips. Bismuth precursors were developed for deposition of Bi_2O_3 and bismuth-containing multicomponent oxides like $Bi_4Ti_3O_{12}$,[11] $SrBi_2Ta_2O_9$,[VI] and $BiFeO_3$ [12,13] that may be used in memory applications. A silver precursor was needed to enable the growth of metallic silver films for surface-enhanced Raman spectroscopy (SERS) and various other applications.[VIII,IX,14–16] Group 15 and 16 elements As, Sb, Se and Te [X] lacked proper precursors to deposit materials like germanium telluride [17] and germanium antimony telluride (GST) [X,18] that are materials for phase change memories (PCRAM), and Bi_2Te_3,[19] and Bi_2Se_3,[20] thermoelectric materials, $Cu(In_xGa_{1-x})Se_2$, a semiconductor material for solar cells, and GaAs,[21] a semiconductor material for various applications.

As a background for the study, general aspects of making thin films by ALD from the precursor chemist's point of view and precursor chemistry involved in ALD are reviewed. Essential precursor properties and ways to pursue those are discussed.

The experimental part of this thesis is divided into five parts. In the first part, studies on magnesium β-diketonates as potential precursors for ALD are summarized.[II,III] The second part deals with cyclopentadienyl compounds of strontium and barium.[I,IV,V] In the third part, studies on bismuth precursors are described.[I,VI,VII] The fourth part describes silver precursor chemistry studied,[I,VIII,IX] and finally, in the last fifth part, new precursors for selenium, tellurium, arsenic, antimony, and bismuth are described.[I,X] For the last, results are summed up in chapter 5. In addition to results published in the papers I – X, some results unpublished and published in other articles are reported.

2 General background

2.1 Chemical vapor deposition and atomic layer deposition

The name chemical vapor deposition (CVD) describes the main characteristics of the methods under it. “Chemical” implies that the growth of the film takes place through chemical reactions. “Vapor” implies that the precursors forming the film are in vapor form. Precursor compounds are transported through the gas phase to the substrate where the precursors react to form a solid thin film.

There are many methods which differ only slightly from each other, but all together they may be called chemical vapor deposition methods. Some of the names and acronyms for the methods are Metal-Organic Chemical Vapor Deposition, MOCVD, Organometallic Chemical Vapor Deposition, OMCVD, Metal-Organic Vapor Phase Epitaxy, MOVPE, Plasma Enhanced Chemical Vapor Deposition, PECVD, Chemical Beam Epitaxy, CBE, Metal-Organic Molecular Beam Epitaxy, MOMBE, low pressure chemical vapor deposition, LPCVD, Atmospheric Pressure Chemical Vapor Deposition, APCVD, Liquid Injection Chemical Vapor Deposition, LICVD, Aerosol Assisted Chemical Vapor Deposition, AACVD and Atomic Layer Deposition, ALD. Main differences between the differently named methods above are in the precursors used, reaction initiation or promotion method, the structure of the resulting film, system pressure, and the way of introducing the precursors.

In conventional CVD and most of the CVD methods mentioned above, excluding MOMBE, CBE, and ALD, the precursors are (if more than one precursors are used) evaporated, transported through the vapor phase, and introduced to the substrate simultaneously. In the vicinity of the heated substrate or on the substrate surface, the precursors react or decompose to form a solid material.[22,23] Because the precursors are delivered continuously under fixed conditions, the films grow continuously, and the thickness of the films is determined by the growth time. The growth rate and properties of the films are affected by the precursor properties, precursor delivery rate (evaporation temperature), growth temperature, total pressure, partial pressures of precursors, surface conditions, reactor design, and so on. Control parameters are numerous. The main advantages of chemical vapor deposition usually mentioned are high speed and the ability to coat large area substrates and surfaces of complex structures uniformly and conformally without compositional gradients. In comparison, physical methods are line-of-sight methods usually incapable of coating complex structures conformally.[24] PVD methods, however, have the advantage that the films are generally very pure.

Atomic layer deposition (ALD) is unique among the chemical vapor phase methods because it has some major differences compared to the other CVD methods. In ALD, each precursor used is brought to the surface separately. Between the introduction of the different precursors, all the excess precursor and reaction products are purged or pumped away. In an ideal ALD process, during the individual precursor pulse, the precursor adsorbs or reacts with the surface until the surface is filled so that no more precursor can adsorb. The precursors never meet in the gas phase but only on the surface of the substrate. From this, it follows that the growth of the films takes place only through saturative surface reactions. The growth proceeds in cycles

depositing one monolayer or a fraction of a monolayer per cycle (same amount of material in every cycle), and at constant conditions, the film thickness is controlled by the number of growth cycles.[2,25,26] Ideally, the growth rate is not affected by the precursor delivery rate, pressures, or rector design.

Advantages of ALD over conventional CVD methods are the superior capability to coat substrates with extremely demanding features conformally and uniformly with very precise ångström level thickness control. Typically, ALD processes also require much lower temperatures than CVD, although usage of plasma activation lowers the applicable temperatures in CVD, as it also does in the case of ALD. Sometimes the usually much higher growth rate and high throughput of conventional CVD methods are mentioned as advantages over ALD. However, the slowness of ALD may also be considered as an advantage because it is the thing allowing the repeatable and precise deposition of ultra-thin films (<10 nm). Throughput of ALD may also be rendered higher because the nature of ALD allows usage of batch reactors where many substrates may be coated simultaneously.[2] Also, spatial ALD is possible.[27]

As already mentioned, in all the chemical vapor phase methods, the role of the precursors is crucial. The success of the process and the characteristics of the resulting thin films depend largely on the precursors and especially the way how the precursors are combined. The choice of the precursors together with other growth parameters determine the structure, morphology, composition, and conformality of the deposited films which again determine the various properties like electrical, optical, thermal, magnetic, chemical and mechanical properties and the performance of the films in different applications.

All CVD methods, including ALD, inevitably require volatile precursor compounds with adequate thermal stability and reactivity. While as good as possible volatility is most advantageous for both conventional CVD and ALD, due to the differences between the methods mentioned above, thermal stability and reactivity requirements are somewhat different for the two methods. The main requirements for CVD and ALD precursors, i.e., volatility, thermal stability, and reactivity are discussed in the following chapter.

2.2 Requirements for ALD precursors

Main requirements for the precursors for ALD [2] are

- volatility (2.2.1)
- good thermal stability (2.2.2) and
- high reactivity (2.2.3)

All of these three properties are affected by the structures of the compounds and steric and electronic effects present. Other requirements [2] are

- no etching of the film or substrate material
- unreactive and volatile byproducts
- no dissolution into the film or substrate
- sufficient purity
- low price (high yield, simple, scalable synthesis)
- easy to handle (contradictory with the requirement of high reactivity)
- stable during storage
- nontoxic and environmentally friendly

Combining these properties in one molecule is many times a challenging task, and usually one has to compromise between the different properties. In the following, the first three main requirements are discussed in more detail. The differences and similarities with precursors aimed for conventional CVD are considered.

2.2.1 Volatility

Volatility is a common requirement for ALD and CVD precursors. Good volatility is needed for efficient transportation of the precursor. The most preferred precursors are gases and liquids because they usually supply a stable flux. The surface area and particle size of a solid precursor may be varying from a synthesis batch to batch and change when heated/evaporated. This causes variations in the precursor fluxes. Enrichment of less volatile or non-volatile impurities to the surfaces of solid particles during sublimation also causes a change in the sublimation rate. While CVD is quite sensitive for the precursor flux variations, ALD tolerates those better. That is because of the nature of the method: ALD is a self-limiting growth method, and small variations in precursor fluxes should not affect the growth as long as the precursor doses are high enough.

In CVD the precursors should be stable up to the deposition temperature so that they may be transported cleanly. To maintain the self-limiting growth conditions, in ALD, the precursors should be thermally stable at the deposition temperature too (See chapter 2.2.2).

Volatility is a property of liquid and solid substances measured with vapor pressure. The vapor pressure of a solid or a liquid substance is the pressure, which the vaporized part of the substance generates when the gas and condensed phases are in dynamic equilibrium. The vapor pressure is a function of temperature and rises exponentially with the temperature. In ALD the lowest applicable vapor pressure of a precursor is typically 0.1 torr at the highest applicable

evaporation temperature, which is typically 300 °C and sometimes up to 500 ºC.[2] The vapor pressure of a substance is mainly affected by the interactions between the molecules in the solid or liquid phase and the molecular mass. Typically, the most volatile compounds have strong covalent bonds, low molecular mass, and as little as possible intermolecular interactions. Thus, while pursuing the best possible volatility, one must try to prepare a monomeric non-polar compound or a compound with well "shielded" metal-ligand bond if the bond is polar. To keep the molecular weight low, as small as possible ligands should be used, and a balance between the weight and the shielding that prevents the oligomerization should be found.

For many metals, finding volatile compounds is not difficult as even the simplest compounds like halides show sufficient volatility. In some cases also the elements themselves (e.g., Zn, Cd, Hg) possess adequate volatility.[28] However, many metals like the larger alkaline earth metals Ca, Sr, and Ba tend to form oligomeric or polymeric compounds which have low volatility. This tendency arises from the nature of the metals. Large ionic radius combined to small charge causes the metal centers of the complexes to be coordinatively unsaturated in the monomers. To compensate this coordinative unsaturation, the compounds of these metals form oligomers (Figure 1). The electropositivity, i.e., low electronegativity values of the metals causes the metal to ligand bonds to be highly polar, which also makes the compounds prone to interact with surroundings.[29]

To prevent oligomerization and to make monomeric compounds (an example of a monomer is shown in Figure 1) two major strategies have been traditionally used: sterical shielding and filling the coordination sphere of the metal.[30,31]

In the concept of sterical shielding, large organic ligands are used to increase the distance between the polar metal to ligand bonds so that the oligomerization is prevented. The bulk of the ligands hinders the possibility of donor atoms to act as bridging. The concept is effective, but the metal atom usually stays coordinatively unsaturated. Consequently, small molecules like, for example, H_2O, O_2, or NH_3 may coordinate and react with the metal complexes, and cause oligomerization or decomposition. In CVD literature, this is sometimes mentioned as a downside because such precursors may be difficult to handle (exclusion of air and moisture is needed), and are too reactive for controlled deposition.[30] However, considering the ALD usage, the reactivity with small molecules is a clear advantage, and handling issues are secondary compared to the reactivity requirement.

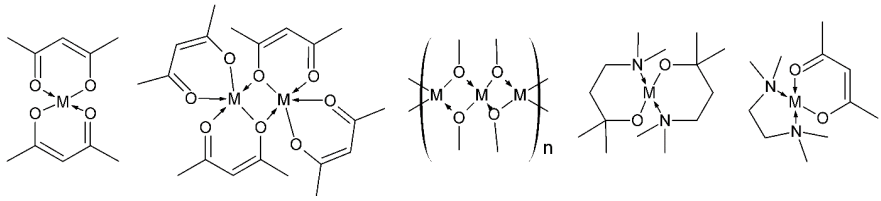


Figure 1 *Examples of a monomer and dimer with chelating β-diketonate ligands, polymer, a metal complex with a donor-functionalized ligand, and an adduct.*

In the concept of filling the coordination sphere of the metal neutral Lewis base or bases are added so that oligomerization is prevented. In other words, Lewis base adducts (Figure 1 shows an example of an adduct) are formed. Multidentate ligands, e.g., polyethers and polyamines with a suitable number of donor atoms, are typically used. Optionally donor-functionalized

ligands, e.g., alkoxy ligands, which have additional ether or amine functionalities (Figure 1), can be used. Coordinating donor ligands also transfer charge to the metal ion and cause the polarizing strength of the metal to reduce. This results in a reduction of intermolecular interactions and enhanced volatility.[32] For this concept, it is essential that the Lewis bases bond to the metal strongly enough so that they will not dissociate during sublimation/evaporation of the complex. Donor-functionalized ligands may have an advantage over the separate ionic ligands and neutral Lewis base ligands in a sense that there is no separate neutral ligand that could dissociate and get lost. However, the coordinated ancillary donor atom may detach from the metals coordination sphere leading to a loss of the coordinative saturation. A disadvantage of using this concept is the possibility that the multidentate ligands may instead of coordinating to one metal center form a bridge between metal centers and cause oligomerization.[30]

Also or connected to the above strategies, prevention of oligomerization and enhancement of volatility may be pursued by tuning the electronic properties. Complexes with ligands making less polar bonds with the metal are likely to be more volatile. A smaller difference between the electronegativities of the metal and donor atom makes the metal to ligand bond polarity lower. While the metal in question and the coordinating atom of the ligand mostly affect the bond polarity also the structure and substituents on the ligand do have some effect. Having electron-withdrawing or donating groups in the ligand affects the basicity, i.e., electron donation properties of the ligand. Electron donating groups, e.g., ^{t}Bu, increase the electron density at the donor atoms and make the ligands stronger electron donors (more basic). This also means slightly less polar metal to ligand bonds. On the negative side, higher basicity of the donor atom causes increased bridge forming tendency for the donor atom.[31] Electron withdrawing substituents make the ligands weaker electron donors (less basic) and thus the metal-ligand bonds more polar, which is considered as a negative effect. However, some electron-withdrawing groups may also have positive effects. Fluorinated ligands, i.e., ligands with electron-withdrawing substituents, are used quite commonly to increase volatility. That is because fluorine is an electron-rich substituent, which causes the ligands to repel each other, thus decreasing the intermolecular interactions and promoting the volatility of the complexes. Lower basicity of the donor atom also makes the ligand less likely to act as a bridge forming ligand.[31] Another positive effect is that due to the lower basicity of the ligand and consequent higher acidity of the metal center, Lewis bases coordinate more strongly to metals with fluorinated ligands. For example, polyether adducts of $Ba(thd)_2$ are thermally unstable and lose polyethers in sublimation while polyether adducts of $Ba(hfac)_2$, in contrast, sublime intact.[30] The downside of the fluorinated ligands, however, is that fluorine may be incorporated in the films. Though the fluorine atoms in the ligands repel each other, they may interact with the metal atoms.[33,IX]

Ligands to be avoided for the sake of volatility are those containing aromatic groups because they quite usually show intermolecular π-stacking interaction.[34] The ligand choice may also affect the melting point of a compound. Ligands with more degrees of freedom and less symmetry tend to have lower melting temperatures.[35]

In addition to pursuing sufficiently volatile compounds, technical solutions allowing usage of compounds with lower volatility as precursors have been developed. Such methods are, for example, aerosol assisted CVD (AACVD) [36] and liquid injection CVD (LICVD).[37]

2.2.2 Thermal stability

Precursors used in all chemical vapor deposition processes should ideally be stable at the evaporation temperature, i.e., source temperature, and at the transport temperatures. At the deposition temperature, the stability requirement is usually completely different for conventional thermal CVD and ALD. In ALD the precursors ideally should not decompose but adsorb on the substrate surface. The precursor decomposition destroys the self-limiting growth mechanism characteristic of ALD. In contrast, in thermal CVD, decomposition is usually a requirement. In many cases precursors with high volatility and low thermal decomposition temperature are searched for – in the majority of CVD processes, precursors should decompose cleanly at the deposition temperature without leaving any impurities in the films. Obviously, this is not always the case – many CVD processes rely on reactions between two or more precursors. For example, Al_2O_3 is deposited using $AlCl_3 + CO + H_2$. At the heated reaction zone, CO and H_2 form H_2O, which hydrolyzes $AlCl_3$. This process circumvents the problem of otherwise too high reactivity between $AlCl_3$ and H_2O.[38] Though an ideal ALD precursor does not show any thermal decomposition at the deposition temperatures, in practice some decomposition may be allowed. The extent of tolerated decomposition depends on the process, material, and application. In many cases, processes which are operating at temperatures where precursors decompose slowly, are quite viable as long it is possible to keep the precursor exposure times short, i.e., the reaction forming the film is fast. As the degree of decomposition increases with time, long exposure times result in more decomposition.[2]

Thermal stability of a substance may be defined as resistance to a permanent change in the properties caused solely by heat. In thermal decomposition, also called thermolysis, a compound undergoes a thermally activated internal reaction, which accelerates with increasing temperature, and increases linearly with time. The standard measure of thermal stability is the temperature at which a compound starts to decompose substantially, i.e., decomposition temperature. It is said substantially because, in practice, it is quite impossible to define a temperature where the decomposition exactly starts but a point where it is occurring with a certain rate may be determined. While most compounds show gradually increasing decomposition with rising temperature, some compounds show a clear threshold temperature for decomposition. If the decomposition process is highly exothermic, it is likely that the decomposition is very fast because the released heat accelerates the decomposition reaction. Also, the decomposition products may further accelerate the decomposition.

Thermal stability may be different in the solid state, in the gas phase and when adsorbed on the surface. This is because of the various interactions the compounds are experiencing. In the gas phase, the partial pressure may also affect the stability if there is a possibility that individual precursor molecules react with each other or other gas molecules: the more molecules, the more collisions, and the more reactions. It seems that thermal stability in the gas phase is quite often lower than in the solid phase.

For approaching the thermal stability issue, there does not seem to be any common strategies. Obviously, the choice of ligands is crucial when trying to make a compound with better thermal stability, but the preference is usually different for each metal. However, in general, one could say that it is beneficial to have strong metal to ligand bonds and a ligand which itself has no weak points. One may also design the ligands so that the possible mechanisms through which the thermolysis may take place are hindered. For example, in the

case of amidinates and guanidinates, ligand design has been used to block the primary decomposition pathways of β-hydrogen elimination and deinsertion.[39] The compounds prepared had better thermal stability compared to compounds where those mechanisms are possible.

Thermal decomposition of the ligand may limit the thermal stability of a compound, but in most cases, the thermal decomposition is connected to the stability of the metal complex as a whole. In some cases, the ligands may be so large that the steric strain causes them to be unstable. As an example, alkoxy ligand tritox, tri(tertbutyl)methoxy, may be mentioned.[40] Adduct compounds have quite often low thermal stability as the ancillary Lewis base ligands tend to dissociate. In many cases, fluorine in the primary charged ligands clearly enhances the stability of the adduct complexes. This has been said to be due to the increase in the Lewis acidity of the metal center which causes the Lewis bases to coordinate more strongly to the metals.[29,32] Generalizing, using charged ligands with less basic donor atoms may enhance the stability of the adducts.

For predicting the thermal stabilities of different molecules, computational chemistry may prove useful. Metal to ligand bond strengths and bond strengths in the ligand, thermal decomposition energy, and activation barrier may be calculated.[41] From the determined crystal structures and bond lengths therein, one might be able to estimate bond strengths and thermal stabilities in relative terms.

The strict thermal stability requirements of conventional CVD and ALD have been circumvented by inventing technical solutions like the above mentioned LICVD and AACVD methods.[36,37] LICVD tackles the long term thermal stability issues. The precursors dissolved in some suitable solvent are kept at room temperature and delivered into the reactor as needed by injecting the solution into a heated evaporator. AACVD allows usage of thermally stable compounds that do not otherwise have sufficient volatility. Also, by using activated co-precursors like O_3 or plasma gases, lower growth temperatures may be used, and thus precursors with lower thermal stability may be used.

2.2.3 Reactivity

In ALD, reactivity is determined as the tendency of the precursor to undergo a chemical reaction with a co-precursor, i.e., the reactivity of a precursor can only be considered relative to the co-precursor. In both methods, ALD and conventional CVD, the precursors should react on the substrate surface (or in its vicinity) cleanly and leave no impurities. In the cases of CVD where multiple precursors are used too reactive combinations of precursors must be avoided – too high reactivity causes precursors to react in the gas phase, which in turn causes powdery films to form.[22,42] Conformal growth in three-dimensional substrates will also get very difficult if not impossible. In ALD where the precursors are never simultaneously present in the gas phase, usage of highly reactive precursor combinations is possible and usually beneficial. Fast, aggressive reactions ensure rapid completion of reactions and thereby short cycle times and effective precursor utilization, which are crucial for achieving high throughput important for industry.

Reactivity is characterized by thermodynamics and kinetics. Thermodynamics, i.e., the change of the Gibbs free energy (ΔG) in the reaction, tells whether a reaction is favorable. The

more negative the energy is, the more favorable the reaction is, i.e., the products are more stable compared to the precursors. While negative ΔG is usually essential for good ALD reaction, it may not be used solely to predict whether some reaction is good. This is because Gibbs free energy tells nothing about the kinetics, i.e., the rate of a reaction.[2] It may be that the reaction is too slow to be good for ALD. Increasing the growth temperature may be used to enhance the rate of the reaction but only up to the limit set by the thermal decomposition of the precursor.

The nature of bonding between elements varies due to the properties of the elements. While the electropositive s block metals form complexes, which have a lot of ionic character in their bonds with ligands, many of the more electronegative metals/metalloids form bonds with quite a lot covalent character. These differences highly affect the reactivity of different compounds toward different co-precursors. Compounds with highly covalent character hardly follow the same predictions as the ionic compounds.

Considering ALD precursors, it is usually better to use large sterically demanding ligands than try to fill the coordination sphere of the metal with ancillary donor ligands or by using donor-functionalized ligands. For CVD, the opposite is many times true. Complexes synthesized using the first strategy are usually more reactive against small molecules like H_2O while compounds synthesized using the other strategy more often may lack the reactivity – unless donor-functionalities detach from the metal coordination.

The electronic factors may be used to affect the reactivity of metal complexes towards surface groups and small molecules, e.g., hydroxyl groups and H_2O. Electron withdrawing groups (e.g., CF_3) in the ligand are likely to lower the reactivity toward H_2O and OH groups while electron-donating groups in the ligand should increase the reactivity. The above is connected to the pK_a values (Brønsted acid character) of the protonated ligands. The less acidic the protonated ligand (i.e., the more basic the conjugate base) is, the higher the reactivity is. In other words, the reaction equilibrium is on the side of the protonated ligand and metal oxide, and the ΔG is more negative. Along this theory for example descending pK_a values [43] of $^{i}Pr_2NH$ (36 measured in THF), Hbtsa (26 measured in THF), $^{t}BuOH$ (17), CpH (15), Hacac (9), Htfac (7), Hhfac (7), and AcOH (4.76) indicate descending reactivity of the complexes with the corresponding ligands towards surface OH groups and H_2O. Obviously, the pK_a values can be used to estimate reactivity only roughly. Also, the theory does not seem to apply to all cases, e.g., metal halides. To get a better estimation, one should consider the whole reaction, not just the favorability of formation of the free ligand.

Computational chemistry has been used to predict the reactivity.[44,45] By sketching the possible reaction schemes and calculating the energies of species involved, thermodynamic favorability may be predicted. By sketching the possible reaction intermediates and calculating their energies, it may be possible to predict the kinetics of the reactions. The effect of the electron-donating and electron-withdrawing groups in the ligands is reflected in the pK_a values as mentioned above, but also the energies related may be calculated. By calculating the energy connected with the Brønsted basicity of the deprotonated ligand ($L^- + H_2O \rightarrow H\text{-}L + OH^-$) and the energy connected with the Lewis basicity ($MOH + L^- \rightarrow ML + OH^-$), the total hydrolysis energy that predicts the reactivity more reliably may be obtained.[46,47]

One may also predict the reactivity by considering the compounds reacting and forming in the light of the Lewis hard–soft acid–base (HSAB) theory. If in the reaction hard–soft and soft–hard acid-base pairs turn into hard–hard and soft–soft pairs, the reaction is likely to be

favorable. Unfavorable reactants and favorable products mean more negative Gibbs free energy and good reaction for ALD.[48] Also a precursor compound with unfavorable HSAB combination is likely to be more reactive.

Many times the difficulty to find reactive precursor combinations has been solved by using activated co-precursors, e.g., radicals, plasma, or ozone.

2.3 Precursor design and development

Starting to develop a new ALD process for a specific material there is, of course, some reason for it. The material may be new for ALD or the processes developed so far might be unsuitable or non-ideal for the application intended. If the case is the latter, the first thing is obviously to identify the problems of the existing processes and try to find the reasons behind these problems. If the problem is precursor-related, is it the volatility, stability, or reactivity? This gives directions for the molecular design to be done. This chapter describes the process of designing and developing precursors for ALD. Figure 2 sketches the process.

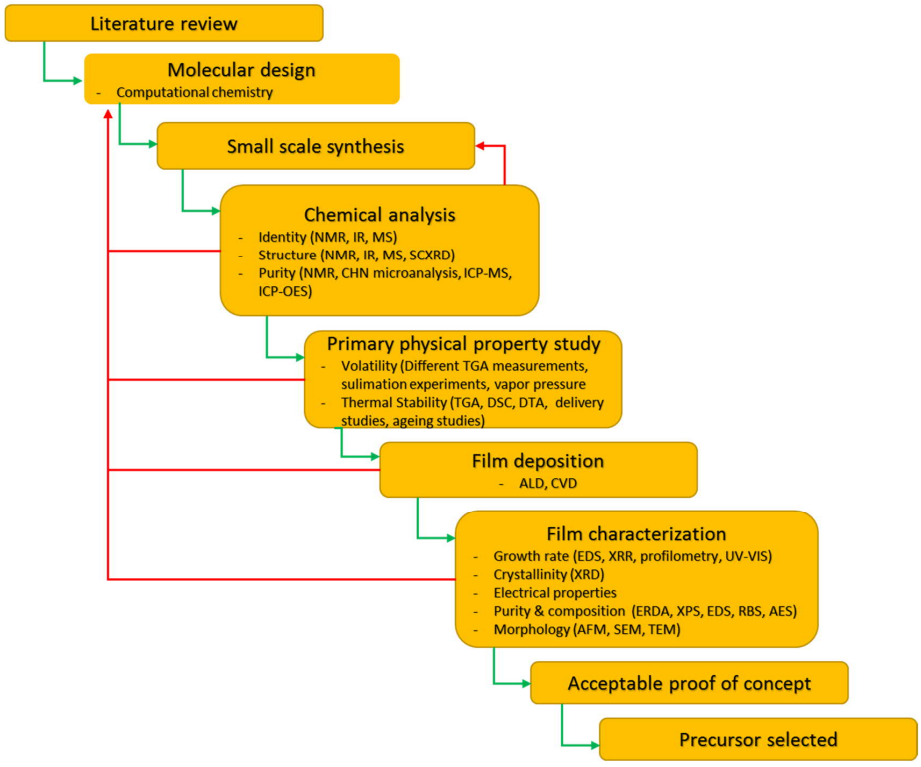


Figure 2 *Precursor design and development cycle. Modified from the Chart presented by Kanjolia et al.[49]*

The first thing to do is a literature review. The literature on ALD and CVD processes discussing materials containing the constituents of the material aimed for should be searched. Precursors used in thermal CVD processes may or may not work in ALD. CVD precursors probably have proper volatility, but quite often their thermal stability and reactivity are not optimal for ALD. Deposition temperatures used in thermal CVD may give some idea about the decomposition temperature of a compound. A high temperature needed in CVD is good considering the thermal stability requirement of ALD. Notes on reactions between different precursors in the gas phase, making the film growth difficult, prove high reactivity, which is also good news from the ALD point of view.

If there is no CVD or ALD literature on the required element or if it is clear that none of the known precursors is good for the application intended one should look for literature about the coordination and organometallic compounds of the element. Synthesis publications with some volatility data (e.g., purification by sublimation) and thermal analysis papers may be helpful. Already a comment on that a compound is volatile is good. If an oxide process is aimed for, any mentions of air or moisture sensitivity predict good reactivity. One should also work out the properties of the element/metal concerned and find out what would be the main problems to expect with various compounds of the element. Are the issues related to volatility, thermal stability, or reactivity? Next one should try to assess the properties of the known compounds. It is quite possible that known compounds are suitable precursors, but they just have not been found yet for the application.

Before the synthesis, one may try to estimate the thermodynamic favorability of different process options. There may be thermodynamic data available for some possible precursor compounds in the literature. There are even computer programs which utilize literature data and can be used to calculate thermodynamic data under different conditions.[50] For example, data on transformation from solid or liquid to gas phase species gives vapor pressure of a compound. One may also conduct computational studies. Theoretical calculations may predict, e.g., bond strengths, thermolysis energies, and barriers, chelation energy, hydrolysis energy, formation energy, *etc*., which are related to the stability and reactivity of the precursors.[41]

After the careful literature survey, possible computational studies and possibly checking the thermodynamics, one should exploit the outcome to choose the compounds for synthesis study. After synthesis, isolation, and purification, the compounds should be analyzed to identify them and to find out their structures. Methods usually used are solution NMR, MS, IR, elemental microanalysis, and single crystal X-ray diffraction (SCXRD), which will most certainly prove the identity and structure of the synthesized compound. The purity of the prepared compound is essential for many applications and may be assessed using ICP-MS or ICP-OES. Next, the physical characteristics of the compound should be studied. These include volatility, thermal stability, and reactivity. Volatility and thermal stability are easily studied by using thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) or differential thermal analysis (DTA).

A simple dynamic TG measurement with a constant heating rate will reveal whether a compound evaporates as an intact molecule or if the compound shows ligand dissociation or thermal decomposition. A TG curve with one step, exponentially increasing rate of weight loss and zero residue indicates that the compound is volatile and thermally stable under the used conditions at least up to the temperature at which the evaporation is complete. Any residue or multiple steps in the TG curve of a pure compound usually indicate decomposition of the

compound. Thermal stability may be further studied by conducting the TG measurements in crucibles with lids that have a small orifice through which the evaporation takes place. Another option is to use larger samples. Crucibles with lids and larger samples may also be combined. When larger samples are measured, or crucibles with lids are used, part of the sample inevitably experiences higher temperature than in the case of smaller sample or crucible without a lid. If in such an experiment, the residue is larger compared to the measurement without a lid, it is an indication of thermal decomposition. TGA may also be used to study long-term thermal stability and evaporation rates of compounds by making isothermal or stepped isothermal measurements. Evaporation rates, in turn, may be used to estimate the vapor pressures of the compounds.[51–53] Accurate vapor pressures of compounds are most relevant information but measuring low vapor pressures of solid and liquid compounds may be quite complicated and require special equipment.[54] A TG curve measured under vacuum is also valuable because it may be considered as a simulation of the actual conditions in an ALD reactor. Vacuum TGA is valuable also because many potential precursors that show decomposition in normal pressure TGA may evaporate/sublime under reduced pressure. However, TGA equipment with good leak-free vacuum and capability of measuring samples not releasing gases but vapors of normally solid or liquid compounds are not usually available. In the absence of vacuum TGA, sublimation experiments under vacuum can be used to study the volatility and thermal stability. Important things to observe are the sublimation yield and composition before and after sublimation. DSC or DTA measurements are also informative when studying thermal stability. Temperatures and energies connected with processes like melting, evaporation, other phase changes, reactions, and decomposition may be observed.

In connection to TGA thermolysis mechanisms may be studied in-situ by evolved gas analysis (EGA) using, e.g., in-situ (GC)MS or IR, or ex-situ by NMR analysis.[39] MS with controlled heating of the sample works too: by observing intensities of different ions decomposition temperatures of compounds may be estimated. Such measurements have been used even to suggest decomposition mechanisms.

Thermal stability as a function of time (aging) or raising temperature may also be studied without any actual thermal analysis equipment. In such an experiment, the sample is heated, and the composition is checked ex-situ using, e.g., NMR, IR, or TGA/DSC. To study the thermal stability in the gas phase, a system with a temperature gradient oven has been used.[55] A precursor sample was placed in an evacuated and sealed ampoule which was inserted in the oven so that the precursor at one end of the ampoule was at a convenient evaporation temperature. During the experiment, the precursor evaporated, diffused toward higher temperatures and produced visually observable deposits to the walls of the ampoule or substrate pieces placed at the bottom of the ampoule at temperature zones where decomposition took place. This system was designed to mimic the ALD reactor environment. A simple zone oven with MS connected may also be used to study the thermal stability in the gas phase.[56]

Some hints of the reactivity (both kinetics and thermodynamics) may be acquired before going into the ALD experiments by mixing the precursors in solution and observing whether there is any reaction and how fast this reaction is.

Finally, when a good candidate for a new process has been found, it will be tested in ALD experiments, and the film quality and properties will be characterized. It might be that several co-precursor options have to be tested. Only this last step can give the final answer whether a process/precursor is good. The feedback obtained in the different phases of the precursor characterization is used to design and synthesize better precursors. Thus, a cycle of precursor development is created (Figure 2).

2.4 Precursors for ALD

In general, the precursors may be classified on the bases of what they are supposed to deliver into the growing film. Three main categories are 1) metal precursors, 2) non-metal precursors and 3) other precursors, which include, e.g., reducing agents, or precursors eliminating the ligands when metal films are aimed.

In ALD, typically, one precursor delivers one element into the growing films, but there are also single source precursors, which deliver several components in one precursor. Components may be different metals or metal/metals and non-metal/non-metals. Single source precursors are quite rare in ALD but common in conventional CVD.

Other precursors used are molecule precursors used in depositing fully organic materials or hybrid materials. However, deposition of these materials is molecular layer deposition (MLD), which is similar to ALD, but instead of layering atoms, molecules are layered.

There are some reviews where precursors used in ALD have been listed extensively.[28] Precursors for elements dealt with in the experimental work presented in this thesis have been reviewed for some extent in the articles I – X. Below precursors are represented only in general level.

2.4.1 Metal precursors

As noted above, when making precursors compounds for ALD, different metals have different challenges. Anyhow, the main challenge is to combine all the required properties in one compound – to find a balance between all the wanted properties. For some metals, it may be quite easy to find volatile compounds, but these are not necessarily thermally stable enough or reactive with appropriate co-precursors, or vice versa. In Figure 3, most general classes of metal precursors are shown.

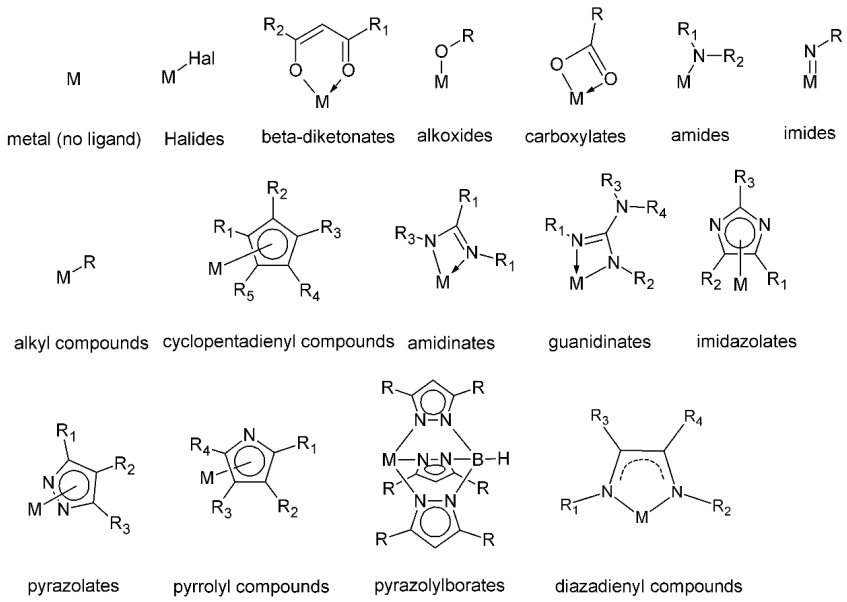


Figure 3 *General classes of metal precursor compounds frequently used.*

If a compound consists only one kind of ligands, it is called homoleptic. If there is two or more different kind of ligands, the compound is called heteroleptic. In general, homoleptic metal precursors can be classified into three types: inorganic precursors which do not contain carbon, metal-organic precursors which contain an organic ligand but do not possess metal-carbon bonds, and organometallic precursors which possess organic ligands and metal-carbon bonds. Though certain ligands have their intrinsic geometries and ways to bond, the structures and properties of the forming metal complexes depend on both the ligands and the metals themselves. As discussed already above, properties of the metals, which particularly affect the properties and structures of the forming complexes, are ionic radius, electron configuration, and charge density. These properties govern the nature of the bonds, which form between the metal and certain ligand. For example, the electronegativity difference determines the amount of ionic character or covalency, and the availability of d-electrons for bonding cause d-block elements to bond strongly with some neutral ligands (e.g., CO) that have only weak interactions with main group elements. Because the properties of metal complexes depend so much on the metal itself, it is not possible to make general conclusions on the properties of a certain compound group as a whole.

A large set of known ligands may be used as building blocks while designing new precursors. Also, one may develop new ligands. In tailoring the properties of compounds, heteroleptic compounds are becoming increasingly important. With the right combination of ligands appropriate reactivity, thermal stability and volatility may be pursued. It is thought that the best properties of each ligand could be combined in the heteroleptic compound. Adducting the complexes with neutral ligands not to mention donor-functionalized ligands should not be forgotten either. Options are numerous.

Multimetal single-source precursors still wait for their breakthrough in ALD. These compounds have their downsides like inability to control the stoichiometry between metals, and upsides like the possibility for faster growth and the possibility, that while it may be difficult to find volatile and thermally stable compounds for a single metal, multimetal compounds of the metal may possess such properties.

2.4.2 Non-metal precursors

The most frequently used non-metal precursors in ALD are hydrides like H_2O, H_2S, and NH_3 used for oxides, sulfides, and nitrides, respectively. For oxides, also O_3 is used frequently. Elements O_2, S, Se, Te, As and Sb have been used for the corresponding compounds. Alcohols, H_2O_2, HCOOH, CH_3COOH with alkoxides and N_2O have been used for oxides, HF, TiF_4 and TaF_4 for fluorides, alkylamides of Te, Te alkyls, $tBuAsH_2$, $tBuPH_2$ and alkylsilyl compounds of As, Sb, Se and Te for corresponding pnictides and chalcogenides.[28] The usage of plasma activated gases (oxygen, nitrogen, ammonia) has also become increasingly frequent.

Some compounds used as a metal precursors may also act in the role of nonmetal precursor. The role depends on the combination of the precursors. Examples of such cases are deposition of metal fluorides (e.g., MgF_2, CaF_2), using TiF_4 or TaF_5 as fluorine precursors.[57–59] In some cases, metal precursor has provided both the metal and nonmetal, e.g., reactions of metal halides with metal alkoxides to deposit binary or ternary metal oxide films.[28,60]

2.4.3 Other precursors

Precursors used as reducing agents and for eliminating the ligands when depositing metal films are yet another class of precursors. Examples of such precursors are hydrogen, formic acid, $BH_3(NHMe_2)$, hydrazine, tert-butylhydrazine, N,N'-bis(trimethylsilyl)dihydropyrazine, 1,4-bis(trimethylsilyl)-2-methyl-2,5-cyclohexadiene and plasma-activated NH_3, N_2, and N_2/H_2.[28,61–64]

3 Experimental

All preparations and manipulations of air and moisture sensitive compounds were done under rigorous exclusion of air and moisture using standard Schlenk techniques, and Ar or N_2 filled glove box. Dried solvents were used. Reagents used in synthesis were purchased from Sigma-Aldrich, Strem, Acros, Merck, and Alfa-Aesar, and purified using conventional methods when needed. NMR (^{1}H and ^{13}C), MS, CHN elemental microanalysis, TGA/SDTA, IR, and single crystal X-ray diffraction were used to analyze and characterize the synthesized compounds. Compounds showing properties suitable for ALD were tested in growth experiments using ASM Microchemistry F120 reactor or Beneq TFS-200 reactor. Detailed descriptions of the experimental procedures and equipment used can be found in the original publications (II – X).

4 Results and discussion

4.1 Group II metals Mg, Ca, Sr and Ba

Technologically interesting thin film materials containing alkaline earth metals are many. Materials and applications have been listed in the articles I – V. For example, MgO can be used in buffer layers for ferroelectric materials,[65,66] ternary and quaternary oxide materials like $SrTiO_3$, $BaTiO_3$, $(Sr_xBa_{x-1})TiO_3$ are high permittivity dielectrics and ferroelectrics, which may be used in future DRAMs and FRAMs,[67,68] CaS, SrS, and BaS are host materials for luminescent materials,[69,70] and MgF_2 and CaF_2 are wide band-gap low refractive index materials for optics.[71]

The larger alkaline earth metals Ca, Sr and Ba are especially challenging from the CVD/ALD precursor chemistry point of view because due to the coordinative unsaturation many of their compounds tend to form oligomeric species, which have low volatility. This, in turn, is due to the properties in Table 1: small charge combined with a large radius and electropositive nature of the elements. Thus, sufficiently volatile, thermally stable and reactive compounds of alkaline earth metals are not that common.

Table 1 *Ionic radius,[72] charge/ionic radius ratio, Pauling's electronegativity [73] of Mg, Ca, Sr and Ba and calculated iconicity [74] of M – O, and M – C bonds.*

Metal ion	Ionic radius [Å]/coordination	Charge/ionic radius [e/Å]	Electronegativity (Pauling)	Ionicity* of M – O bond [%]	Ionicity* of M – C bond [%]
Mg	0.72/6	2.78	1.31	67.8	31.9
Ca	1.00/6	2.00	1.00	77.4	45.1
Sr	1.18/6	1.69	0.95	78.8	47.3
Ba	1.35/6	1.48	0.89	80.3	49.8

*Ionicity calculated from Pauling's equation $Q = 1 - e^{-1/4(x_A - x_B)^2}$ where x_A and x_B are electronegativities of the elements involved.[74]

In addition to general curiosity, our interest to the precursors for group II metals originated from the industry needs. At the time beginning the studies, apart from a few exceptions (Mg and $MgCp_2$),[75–79] the only precursors that had been used in ALD for group II metals were β-diketonates which had been used to deposit fluorides using HF as the fluorine precursor,[80] and sulfides using H_2S as the sulfur precursor.[70–87] Processes for alkaline earth metal oxides were practically missing.

At first, the alkaline earth metal containing materials of interest in our laboratory were alkaline earth sulfides used as hosts in electroluminescent materials. For this purpose, β-diketonates had been found generally suitable but by no means perfect precursors.[88] Among other things, the varying quality and aging of the precursors were issues hampering the usage of plain β-diketonates. Precursors resulting in better quality films without any repeatability issues were desired. Motivated by these needs, synthetic studies on β-diketonates of alkaline earth metals were conducted.[II,III,87] In addition to aiming better precursors, the idea was to

get some experience, insight, and deeper understanding of β-diketonates and synthetic precursor chemistry overall.

While still studying the β-diketonates, interest in making oxides of alkaline earth metals by ALD was raising. Materials known for some time, like high-temperature superconductors and high permittivity dielectrics, received increasing attention and microelectronics industry started to show a growing interest, for example on ALD of $SrTiO_3$ thin films. At this point, it was realized that the β-diketonates were not suitable precursors for depositing oxides, because of the lack of reactivity with H_2O, and new more reactive precursors were needed. Based on literature searches, cyclopentadienyl compounds were chosen to be studied.

4.1.1 Precursors used in ALD and other volatile compounds

Precursors used in ALD of alkaline earth metal containing materials until 2012 were listed in the publication I and after that only a few additions have emerged. Basically the precursors used have been restricted to β-diketonates and cyclopentadienyl compounds with only a few exceptions which are elemental Mg,[75,76] Sr-Ta double metal alkoxides,[89–92,VI] and more recent additions of pyrrolyl compound of Ba,[93] amidinates of Mg and Ca,[94] pyrazolylborates[95,96] and imidazolates.[97] Processes published since 2013 are gathered in Table 2.

Many of the β-diketonates of alkaline earth metals have sufficiently good volatility and thermal stability to be used as ALD precursors. β-diketonates have sufficient reactivity against H_2S, HF, TiF_4, and TaF_5, and by using these co-precursors sulfides and fluorides have been deposited. With the most common and preferable oxygen precursor, H_2O, β-diketonates do not react efficiently, and with ozone carbonate contamination of the films is substantial in the case of Ca, Sr, and Ba.[98,99] With oxygen plasma carbon contamination might be avoided.[100,101] Cyclopentadienyl compounds, by contrast, have high reactivity against H_2O and most likely many other co-reactants as well. Also, many of them are quite volatile and very stable thermally.

The most common compounds used in CVD are β-diketonates, β-ketoiminates and other related compounds, which are less suitable for ALD due to insufficient reactivity or thermal stability. In addition to these compounds, there are quite a lot of volatile compounds used in CVD and compounds which have been considered as possible precursors for CVD and ALD.[30] The large list of potential or rarely used precursors includes silylamides and silyl phosphides, carbazolyl compounds, cyclopentadienyl compounds, alkoxides, β-diketonates, β-ketoiminates, β-diketiminates, carboxylates, *etc.*

Heteroleptic compounds with proper volatility and thermal stability have also been synthesized. Ligand combinations are, e.g., thd and donor-functionalized alkoxy ligand, Cp ligand, and thd ligand.[102,103]. Sr(demamp)(thd), a compound with alkoxy and β-diketonato ligand has been successfully used to deposit $SrTiO_3$ by ALD.[104,105]

Table 2 *Alkaline earth metal containing ALD processes reported from 2013 forward.*

Metal precursor	Other precursor(s)	Material deposited	Reference
$Mg(C_5H_5)_2$	H_2O	MgO	106,107
$Mg(EtC_5H_4)_2$	H_2O	MgO	108
	HF-py	MgF	109
	HF	MgF	110
$Mg(^sBuNCMeN^sBu)_2$	$Ca(^iPrNCHN^iPr)_2$, H_2O	$Mg_xCa_{1-x}O$	94
$Ca(thd)_2$	tereftalic acid	Ca-tereftalate	111
	O_3	$CaCO_3$	98
	O_3	$CaCO_3$	112
	O_3, H_2O, TMPO	$CaLaPO_4$	113
$Ca(^iPrNCHN^iPr)_2$	H_2S	CaS	114
	$Mg(^sBuNCMeN^sBu)_2$, H_2O	$Mg_xCa_{1-x}O$	94
$Sr(thd)_2$	$Co(acac)_3$, O_3	$SrCO_3/CoO_x/SrCoO_3$	115
Sr(demamp)(thd)	$Ti(Me_5C_5)(OMe)_3$, H_2O, O_3	$SrTiO_3$	104,105
$Sr(^iPr_3C_5H_2)_2$	H_2O	SrO	116
	$Ti(O^iPr)_4$, O_3	$SrTiO_3$	117
	$Ti(NMe_2)_4$, H_2O	$SrTiO_3$	118
	$Ti(NMe_2)_4$, H_2O	$SrTiO_3$	119
	$Ti(O^iPr)_4$, H_2O	$SrTiO_3$	120
	$Ti(O^iPr)_2(thd)_2$ H_2O for Sr O_3 for Ti	$SrTiO_3$	121
	$(Me_5C_5)_2Ti(OMe)_3$ H_2O for Sr O_3 for Ti	$SrTiO_3$	108,122,123
	$Ti(O^iPr)_4$, La(amidinate)$_3$, H_2O	$LaSrTiO_3$	124
	(DMPD)(EtCp)Ru, RuO_4, O_2	$SrRuO_3$	125
$Sr(^iPr_3C_5H_2)_2$(DME)	$(Me_5C_5)Ti(OMe)_3$, O_2–plasma	$SrTiO_3$	126
	$(Me_5C_5)_2Ti(OMe)_3$, O_2–plasma	$SrTiO_3$	127
	$(Me_5C_5)_2Ti(OMe)_3$, O_2–plasma	$SrTiO_3$	128
	$(Me_5C_5)_2Ti(OMe)_3$, O_2–plasma	$SrTiO_3$	129
$Sr(^tBu_3C_5H_2)_2$	$Ti(OCH_3)_4$, H_2O	$SrTiO_3$	130,131
$Ba(^iPr_3C_5H_2)_2$	$Ti(O^iPr)_4$, H_2O	$BaTiO_3$	132
	$Ti(O^iPr)_4$, H_2O	$BaTiO_3$	133
	$Ti(O^iPr)_4$, O_2-plasma	BaO, $BaTiO_3$	134
Pyrrole-Ba	$Ti(O^iPr)_4$, H_2O	$BaTiO_3$	93

4.1.2 Bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II) and adducts [II, III]

Magnesium is a smaller (see Table 1) and thus easier to cope metal compared to the larger Ca, Sr and Ba. At the beginning of my precursor chemistry studies, this was one reason choosing Mg as a starting point. Another reason was that at that moment, studies of Mg β-diketonate compounds were rarer than studies of Sr and Ba β-diketonate compounds.

Before our work, the structure of $Mg(thd)_2$ was not known, and there were controversial characteristics reported. In our studies, $Mg(thd)_2$ was introduced to ALD for the first time, and the adducts prepared were also new.

4.1.2.1 About β-diketonates

As mentioned above, for the group II metals β-diketonates are the most common precursors used in CVD and the first ones used in ALD. This is probably because of the easy synthesis, simple handling (though sometimes even too careless), sufficient volatility and thermal robustness of the compounds.

The most important feature of the β-diketonato ligand is the ability to bond through both oxygen atoms to metal and delocalize the charge of the ligand in the formed C_3O_2M ring. This feature gives the β-diketonato compounds their unique covalent like characteristics, i.e., solubility to organic solvents, sufficiently high volatility, and exceptional stability among metal-organic compounds.

The β-diketonato ligand may act as a terminal or bridging ligand usually between 2 – 3 metal atoms. When the ligand is terminal, it usually bonds to the metal through both of the two oxygen atoms and the charge is delocalized in the six-member chelate ring. When the ligand is bridging, usually both oxygen atoms are bonded to the same metal, and additionally, either only one or both of the oxygen atoms are bonded to other metal centers. However, there are cases where one oxygen of the bridging ligand is bonded to one metal atom and the other oxygen to another metal atom.[135,136] To conclude, there are many possibilities to form bridges, and thus, several different oligomeric structures are possible.

Like alkoxides, β-diketonates may not branch from the α-position regarding the metal. However, β-diketonates always have the possibility of chelation and thus a better ability to cover the metal. The tendency to act as a terminal ligand follows the same line with the alkoxides: large and fluorinated ligands are the most probable terminally acting ligands because of steric effects and reduced oxygen basicity.[31] Structures of plain unadducted β-diketonates of alkaline earth metals Mg – Ba vary from dimeric to oligomeric and polymeric. β-diketonates with the most simple acetylacetonato ligand are trimeric (Mg),[137] oligomeric or polymeric, and practically involatile. Growing the steric hindrance of the ligands increases the volatility by lowering the oligomerization degree. In the solid state with the most common sterically demanding β-diketonato ligand, 2,2,6,6-tetramethylheptane-3,5-dionato, magnesium forms a dimer,[II] calcium [87,138] and strontium[139] trimers, and barium a tetramer.[140–142] An apparent trend of decreasing volatility and increasing degree of aggregation is seen while going from magnesium to barium.

While synthesizing β-diketonates of the alkaline earth metals, the products have been quite different depending on the synthesis, and purification methods and conditions. This is due to the tendency of the metal ions to take solvents and other Lewis base molecules into their coordination sphere, and react with them (e.g., H_2O reacts to form OH or O bridges and causes a release of β-diketone). Compounds referred as, for example, "$Ba(thd)_2$" have been instead of the pure $[Ba(thd)_2]_4$, for instance, $Ba_5(\mu^5\text{-}OH)(thd)_9(H_2O)_3$,[143] $Ba_6(O_2)(thd)_{10}(H_2O)_6$ [144,145] or $Ba_5(thd)_9Cl(H_2O)_7$.[146] β-diketonates have also been said to suffer from extensive aging already at quite low temperatures, but this may have been at least partly because of the impure compounds or improper handling of the compounds. Quite many of the β-diketonates of the larger alkaline earth metals are sensitive to moisture, and possibly oxygen and carbon dioxide.

The most volatile unadducted β-diketonates are those with fluorinated ligands. The extent of the fluorination correlates almost without exceptions with the volatility. Though fluorinated ligands are good for pursuing volatility, they have a downside of causing possible fluorine contamination in the thin films. For this reason, fluorinated β-diketonates have almost completely been ignored in ALD of alkaline earth metal containing films, an exception being the case where a fluoride film was aimed.[147]

The volatility of β-diketonates has been extensively pursued using the concept of filling up the metal coordination sphere. This has been done by using multidentate Lewis bases and by adding a lariat chain containing donor-functionalities to the β-diketonato ligand. Depending on the bulkiness of the β-diketonato ligands and the adduct forming ligand(s) the number of donor atoms needed in the Lewis base to fulfill the coordination sphere of a given metal to form a monomeric compound varies. Magnesium β-diketonates turn monomeric with one bidentate or two monodentate adduct ligands (CN = 6). Monomeric β-diketonates of calcium are seen with a coordination number 6 at the lowest while monomeric strontium and barium β-diketonates are seen with a coordination number 7 at the lowest. The highest coordination numbers observed are 6, 10, 10, and 12 for Mg, Ca, Sr, and Ba, respectively.[30] Considering the volatility, the best results have been gained using fluorinated β-diketonato ligands and polyamines or polyethers as the adduct forming ligands. The most volatile barium compound known is probably $Ba(tdfnd)_2$(tetraglyme) (tdfnd = 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dionato) which sublimes intact at 90 °C/10^{-2} torr or 160 °C/760 torr.[148,149] Quite often, adducts also show lower melting point temperatures. Adding multidentate Lewis bases to non-fluorinated β-diketonates of strontium and barium have given less successful results as typically these compounds show dissociation on an attempted sublimation. The difference between the adducts with the fluorinated and non-fluorinated β-diketonato ligands is because of the less basic oxygen donor atoms on the fluorinated β-diketonato ligands which cause higher acidity of the metal center, which again causes Lewis bases to coordinate more strongly. In the case of magnesium and calcium, which are more acidic in the Lewis sense, thd complexes with diamines and polyamines have been shown to sublime intact below certain threshold temperatures.[III,87] There have been some non-successful [150,151] and successful attempts to enhance volatility using β-diketonato ligands with polyether lariat appendages: $Sr(MEthd)_2$ (MEthd = 1-(2-methoxyethoxy)-2,2,6,6,-tetramethylheptane-3,5-dionato) is a dimeric compound evaporating intact at temperatures similar with $Sr(thd)_2$.[152–154] The compound has also been used in ALD combined with plasma activated oxygen.[100] In addition, some β-ketoiminates, close relatives of β-

diketonates, with polyether side chains connected to the nitrogen atom are known to have enhanced volatility. The barium β-ketoiminates have dimeric or monomeric structures depending on the length of the polyether appendage.[155–157] However, thermal stabilities of the β-ketoiminates have been low, and they have not been used in ALD.

4.1.2.2 Synthesis and properties of bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II) and adducts

Bis(2,2,6,6-tetramethylheptane-3,5-dionato)magnesium(II) was synthesized using the traditional and simple metathesis route.[158] $MgSO_4$ was reacted with Na(thd) in $EtOH/H_2O$ solution. $Mg(thd)_2$ was also synthesized by the reaction of $MgBu_2$ with Hthd in toluene.[57] The latter non-aqueous method gave close to 100% yield without any purification step needed while the aqueous route required purification by sublimation and resulted in ~60% yield. This proves that the non-aqueous route is much more viable in laboratory scale synthesis. Adducts of $Mg(thd)_2$ were synthesized by reacting $Mg(thd)_2$ with appropriate Lewis bases (ethylenediamine, en; N,N'-dimethylethylenediamine, dmeda; N,N'-diethylethylenediamine, deeda; N,N,N',N'-tetramethylethylenediamine, tmeda; diethylenetriamine, dien; triethylenetetraamine, trien; 1,2-ethanediol, 1,3-propanediol) in hexane or EtOH. Dmeda and tmeda adducts were also prepared by one-pot synthesis where the adduct forming ligand, $MgSO_4$ and Na(thd) were reacted in aqueous solution. Yields of the synthesis were quantitative. To see whether the method is applicable to all alkaline earth metals, also adducts of $Ca(thd)_2$, $Sr(thd)_2$ and $Ba(thd)_2$ were prepared. Polyamines dien and trien were used, and the general applicability was confirmed. Benefits of the method are that it is simple and makes it possible to synthesize water, hydroxyl group, and oxygen atom free metal β-diketonato adducts in water solutions with good yields. In using this method, it is essential that proper multidentate Lewis bases capable of driving H_2O off the coordination sphere are used. Earlier the one-pot method had been used to synthesize tetraglyme adducts of $Sr(hfac)_2$ and $Ba(hfac)_2$.[159]

$Mg(thd)_2$ was found to have a dimeric structure in a solid (Figure 4), so actually, the molecular formula should be written as $Mg_2(thd)_4$. Magnesium atoms are five and six coordinated. All the adducts prepared whose structures were solved (EtOH, en, tmeda, trien, 1,2-ethanediol), had six coordinated magnesium. Adducts $Mg(thd)_2(EtOH)_2$ (Figure 5a) and $Mg(thd)_2$(tmeda) (Figure 5b) were strictly monomeric. When a polydentate ligand with more than two donor atoms was used as the adduct forming ligand (trien), two of the donor atoms coordinated to one Mg center while the other two stayed uncoordinated (Figure 5d). The NH_2 group at the free end of the trien ligand was found to be 3.766 Å from the neighboring Mg. Ethylenediamine adduct, $Mg(thd)_2$(en) (Figure 5c), and the two diol adducts, $Mg(thd)_2$(1,2-ethanediol) (Figure 6) and $[Mg(thd)_2(EtOH)]_2$(1,3-propanediol), show hydrogen bonding between the ligands of the neighboring structure units (OH···O 1.968 and 1.856Å).

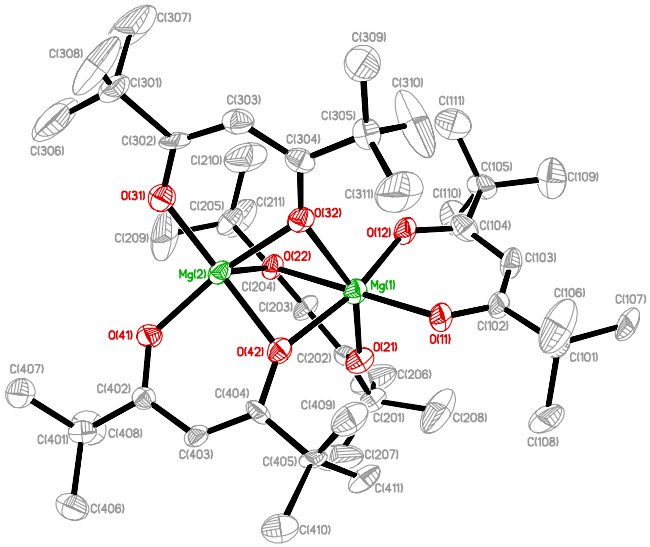


Figure 4 *Structure of $Mg_2(thd)_4$.[II] Hydrogen atoms are omitted for clarity, thermal ellipsoids are at 30% level.*

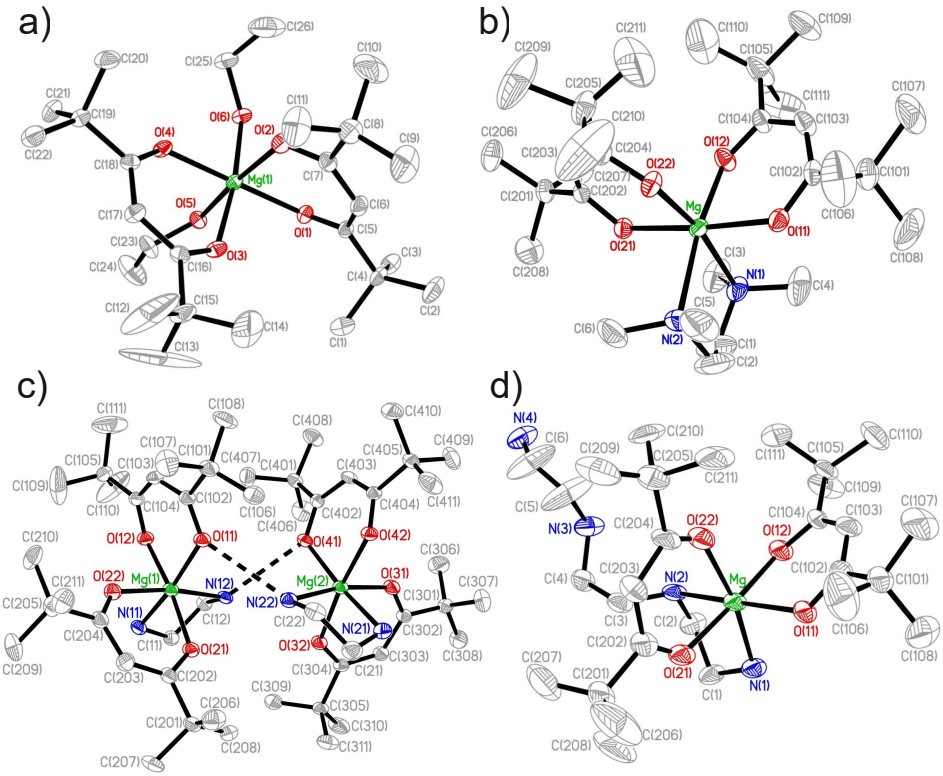


Figure 5 *Structures of a) $Mg(thd)_2(EtOH)_2$, b) $Mg(thd)_2$(tmeda), c) $Mg(thd)_2$(en) and d) $Mg(thd)_2$(trien).[II,III] Hydrogen atoms are omitted for clarity, thermal ellipsoids are at 30% level.*

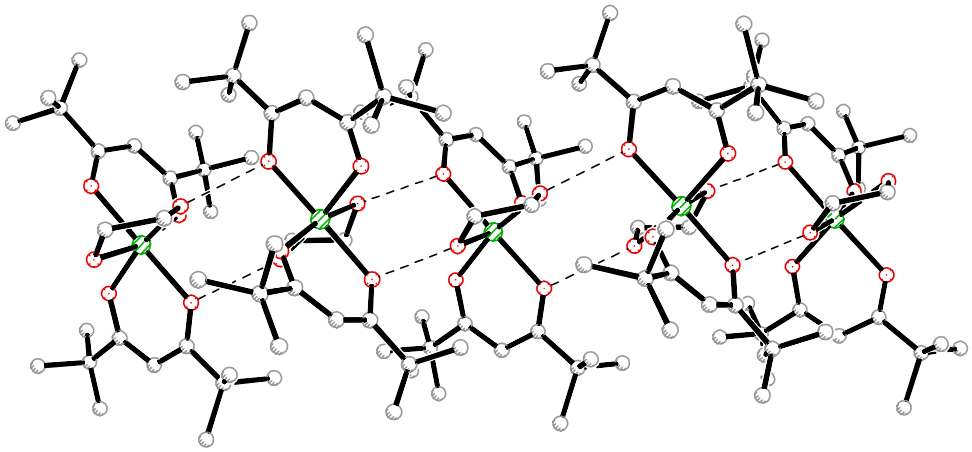


Figure 6 *Structure of $Mg(thd)_2$(1,2-ethanediol) [III]. Hydrogen atoms are omitted for clarity.*

Volatility and thermal stability of $Mg_2(thd)_4$ was found to be ideal considering the usage in ALD. TGA (10 °C/min, flowing N_2, 1 atm) for $Mg_2(thd)_4$ (Figure 7) showed pure evaporation behavior with zero residue and completion at approximately 300 °C indicating that as a liquid (mp 122 – 126 °C) the compound is thermally stable at least up to this temperature. Monodentate adducts $Mg(thd)_2(EtOH)_2$ and $Mg(thd)_2(H_2O)_2$ showed first a loss of the adduct forming ligands and then evaporation of the $Mg_2(thd)_4$ species (Figure 7) – no reactions to form oxo or hydroxy bridged oligomers, like in the case of larger alkaline earth metals,[160–162] took place. In addition, all the amine adducts showed practically complete volatility in TG measurements. Diamine adducts, however, showed two overlapping steps indicating dissociation of the amines at temperatures above ~220 °C. For the dien and trien adducts, only one step was seen, but it is not likely that intact compounds evaporated as vacuum sublimation at lower temperatures resulted in partial dissociation (see below) – more likely the thd complex and amine evaporate separately at the same temperature range. TG curves measured for the 1,2-ethanediol and 1,3-propanediol adducts showed decomposition, though the residues at the end of the TG measurements were quite low (5.4 and 2.2%, respectively). The behavior of $Mg(thd)_2$(1,2-ethanediol) may be explained in terms of internal hydrolysis reactions which are promoted by the hydrogen bonding seen in the crystal structure.

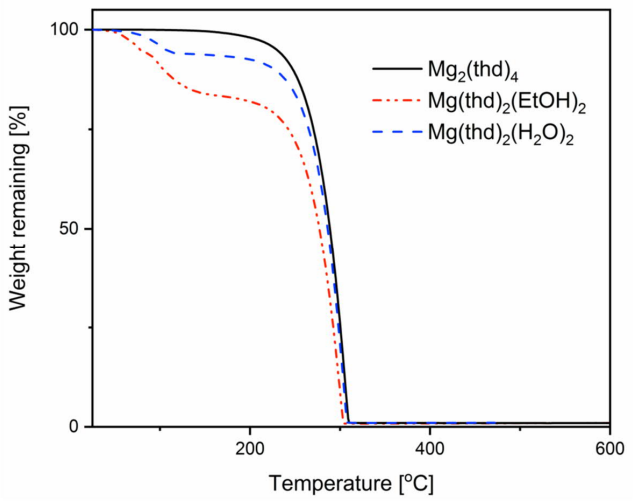


Figure 7 *TG curves measured for $Mg_2(thd)_4$, $Mg(thd)_2(EtOH)_2$ and $Mg(thd)_2(H_2O)_2$.*

While in atmospheric pressure TGA the evaporation and probable dissociation of the amine adducts was seen at temperatures above 200 °C, vacuum sublimation of the compounds could be done at much lower temperatures (75 – 170 °C/0.18 – 1.20 mbar). Sublimation of plain $Mg_2(thd)_4$ and diamine adducts resulted in sublimates identical with the unsublimed compounds proving that below a certain dissociation temperature the compounds do evaporate intact. Diamines and the triamine dien also seemed to enhance the volatility as indicated by the lower vacuum sublimation onset temperatures.[III] $Mg(thd)_2$(dien), however, showed partial dissociation, i.e., loss of the adduct forming ligand dien, and $Mg(thd)_2$(trien) turned into $[Mg(thd)_2]_2$(trien). Mass spectrometry for $Mg_2(thd)_4$ did show the molecular ion but the base peak seen was $[Mg(thd)_2 - {}^tBu]^+$. For the amine adducts, $[Mg(thd)_2(A)]^+$ and $[Mg(thd)(A)]^+$ ions containing the amine were seen corroborating the evaporation of the intact adducts. However, small peaks originating from $[Mg_2(thd)_3]^+$ and $[Mg_2(thd)_4]^+$ were also seen indicating possibly some dissociation.

No ALD growth was observed when $Mg_2(thd)_4$ was combined with water. ALD growth experiments done, using $Mg_2(thd)_4$ and 30% H_2O_2 solution as precursors, resulted in ALD type growth of MgO at temperatures between 325 and 425 °C. Other synthesized magnesium complexes were not tested because of the discouraging results and better emerging precursors. In addition, the TG measurements indicated that the adducts tended to dissociate at temperatures well below the temperatures where the film growth from $Mg_2(thd)_4$ took place. The low growth rate of 0.1 Å/cycle observed with $Mg_2(thd)_4$ was said to be due to steric limitations between the adsorbed $Mg(thd)_x$ species [III] but rethinking it is more likely due to the low reactivity of $Mg_2(thd)_4$ or $Mg(thd)_2$ towards the surface OH and H_2O_2. An increase of the growth rate indicating decomposition of the precursor was seen at 450 °C, and also when the pulse lengths at 450 °C were increased. It was noted that $Mg_2(thd)_4$ alone does not decompose to MgO at 450 °C since pulsing of only $Mg_2(thd)_4$ did not result in any film growth. It was concluded that the MgO film formed in the reactions between $Mg_2(thd)_4$ and H_2O_2 catalyzes the $Mg_2(thd)_4$ decomposition.

4.1.2.3 Conclusions

With magnesium, volatility is easier to achieve than with Ca, Sr, and Ba because of the smaller size and lower electropositivity of magnesium. With the thd ligand, a dimeric compound [II] is formed while Ca, Sr and Ba form trimeric and tetrameric structures.[138–142] The highest coordination number observed for magnesium was six while coordinative saturation of Ca, Sr and Ba require 8 – 13 coordinating atoms. Adducts of Mg, Ca, Sr and Ba may be synthesized conveniently with excellent yields using a one-pot method and aqueous conditions providing the adduct forming ligands are capable of saturating the metals coordination sphere. While adducts of $M(thd)_2$ (M = Sr, Ba) tend to dissociate when sublimed, some diamine adducts of $Mg(thd)_2$, similarly to $Ca(thd)_2$(tetraen),[87] can be sublimed intact under reduced pressure. This observation corroborates the assumption that the thermal stability of the adducts gets weaker while going from Mg to Ba as the Lewis acidity of the metal ions gets lower. Adducting with diamines and dien also seem to enhance the volatility of $Mg(thd)_2$ slightly. However, using the adducts as ALD precursors would not make sense because they still do dissociate at temperatures well below viable growth temperatures. Thus there hardly would be any difference between using an adduct or plain $Mg_2(thd)_4$. Adducting $Mg(thd)_2$ in order to make a compound that is not sensitive to moisture may be rational. Though $Mg(thd)_2(H_2O)_2$ is stable at least for short periods on storage and releases H_2O reversibly when heated, storing for a long time may cause deterioration. What comes to ALD, $Mg_2(thd)_4$ does not react with H_2O to form MgO, and with H_2O_2 the reaction is quite inefficient, leading to low growth rate at temperatures below the decomposition temperature. $Mg_2(thd)_4$ seems to be stable at least up to 425 °C. Oxides may be deposited using $Mg_2(thd)_4$ if a more efficient oxygen source like O_3 or oxygen plasma is used – as shown later on by Putkonen *et al.*[163] Unlike $Sr(thd)_2$ and $Ba(thd)_2$, $Mg(thd)_2$ combined with O_3 deposited pure MgO without carbonate contamination. However, substantially long O_3 pulses were needed to achieve saturative growth.

4.1.3 Cyclopentadienyl compounds of Strontium and Barium [I, IV, V]

Realizing the limitations of β-diketonates of alkaline earth metals as precursors for ALD of oxides, i.e., the limited reactivity with H_2O and the tendency to form carbonates when O_3 is used,[98,99] another precursor option was needed. After a literature search, the decision to study and synthesize cyclopentadienyl compounds of strontium and barium was made.

ALD processes using cyclopentadienyl compounds of alkaline earth metals are listed in the publication I and Table 2. Only the usage of $MgCp_2$ was reported before our work.[77–79] In MOVPE $MgCp_2$ had been employed as a dopant for semiconductors GaAs, GaN and AlGaN.[164–167] Cp compounds of alkaline earth metals had been suggested as precursors for CVD frequently starting from beginning of the '90s, but actual reports on using them were absent with the exception of some Japanese patent applications,[168–171] one article on CVD of CaF_2 [172], and one on CVD of BaO and SrO.[173] To date, apart from the papers above still no reports on alkaline earth cyclopentadienyl compounds in conventional CVD exist. This is most likely because of the high reactivity of the compounds, which makes them quite difficult to use in CVD – and also better precursors for CVD do exist. In contrast, high reactivity is highly beneficial for ALD.

4.1.3.1 About cyclopentadienyl compounds

Cyclopentadienyl compounds, in general, are known for most of the metals, and many of them are volatile. Cyclopentadienyl ligands are coordinatively and sterically very demanding ligands compared to most of the other ligand groups. Cyclopentadienyl ligands may be highly substituted as each of the five ring carbon atoms may accommodate a substituent. It is also possible to bridge two rings together to an *ansa*-compound. Usually, the negative charge of the cyclopentadienyl ligand is delocalized to the whole five-membered ring, which is π bonded to a metal through all the five ring atoms in η^5-style. Though the Cp ring is bonded through all the five carbon atoms, it is considered a formal tridentate ligand – Cp ligand is a 6-electron donor and is therefore formally counted as a tridentate ligand when calculating the coordination number of the metal. In the case of Mg (and Be) η^1- or η^2-bonding is seen in several structures with small Cp ligands and ancillary Lewis bases.[174–176] In $MgCp_2$ adducts, the coordination number of Mg varies from 5 – 8. In addition to the Cp ligands, no more than two donor atoms are seen to coordinate to Mg. To compensate the coordination of ancillary Lewis base ligands one of the Cp ligands flip to η^1-, η^2- or η^3-coordination and in some cases even ion-pair compounds are formed. With Ca, Sr, and Ba η^5 is the only primary coordination mode seen, except a few structures with substituted fluorenyl ligands.[177,178] Cp ligands may bridge between two or several metal centers. The bridging may take place through the interaction of the ring carbon atoms or the atoms in the substituents with the adjacent metal centers. Bridging through the ring carbon atoms is seen in the case of the larger alkaline earth metals Ca, Sr and Ba and small Cp ligands. Such a structure is for example known for $[BaCp_2 \cdot Me_2SO]_n$ (catena-(bis(μ^2-η^5,η^5-cyclopentadienyl)-barium dimethylsulfoxide solvate), which is fully polymeric with each barium atom tetrahedrally surrounded by four η^5-coordinated C_5H_5 rings.[179] $Ca(C_5H_5)_2$ is also fully polymeric and each Ca atom is surrounded by two η^5, one η^3 and one η^1 Cp ligands.[180] These bridging and polymeric structures are obviously the reason for the low

volatility of these compounds. In contrast, the smaller magnesium ion forms a highly volatile monomeric compound with the unsubstituted Cp ligand.[176,181]

The tendency of the cyclopentadienyl ligands to act as a terminal η^5-ligand grows with the bulkiness of the ligand. A large number of different substituted cyclopentadienyl ligands starting from the small methylcyclopentadienyl up to large penta(isopropyl)cyclopentadienyl have been introduced to the organometallic chemistry of alkaline earth metals. In publications by Hanusa *et al.* [182–184] a large number of Cp compounds of alkaline earth metals are presented with melting and sublimation temperatures, and some other relevant data.

Comparing the sublimation temperatures, it seems that the volatility of the Sr and Ba compounds increases with the bulkiness of the Cp ligands. Most of the cyclopentadienyl compounds of alkaline earth metals are thermally very stable. It is notable that while the simplest Cp compounds of Ca, Sr, and Ba have low volatility, their thermal stability is still exceptional among all metal-organic and organometallic compounds of these elements. For example, $BaCp_2$ survives sublimation at 440 – 460 °C in high vacuum.[185]

Metallocenes with donor-functionalized cyclopentadienyl ligands have been studied to some extent.[186,187,IV] In most cases, the additional donor atoms coordinate intramolecularly and prevent oligomerization, though the donor atoms in the side chains might also remain uncoordinated or cause intermolecular interactions. Though many adducts of the alkaline earth metal cyclopentadienyl compounds are monomeric, the volatility of the compounds does not increase upon adducting. The adduct forming ligands tend to dissociate before or during the sublimation.

4.1.3.2 Compounds studied: synthesis and properties

Barocenes and strontocenes were prepared by metathesis reactions between appropriate metal iodides and potassium salts of the appropriate cyclopentadienyl ligands in THF. Group II metal iodides and alkali metal cyclopentadienides were used because they have some solubility into coordinating solvents like THF. Group II metal chlorides and bromides have negligible solubility. The compounds synthesized are summarized in Table 3.

All the complexes prepared except those with the donor-functionalized ligands $EtOC_2H_4C_5Me_4$ and $Me_2NC_2H_4C_5Me_4$ have such an open coordination sphere that coordination of solvent molecules was eminent always when crystallized from a coordinating solvent (THF). Unadducted complexes and THF adducts have good solubility in polar solvents THF and toluene. Compounds with larger ligands dissolve easily also to nonpolar solvents like hexane.

Adducts of $Ba(Me_5C_5)_2$ were synthesized by adding the appropriate Lewis base to THF or toluene solution of $Ba(Me_5C_5)_2(THF)_n$. Most of the adducts prepared were found to have surprisingly low solubility despite the monomeric structures observed. They dissolved sparingly to toluene and only moderately to THF. Only the adduct with triglyme was found to have better solubility. The low solubility of adducts has been observed in other studies too.[188,189]

All the complexes prepared were found to be extremely air and moisture sensitive so that even a few seconds exposure to air practically destroyed the samples. Adducting was hoped to lower the sensitivity, but the effect seemed negligible: adding multidentate Lewis base molecules to the coordination sphere of barium in $Ba(Me_5C_5)_2$ did not notably lower the sensitivity.

Table 3 *Cyclopentadienyl compounds synthesized and studied.*

Compound	mp [°C]	T(subl) [°C/mbar]	CN
$Sr(Me_5C_5)_2(THF)_2$	190	120-150/0.05	8
$Ba(Me_5C_5)_2(THF)_2$	188-195	140-230/0.05	8
$Ba(Me_5C_5)_2$(diglyme)	not obs	200-240/0.05	9
$Ba(Me_5C_5)_2$(dien)	not obs	180-260/0.05	9
$Ba(Me_5C_5)_2$(trien)	not obs	200-240/0.05	9
$Ba(Me_5C_5)_2$(triglyme)	207	200-240/0.05	9
$Ba(Me_4C_5CH_2CH_2NMe_2)_2$	249	200-260/0.05	8
$Ba(Me_4C_5CH_2CH_2OEt)_2$	202	150-220/0.05	8
$Ba(^iPr_3C_5H_2)_2(THF)_2$	115	160-210/0.05	8
$Ba(^tBu_3C_5H_2)_2(THF)$	155	160-220/0.05	7
$Sr(^iPr_3C_5H_2)_2(THF)$	98-100	120-160/0.05	7
$Sr(^tBu_3C_5H_2)_2$	136	120-180/0.05	6
$Ba(^tBu_3C_5H_2)_2$ **1**	155	160-220/0.05	7
$Ba(^tBu_3C_5H_2)_2$ **2**	<160	160-220/0.05	7

All the adduct compounds prepared were strictly monomeric and had formal coordination numbers of 7 to 9. Figure 8 shows XRD structures for four adducts of $Ba(Me_5C_5)_2$. In the case of $Ba(Me_2NCH_2CH_2C_5Me_4)_2$ and $Ba(EtOCH_2CH_2C_5Me_4)_2$ where the ligands contain donor-functionalized side chains, solvent molecules do not coordinate to the metal, but the nitrogen/oxygen atoms of the side chains are coordinated (Figure 9). This is frequently seen when Cp ligands with pendant donor atoms are used with alkaline earth metals, even when other substituents are not present.[186] All complexes show bent metallocene geometry typical for Cp compounds of alkaline earth metals.[190,191]

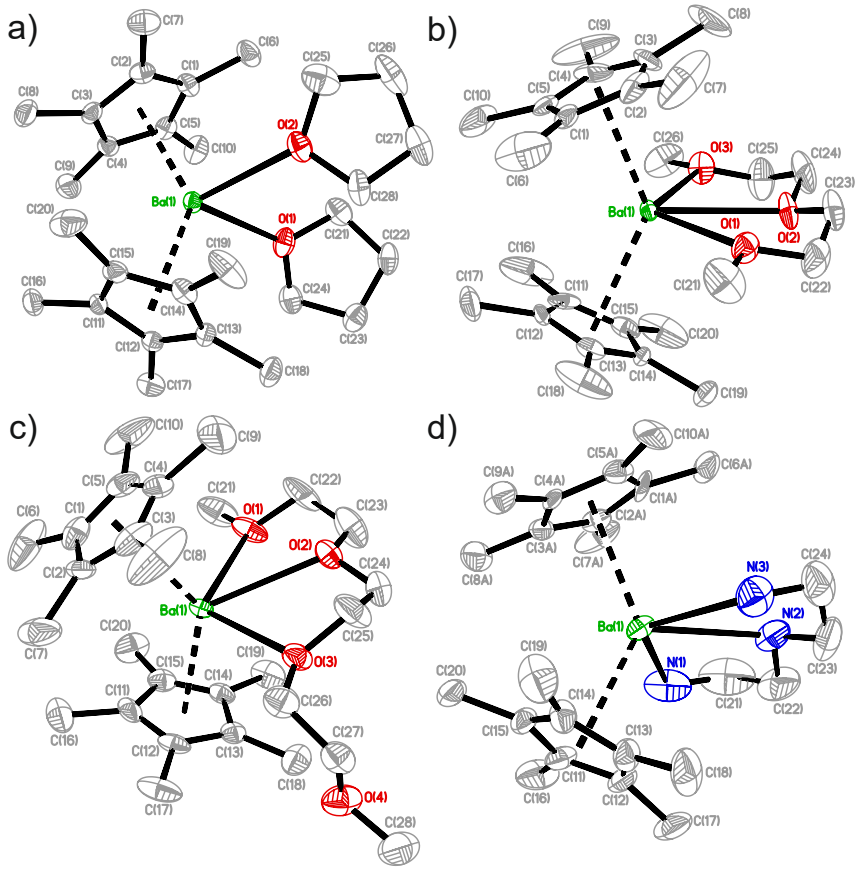


Figure 8 *Structures of a) $Ba(Me_5C_5)_2(THF)_2$, b) $Ba(Me_5C_5)_2$(diglyme), c) $Ba(Me_5C_5)_2$(triglyme), d) $Ba(Me_5C_5)_2$(dien).[IV] Thermal ellipsoids are at 30% level. Hydrogen atoms are omitted for clarity.*

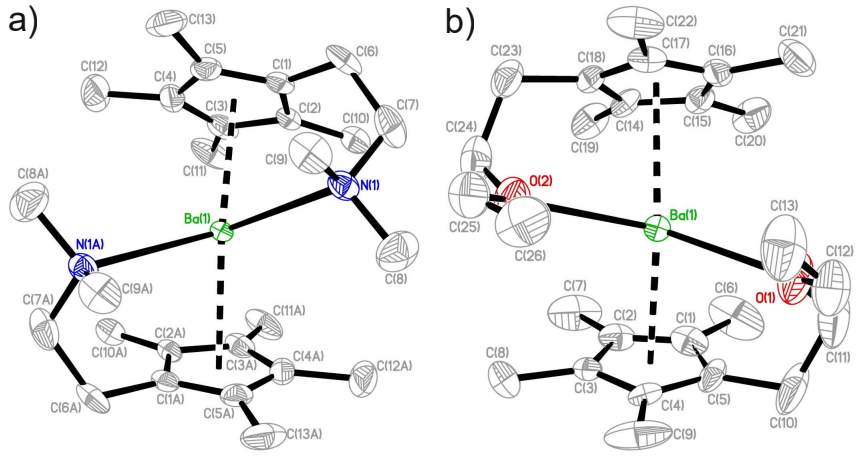


Figure 9 *Structures of a) $Ba(Me_4C_5C_2H_4NMe_2)_2$ and b) $Ba(Me_4C_5C_2H_4OEt)_2$.[IV] Hydrogen atoms are omitted, and thermal ellipsoids are drawn at 30% level.*

Unadducted Sr(^{t}Bu$_3$C$_5$H$_2$)$_2$ was found monomeric, and the Sr atom six coordinated (Figure 10a). In the case of Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$ two different crystal structures were found depending on the way of crystallization, i.e., sublimation and crystallization from a waxy evaporation residue of a toluene solution (Figures 10b and 11). Both structures show weak interactions between barium atoms and methyl carbons of the ligands so that formally the coordination number of the metal is 7. In one structure (Figure 10b), there is internal interaction (3.443 – 3.476 Å) and in the other one (Figure 11) chains are formed (3.352 Å). The Cp(centroid) – M – Cp(centroid) angles for Sr(^{t}Bu$_3$C$_5$H$_2$)$_2$ (average 167.3°) and Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$ (average 162.6°) are larger than those observed for Sr((Me$_3$Si)$_3$C$_5$H$_2$)$_2$, (159.4°) [192] and Ba(^{i}Pr$_4$C$_5$H$_2$)$_2$ (154°) [193] which indicates that the ^{t}Bu$_3$C$_5$H$_2$ is sterically more demanding ligand. Ba((Me$_3$Si)$_3$C$_5$H$_2$)$_2$ has a similar angle (162.2°) as Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$ and only in the extremely crowded cyclopentadienyl compound Ba(^{i}Pr$_5$C$_5$)$_2$ the angle is the largest possible, i.e., 180°.[194]

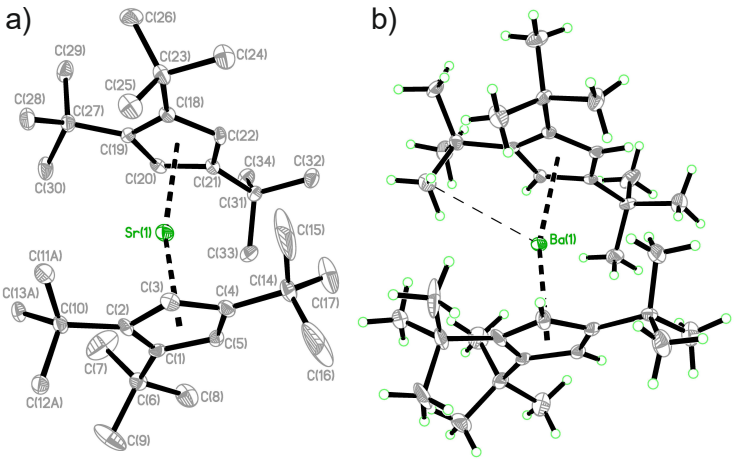


Figure 10 *Structures of a) Sr(^{t}Bu$_3$C$_5$H$_2$)$_2$ and b) Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$.[V] In Sr(^{t}Bu$_3$C$_5$H$_2$)$_2$ hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% level. Interaction between Ba and methyl group of the ligand is indicated for Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$.*

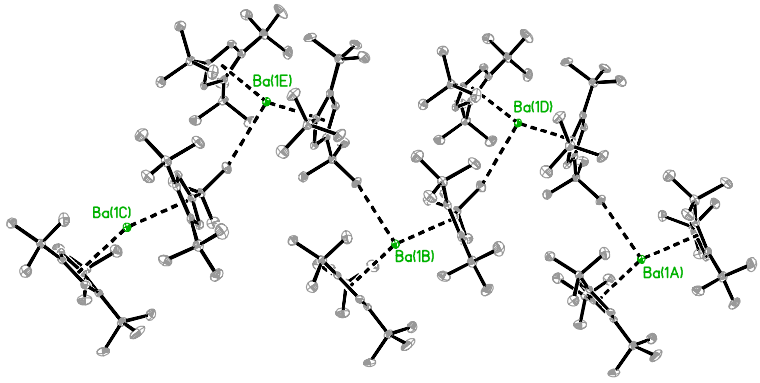


Figure 11 *Structure of Ba(^{t}Bu$_3$C$_5$H$_2$)$_2$.[V] Picture is showing the chains formed in the structure due to weak interactions between barium atoms and methyl groups in the adjacent molecules. Hydrogen atoms are omitted, and thermal ellipsoids are drawn at 30% level.*

Thermal properties of the adducts $Ba(Me_5C_5)_2A$ (A = dien, trien, diglyme, triglyme) were found insufficient considering their usage as ALD precursors. TG measurements revealed that the complexes with pentamethylcyclopentadienyl and ancillary multidentate Lewis base ligands hardly evaporate but decompose (Figure 12). It seems that these adducts, especially polyamine adducts, are thermally stable and stay intact quite well, but apparently, the temperatures of sufficient evaporation and decomposition are close to each other. However, vacuum sublimation of the multidentate adducts at 180 – 260 °C and analysis of the sublimates proved that the compounds were recovered intact although the sublimation yields were low (32 – 63%). Whether the compounds sublimed intact or dissociated and recombined on the cold finger surface cannot be said for sure, but the latter assumption might be supported by the fact that MS did not show any adduct species. Sublimation of the adducts required higher temperatures than the sublimation of $Ba(Me_5C_5)_2$. Also surprisingly, considering the structures of the adducts consisting of discrete monomeric molecules, the melting temperatures of the adducts were very high: the triglyme adduct melted at 207 °C and the others apparently did not melt before decomposition.

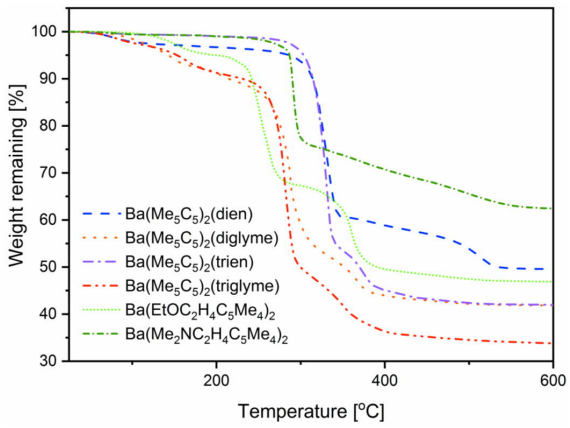


Figure 12 *TG curves measured for $Ba(Me_5C_5)_2A$ adducts (A = THF, dien, diglyme, trien, triglyme) and $Ba(EtOC_2H_4C_5Me_4)_2$ and $Ba(Me_2NC_2H_4C_5Me_4)_2$.*

The barium compounds with the donor-functionalized Cp ligands also showed decomposition in atmospheric pressure TG measurements (see Figure 12). However, under vacuum $Ba(Me_2NC_2H_4C_5Me_4)_2$ could be sublimed with only minor decomposition (yield 94%) while sublimation of $Ba(EtOC_2H_4C_5Me_4)_2$ resulted in poor yield. Thus, it is possible to use $Ba(Me_2NC_2H_4C_5Me_4)_2$ as an ALD precursor.

TGA of the THF adducts of $Sr(^iPr_3C_5H_2)_2$, $Ba(^iPr_3C_5H_2)_2$, $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$ showed a loss of the coordinated THF and then evaporation of the parent compound (Figure 13). The residues were smaller than 10%. $Sr(Me_5C_5)_2(THF)_{1.2}$ and $Ba(Me_5C_5)_2(THF)_2$ behaved similarly, but the residues were much larger (20.6 and 38.2%, respectively). This was because of inferior thermal stability, and also higher sensitivity to air and moisture. Vacuum sublimation of the apparent THF adducts took place at 140 – 220 °C with a loss of THF. The yields were good (70 – 92%) and the minor decomposition observed was considered to be because of minor air leakage into the equipment.

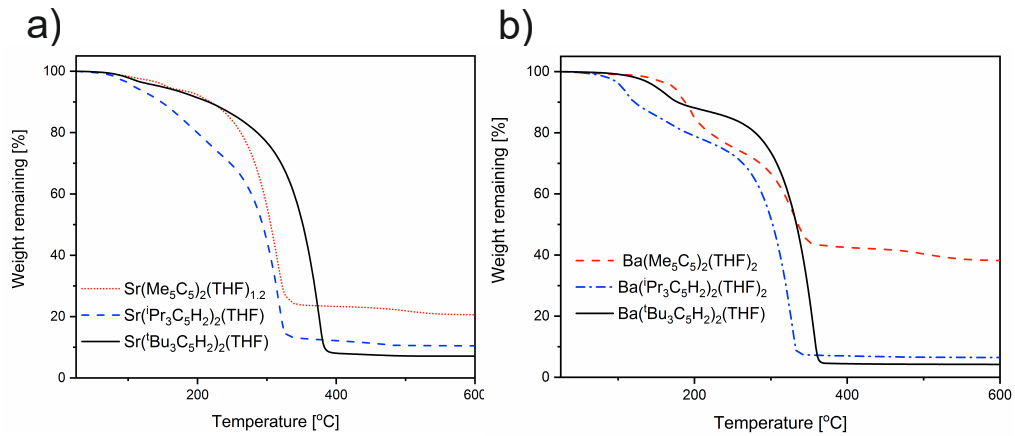


Figure 13 *TG curves measured for a) $Sr(Me_5C_5)_2(THF)_{1.2}$, $Sr(^iPr_3C_5H_2)_2(THF)$ and $Sr(^tBu_3C_5H_2)_2(THF)$, and b) $Ba(Me_5C_5)_2(THF)_2$, $Ba(^iPr_3C_5H_2)_2(THF)_2$ and $Ba(^tBu_3C_5H_2)_2(THF)$.*

TGA of the Lewis base free $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$ revealed single step evaporation and residues below 10% (Figure 14). The two compounds showed weight loss taking place at exactly the same temperature range. As could be expected, $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$ also sublimed well under vacuum. The small residues seen were due to air leaks or exposure to air rather than due to thermal decomposition. For comparison, Figure 14 also shows TG curves for the β-diketonates $Sr(thd)_2$ and $Ba(thd)_2$, which clearly have lower volatility. Based on the TG measurements $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$ can be said to be stable as bulk materials at least up to 350 °C, but they are likely stable at even higher temperatures. As compared with $Sr(^iPr_3C_5H_2)_2$ and $Ba(^iPr_3C_5H_2)_2$, their thermal stability is higher, and volatility is about the same. In general, TGA and vacuum sublimation experiments proved that the Cp compounds of Sr and Ba have higher volatility than the thd compounds.

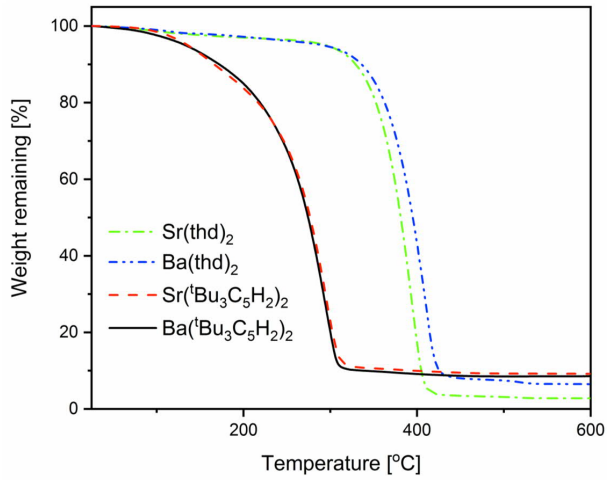


Figure 14 *TG curves measured for $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$. For comparison TG curves for $Sr(thd)_2$ and $Ba(thd)_2$ are also shown.*

Out of the strontium and barium precursors prepared $Sr(Me_5C_5)_2(THF)_x$, $Sr(^iPr_3C_5H_2)_2(THF)$, $Sr(^tBu_3C_5H_2)_2$, $Ba(Me_5C_5)_2$, $Ba(^iPr_3C_5H_2)_2$, $Ba(^tBu_3C_5H_2)_2$ and $Ba(Me_4C_5CH_2CH_2NMe_2)_2$ were studied as ALD precursors. The materials deposited were SrS, BaS, SrO, BaO, $SrTiO_3$, $Sr_xBa_{1-x}TiO_3$ and $BaTiO_3$. Detailed film growth studies may be found from the original publications.[4–6,8,9,195,196,IV]

Strontium and barium sulphides were grown $Sr(Me_5C_5)_2$, $Sr(^iPr_3C_5H_2)_2$, and $Ba(Me_5C_5)_2$ and H_2S as precursors.[4,5] Sufficiently pure sulfide films could be grown. Compared to the previously used thd β-diketonate precursors, the cyclopentadienyl precursors allowed, due to their better volatility and similar thermal stability, much larger growth temperature windows (120 – 400 °C [4] vs. 300 – 450 °C [70, 83–86]). The Cp compounds also gave higher or similar growth rates, depending on the temperature. Roughnesses of the SrS films grown using the Cp compounds were also lower than with the thd compounds. Thermal stability of the three metal precursors studied increased in the order: $Ba(Me_5C_5)_2 < Sr(Me_5C_5)_2 < Sr(^iPr_3C_5H_2)_2$ as the temperatures where decomposition was observed were >300, >350 and >380 °C, respectively.[4] The growth rates in the temperature range of the constant growth, i.e. so-called ALD window, decreased in the order $Sr(Me_5C_5)_2 < Ba(Me_5C_5)_2 < Sr(^iPr_3C_5H_2)_2$. This observation is understood considering the ion and ligand sizes: Ba is a larger cation than Sr, and $^iPr_3C_5H_2$ is a larger ligand than Me_5C_5, requiring larger surface area in the saturatively formed monolayer of the precursor on the surface of the growing film.

Water was used as the oxygen precursor for making the oxide films. For titanium $Ti(O^iPr)_4$ or $Ti(OMe)_4$ was used as a precursor. The strontium and barium precursors used were $Sr(^iPr_3C_5H_2)_2$, $Sr(^tBu_3C_5H_2)_2$, $Ba(Me_5C_5)_2$, $Ba(^tBu_3C_5H_2)_2$ and $Ba(Me_4C_5CH_2CH_2NMe_2)_2$.[6,8,9,195,196,IV] It was found that the best precursors were those with large sterically demanding cyclopentadienyl ligands, i.e. $Sr(^iPr_3C_5H_2)_2$, $Sr(^tBu_3C_5H_2)_2$, $Ba(^iPr_3C_5H_2)_2$, and $Ba(^tBu_3C_5H_2)_2$. Their volatility and thermal stability were the best allowing the highest growth temperatures. Deposition studies of the oxide materials in our group suggested thermal stability of 275 °C for $Ba(Me_5C_5)_2$,[6] and 300 – 325 °C for $Sr(^iPr_3C_5H_2)_2$.[7,9,197,198] For the other precursors, decomposition temperature in ALD growth experiments was not directly established. Subsequent studies have suggested even lower (~280 °C) [195,199] but also higher (>390 °C) decomposition temperatures for $Sr(^iPr_3C_5H_2)_2$.[200] Using $Sr(^tBu_3C_5H_2)_2$, $Ti(Me_5C_5)(OMe)_3$, and O_3 as precursors uniform $SrTiO_3$ was deposited at 370 °C.[201] In most of the studies saturation behavior of the alkaline earth metal Cp precursors have not been thoroughly studied or reported. It is likely that seemingly losing the saturative growth behavior does not necessarily mean thermal decomposition as it may also arise from the hygroscopicity of the film. Anyway, the stabilities of the Cp compounds are so good that in the deposition of high permittivity materials $SrTiO_3$ and $BaTiO_3$ the temperature limiting precursor was the titanium precursor ($Ti(O^iPr)_4$ or $Ti(OMe)_4$) rather than the Sr or Ba precursor: high deposition temperatures were aimed in a desire of materials that are crystalline in the as-deposited state because crystallization by post-deposition annealing often results in nano-cracks in the films. The barium Cp compound with the donor-functionalized ligand $Ba(Me_4C_5CH_2CH_2NMe_2)_2$ was also found suitable for ALD, but its thermal stability was lower, however.

In general, in growing oxide films, the advantages of cyclopentadienyl compounds are high reactivity against oxygen precursors and high thermal stability. In our studies, we used H_2O as the oxygen precursor, but the above applies to O_3 and oxygen plasma too, as has been shown in

several studies ([I], Table 2). The Cp compounds of alkaline earth metals (Mg, Ca, Sr, Ba) enable the growth of oxide films of sufficient purity at reasonable temperatures and growth rates, using water, ozone, or oxygen plasma as the oxygen source, which is very difficult if not impossible with the alternative thd-precursors. Before the introduction of the Cp compounds by us, Sr and Ba containing oxide films had not been deposited by ALD.

4.1.3.3 Conclusions

The best strategy for obtaining volatile and thermally stable cyclopentadienyl compounds of alkaline earth metals is to use cyclopentadienyl ligands with sterically demanding substituents. The Sr and Ba compounds with the $^{i}Pr_3C_5H_2$ and $^{t}Bu_3C_5H_2$ ligands have good volatility, high thermal stability and, like practically all the cyclopentadienyl compounds of alkaline earth metals, high reactivity against many co-precursors, especially water. Adducting does not seem to improve volatility. Cyclopentadienyl compounds with multidentate Lewis bases as the adduct forming ligands seem to stay intact quite well, but apparently at the temperatures where the sublimation is efficient thermal decomposition also takes place. Adducting does not either improve the air/moisture stability of the compounds. Compounds with the donor-functionalized cyclopentadienyl ligands, as exemplified by $Ba(Me_4C_5C_2H_4NMe_2)_2$, may have suitable volatility and thermal stability for ALD. Typically, donor-functionalized Cp ligands prevent coordination of Lewis bases by coordination of the pendant donor atom to the metal center. None of the Cp ligands, Me_5C_5, $^{i}Pr_3C_5H_2$, and $^{t}Bu_3C_5H_2$ without donor-functionalities hinder the coordination of solvent THF molecules in the synthesis. Only one compound prepared, $Sr(^{t}Bu_3C_5H_2)_2$, shows strictly monomeric solid state structure. The analogical Ba compound, $Ba(^{t}Bu_3C_5H_2)_2$, shows interactions between metal and ligand substituents. Though other strictly monomeric cyclopentadienyl compounds of Sr and Ba with even more bulky cyclopentadienyl ligands do exist, it might be beneficial from the ALD point of view that the metal center remains accessible so that the reactivity is not compromised. The high reactivity of the cyclopentadienyl compounds allows the growth of oxide materials of alkaline earth metals. The volatilities of the best Cp compounds are higher than those of the thd β-diketonates.

As a result, we introduced the Cp compounds of Sr and Ba to ALD for the first time. Greatly improved SrS and BaS processes were realized, and strontium and barium containing oxide materials could be easily deposited using the cyclopentadienyl compounds of strontium or barium and water. After introducing the chemistry, making $SrTiO_3$ and $Sr_xBa_{1-x}TiO_3$ as possible future high-k materials for DRAMs and FRAMs has been extensively studied, and the processes have been scaled to large 300 mm silicon wafers.[130] Though some new precursors for strontium and barium have recently emerged, the Cp compounds are still the state-of-the-art precursors for strontium and barium.

4.2 Bismuth

Applications of binary bismuth oxide thin films have been mainly restricted to sensors and solid electrolytes (ionic conductors in solid-state oxide fuel cells) [202–205] while ternary and quaternary bismuth-containing metal oxides have a much broader spectrum of potential applications in, e.g., sensors, oxidation catalysis, superconductors, photocatalysts, high-temperature electrolytes, and DRAM, FRAM, and MRAM data storage devices.[202] Other materials of interest are, e.g., bismuth sulfides, selenides, and tellurides, which find use in sensors and thermoelectrics.[206]

Bismuth is an element that usually forms compounds at an oxidation state +3. Electronegativity (2.02) [73] and charge to ionic radius (1.03 Å, CN = 6) [72] ratio (2.91) are sufficiently high so that bismuth forms readily compounds that are monomeric or have a low oligomerization degree. Using the Pauling's equation [74] ionicity of the Bi – C bond is estimated to be only 6.8%. For the Bi – N bond ionicity would be 22.9% and for the Bi – O bond 39.6%. Thus, finding volatile bismuth compounds is quite easy, and even the simplest compounds like $BiCl_3$, $BiMe_3$, and $Bi(O^tBu)_3$ present substantial volatility. The issues concerning bismuth precursors are therefore insufficient reactivity and low thermal stability.

Our interest in bismuth originated from the desire to deposit multi-component oxide materials that may be used in different microelectronics applications.

4.2.1 Precursors used in ALD and other volatile compounds

Bismuth precursors used in ALD until 2012 were reviewed in publication I. They included $BiCl_3$,[X,207] $Bi(Ph)_3$,[208–210] $Bi(CH_2SiMe_3)_3$,[211] $Bi(N(SiMe_3)_2)_3$,[11,VI] $Bi(thd)_3$,[VII,212,213] $Bi(mmp)_3$ [214–218] and $Bi(OCMe_2{}^iPr)_3$.[VII] Only $Bi(thd)_3$ and $Bi(OCMe_2{}^iPr)_3$ were shown to deposit properly pure binary Bi_2O_3. $Bi(Ph)_3$, $Bi(N(SiMe_3)_2)_3$, and $Bi(mmp)_3$ had been used for ternary and quaternary oxides, and $Bi(CH_2SiMe_3)_3$ for bismuth silicate. $BiCl_3$ had been used to deposit sulfide, selenide, and telluride. Additions to the precursor list after 2012 are bismuth amides $Bi(NMe_2)_3$, $Bi(NMeEt)_3$, and $(Me_3Si)_2NBi(NSiMe_3)_2Bi(N(SiMe_3)_2$ that have been used together with $(Et_3Si)_2Te$ to deposit Bi_2Te_3,[219] and $Bi(Me)_3$ that has been used with $(C_6H_8)Fe(CO)_3$ and H_2O to deposit $BiFeO_3$.[220] In addition, there have been publications where the already known precursors have been used to deposit a variety of bismuth-containing materials.[12,19,20,221–230] It has been shown, for example, that $Bi(Ph)_3$ combined with O_3 may be used to properly deposit pure Bi_2O_3.[221]

The bismuth compounds that had been used or tested in ALD before our input, starting in 2004, were $BiCl_3$,[231] $Bi(Ph)_3$, [208] and $Bi(mmp)_3$.[214] They all had some drawbacks considering the deposition of bismuth-containing oxide materials: $BiCl_3$ deposits oxyhalides, $Bi(Ph)_3$, like all bismuth alkyls and aryls, lacks reactivity with water, and $Bi(mmp)_3$ suffers from aging in a heated source. In general, many of the bismuth compounds have low thermal stability, and also light sensitivity is a frequently observed drawback.

Precursors used in CVD are pretty much the same that have been tested in ALD: bismuth halides, $Bi(Ph)_3$, $Bi(thd)_3$, $Bi(mmp)_3$, and $Bi(Me)_3$.[202,232] In addition, several bismuth amides and other compounds have been mentioned as possible CVD precursors.

4.2.2 Precursors for bismuth [I, VI, VII]

Bismuth compounds belonging to the different compound groups, viz. alkyls, amides, silylamides, thioamidate, alkoxides, β-diketonate and carboxylate, were synthesized and evaluated in order to get an overview on their properties relevant for ALD precursors, and to overcome the limitations of the previous attempts for depositing Bi_2O_3 and other bismuth-containing oxide materials. Preferably, a process using H_2O as the oxygen precursor was targeted. Many of the compounds were known, but all relevant properties of them and suitability for ALD had not been established.

4.2.2.1 Compounds studied: synthesis and properties

Table 4 lists the bismuth compounds studied. At first bismuth alkyls $Bi(^iPr)_3$, $Bi(^tBu)_3$, and $Bi(CH_2SiMe_3)_3$, bismuth amides $Bi(NEt_2)_3$, $Bi(N^iPr_2)_3$, and $Bi(N^tBuC_2H_4NMe_2)_3$ with donor-functionality, thioamidate $Bi(SCMeN^iPr)_3$, and silyl amides $Bi(N(SiR_3)_2)_3$ with different alkyl substituents were synthesized.[VI,211] Simple metathesis reactions between the lithium salts of the appropriate ligands and $BiCl_3$ were used for the synthesis.

Table 4 *Synthesized bismuth compounds. Yields, melting points, sublimation temperatures, molecular weights, and notes on sensitivity.*

Compound	Yield [%]	mp [°C]	T(subl) [°C/mbar]	MW [g/mol]	Sensitivity
$Bi(^iPr)_3$	-	liquid	60-70/5	338.24	O_2, not H_2O
$Bi(^tBu)_3$	-	liquid	43-52/0.2	380.32	O_2, not H_2O
$Bi(CH_2SiMe_3)_3$	98.5	45-51.5	50-75/0.1	470.63	O_2, not H_2O
$Bi(NEt_2)_3$	93.7	liquid	80-82/0.09torr[233]	425.37	O_2, H_2O, light
$Bi(N^iPr_2)_3$	69.0	not obs	not done	509.53	O_2, H_2O, light
$Bi(^tBuNC_2H_4NMe_2)_3$	60.0	not obs	not done	638.73	O_2, H_2O,light
$Bi(N(SiMe_3)_2)_3$	95.8	133-137	110-150/0.05	690.13	O_2, H_2O, light
$Bi(N(SiMe_2Et)_2)_3$	98.0	not obs	110-150/0.05	774.29	O_2, H_2O, light
$Bi(N(SiMe_2{}^nBu)_2)_3$	94.4	liquid	110-150/0.05	942.61	O_2, H_2O, light
$Bi(N(SiMe_2CHCH_2)_2)_3$	94.7	not obs	110-150/0.05	762.20	O_2, H_2O, light+
$Bi(SCMeN^iPr)_3$	39.0	105-115 dec	decomposes	557.60	O_2, H_2O
$Bi(O^tBu)_3$	72.7	139	100/0.05	428.32	O_2, H_2O
$Bi(OCMe_2{}^iPr)_3$	69.5	40	120-130/0.05	512.48	O_2, H_2O
$Bi(OC^iPr_3)_3$	54.8	64.8–70.0	140-160/0.05	680.80	O_2, H_2O
$Bi(thd)_3$	90.8	130.2–133.6	130-150/0.05	758.78	O_2, H_2O
$Bi(O_2C^tBu)_3$	91.8	167.4–170.5	160-210/0.05	512.35/2049.41	not sensitive

It was found that the alkyl compounds were well volatile as also indicated by the TGA (Figure 16a), but, like the literature states, these compounds were unreactive towards H_2O. Other downsides of the alkyls are potential explosion hazard and toxicity.[234] In the case of alkyl amides thermal instability was found to make them unsuitable precursors for depositing oxides using H_2O as the oxygen precursor. Simple alkylamides are highly volatile and may be distilled under vacuum,[VI,219,233] but decomposition starts to take place already around 100 – 120 °C. Accordingly, TGA shows abrupt weight changes in this region, while DTA shows an exotherm (Figures 16b and 16d). ALD at < 100 °C with H_2O would be quite difficult due to slow removal of excess H_2O from the reaction chamber. Also, light sensitivity and extreme sensitivity to air and moisture are problematic features. The thioamidato compound prepared, $Bi(SCMeN^iPr)_3$, whose structure was solved and is shown in Figure 15b, proved to be thermally unstable (Figure 16b). Out of the silylamides studied (Table 1) the one with the most common and simple silylamido ligand, bis(trimethylsilyl)amido, btsa, $N(SiMe_3)_2$, was found to be the most volatile and also the most thermally stable (Figure 16c). Its monomeric XRD structure was solved and is shown in Figure 15a. According to TGA $Bi(N(SiMe_3)_2)_3$ in the condensed state seems to be thermally stable at least up to 240 – 250 °C, but prolonged heating in an ALD reactor seemed to cause decomposition already at 130 °C. Deposition experiments, in turn, indicated that in the gas phase or adsorbed on a surface decomposition destroying the ALD growth took place at 200 °C and above. Thus deposition of BiO_x, $BiTa_xO_y$, $BiSr_xTa_yO_z$,[V] and $Bi_4Ti_3O_{12}$ [11] films, using H_2O as the oxygen precursor, was rationally possible only in a narrow window of 10 – 15 °C around 190 °C. Deposition of bismuth oxide had reproducibility issues, and yet another limitation was the light sensitivity of the silylamide.

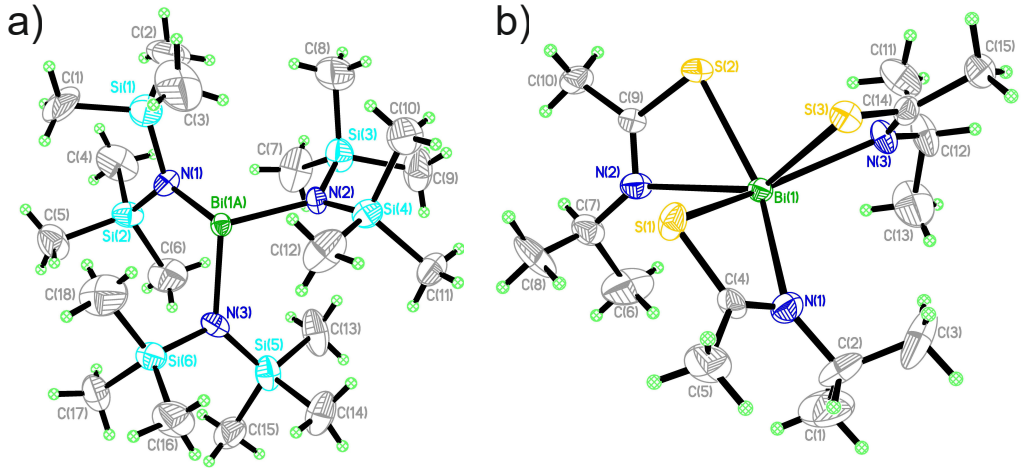


Figure 15 *Structures of a) $Bi(N(SiMe_3)_2)_3$ and b) $Bi(SCMeN^iPr)_3$.[VI] Thermal ellipsoids are drawn at 50% level in both structures.*

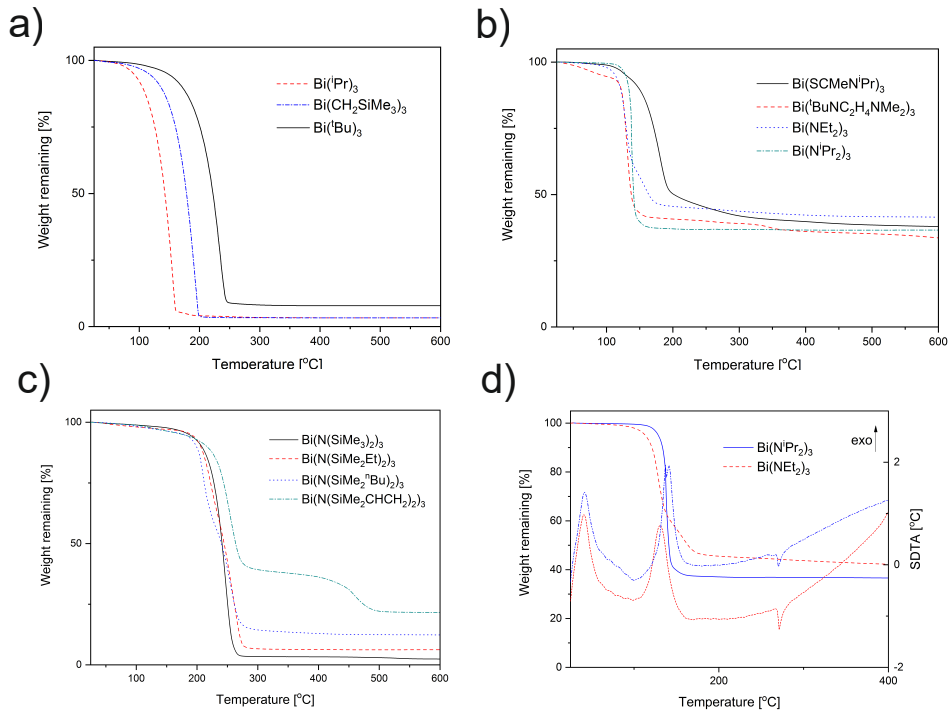


Figure 16 *TG curves of a) $Bi(^{i}Pr)_3$, $Bi(^{t}Bu)_3$ and $Bi(CH_2SiMe_3)_3$. b) $Bi(NEt_2)_3$, $Bi(N^{i}Pr_2)_3$, $Bi(CH_2SiMe_3)_3$ and $Bi(NC_2H_4NMe_2)_3$ and $Bi(SCMeN^{i}Pr)_3$ c) $Bi(N(SiMe_3)_2)_3$ $Bi(N(SiMe_2Et)_2)_3$ $Bi(N(SiMe_2{}^{n}Bu)_2)_3$ $Bi(N(SiMe_2CHCH_2)_2)_3$ d) TG and SDTA curves of $Bi(NEt_2)_3$, and $Bi(N^{i}Pr_2)_3$. SDTA shows an exothermic change in the region of weight change. At 271 °C melting peak of Bi (endothermic) is seen.*

After these trials, bismuth compounds with oxygen donor ligands were taken into study.[VII] Several bismuth compounds with oxygen based ligands are known, and their thermal properties have been studied.[202] There are quite volatile compounds in all the common compound groups, i.e., alkoxides, β-diketonates, and carboxylates. Besides, bismuth compounds with oxygen donor ligands are known to be insensitive to light and mostly reactive with water.[202]

Three alkoxides and β-diketonate and carboxylate were synthesized and characterized (Table 4). Tertiary alkoxides were chosen for the study as it is known that simple primary and secondary alkoxides show poor volatility while even the simplest tertiary alkoxide $Bi(O^{t}Bu)_3$ is volatile.[VII,235,236] Metathesis reactions between $BiCl_3$ and KOR (R = ^{t}Bu, $CMe_2{}^{i}Pr$, $C^{i}Pr_3$) were used for the alkoxide syntheses. Isolation and purification of the products were done by sublimation. The β-diketonate $Bi(thd)_3$ was synthesized from $Bi(N(SiMe_3)_2)_3$ and Hthd. For the carboxylate $Bi(O_2C^{t}Bu)_3$ a metathesis reaction between $KO_2C^{t}Bu$ and $BiCl_3$ was used. It was also found that the synthesis of $Bi(O_2C^{t}Bu)_3$ does not require any exclusion of air and moisture, and the synthesis succeeds even from Bi_2O_3 and free pivalic acid, though a long period of refluxing is needed. In earlier reports $Bi(thd)_3$ and $Bi(O_2C^{t}Bu)_3$ had been synthesized by ligand exchange reactions between $Bi(Ph)_3$ [237] or $Bi(O_2CMe)_3$ [238,239] and the appropriate ligands. The methods we used resulted in pure products with equally good yields (>90%).

According to single crystal X-ray diffraction studies, the Bi alkoxide with the largest ligand $^{i}Pr_3CO$ had strictly monomeric structure (Figure 17a). Structure of $Bi(OCMe_2{}^{i}Pr)_3$ could not be solved because of difficulties to grow high-quality crystals. A tetrameric compound $[Bi_2O(OCMe_2{}^{i}Pr)_4]_2$, with triple bridging μ_3-oxygen atoms (Figure 17b), was found as a result of exposure to residual air or moisture. For $Bi(O^{t}Bu)_3$, a structure with monomeric units interacting with each other was found (Figure 18). This implicates that the structure of pure $Bi(OCMe_2{}^{i}Pr)_3$ should be similar maybe with some weak interactions between monomeric units. One may find a connection between the structural aspects and melting point temperatures: $Bi(O^{t}Bu)_3$ has intermolecular connections and fewer degrees of freedom in the ligands resulting in higher melting point temperature (139 °C) compared to that of $Bi(OC^{i}Pr_3)_3$ (65 – 70 °C) and $Bi(OCMe_2{}^{i}Pr)_3$ (40 °C). The low melting point temperature of $Bi(OCMe_2{}^{i}Pr)_3$ has an obvious connection with the inability to get proper crystals from the compound. In respect of volatility, interactions between the monomeric units in all three compounds are weak and insignificant. More than anything else, the molecular weight affects the volatility.

Structures of $Bi(thd)_3$ and $Bi(O_2C^{t}Bu)_3$ were also solved and found similar with those already known in the literature: $Bi(thd)_3$ forms a loose dimer and $Bi(O_2C^{t}Bu)_3$ a tetramer.[240,241] Melting point temperatures of the compounds are fairly high while their core structures are quite rigid. Along with the relatively low pK_a value of $^{t}BuCO_2H$ (5.03) [242] the oligomeric structure and good shielding of the Bi atoms (CN = 6) may partly explain the sufficiently good stability against air and moisture. Also, the high reactivity of $Bi(thd)_3$ which is in contrast with most metal β-diketonates can be partially explained by the structure: in the monomer, the Bi center is very poorly shielded from the side where the lone electron pair of Bi(III) resides.

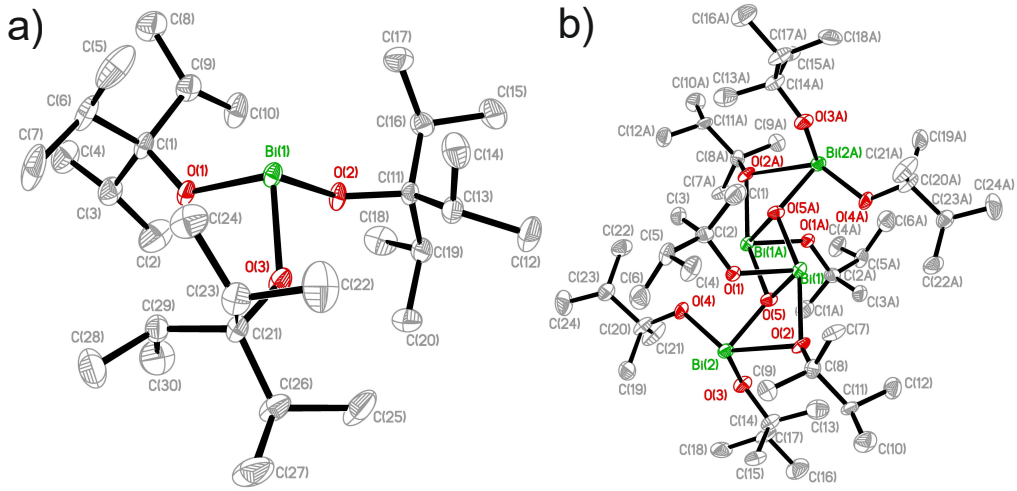


Figure 17 *a) Structure of $Bi(OC^{i}Pr_3)_3$. Thermal ellipsoids are drawn on the 50 % probability level. Hydrogen atoms are omitted for clarity. b) Molecular structure of $[Bi_2O(OCMe_2{}^{i}Pr)_4]_2$.[VII] Thermal ellipsoids are drawn on the 50% probability level. Hydrogen atoms are omitted for clarity.*

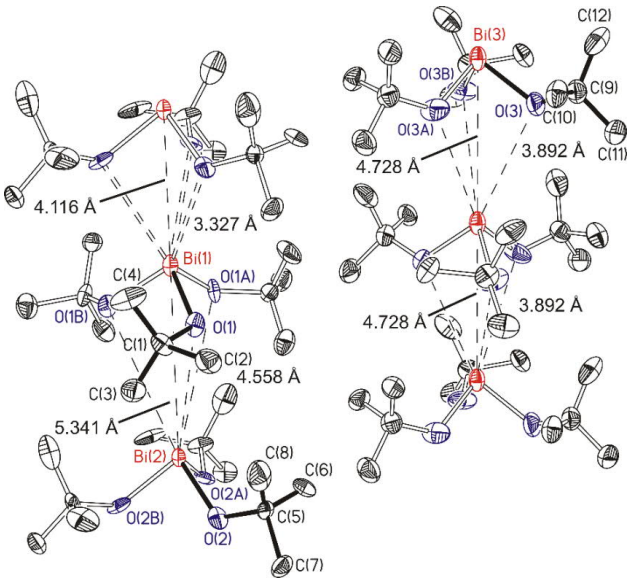


Figure 18 *Structure of Bi(O^{t}Bu)$_3$.[VII] Thermal ellipsoids are drawn on the 50% probability level. Atoms labeled form the asymmetric unit. Parallel to c-axis, there is a three-fold axis running through Bi(1) and Bi(2), and a six-fold rotational axis running through Bi(3n). Through symmetry, complete molecules are formed. Some distances in the structure are shown in the figure.*

As already mentioned, the TG measurements (Figure 19) clearly indicated that the volatility of the tertiary alkoxides decreases with increasing molecular weight. The same seems to apply to Bi(O$_2$C^{t}Bu)$_3$, Bi(OC^{i}Pr$_3$)$_3$, and Bi(thd)$_3$ although the volatilities are close to each other. Residues left after the TG measurements may be interpreted to mainly indicate thermal decomposition of the samples. While Bi(OCMe$_2$^{i}Pr)$_3$, Bi(thd)$_3$ and Bi(O$_2$C^{t}Bu)$_3$ left negligible residues, for Bi(O^{t}Bu)$_3$ and Bi(OC^{i}Pr$_3$)$_3$ that was not the case. Thermal stability of the synthesized complexes was also studied by conducting TG measurements with crucibles with lids having a small orifice through which the evaporation took place (Figure 19b). Compounds leaving higher residues in measurements done with lids are most likely decomposing at the apparent temperatures. By comparing these results with those obtained using crucibles without lids, it was concluded that: 1) Bi(O^{t}Bu)$_3$ maybe shows some decomposition already below 200 °C, but the increase in the rate of decomposition is not that large even at 270 °C. 2) Bi(OCMe$_2$^{i}Pr)$_3$ shows almost no decomposition up to 230 °C but at least at 300 °C decomposition is substantial. 3) Bi(OC^{i}Pr$_3$)$_3$ shows substantial decomposition well below 280 °C, probably much earlier. 4) Bi(thd)$_3$ does not show notable decomposition below 300 °C but around 350 °C decomposition is substantial, and 5) Bi(O$_2$C^{t}Bu)$_3$ is showing very little or no decomposition even at 370 °C.

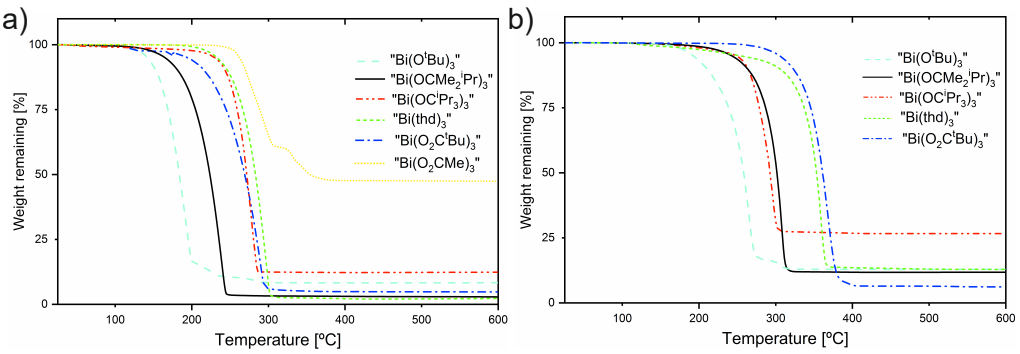


Figure 19 *a) TG curves measured for Bi(O^{t}Bu)$_3$, Bi(OCMe$_2$iPr)$_3$, Bi(OC^{i}Pr$_3$)$_3$, Bi(thd)$_3$, Bi(O$_2$C^{t}Bu)$_3$, and Bi(O$_2$CMe)$_3$. b) TG curves measured for the same compounds using crucibles with lids.*

Because all the compounds studied showed volatility in normal atmospheric pressure TG measurements, it was evident that also vacuum sublimation of the compounds would be successful. In the case of the alkoxides, the sublimation onset temperatures followed the order observed in atmospheric pressure TGA (Table 4). Sublimation yields for all compounds were 80 – 99 %. For Bi(O^{t}Bu)$_3$, Bi(thd)$_3$, and Bi(O$_2$C^{t}Bu)$_3$, the thermoanalytical and sublimation results were in agreement with the previous literature reports.[241,243,244]

All the oxygen donor ligand compounds prepared were tested in ALD film growth experiments with water as the co-precursor. Bi(O^{t}Bu)$_3$ could be used to grow BiO_x films, but the precursor suffered from aging during evaporation at 70 °C, thus making reproducible ALD growth impossible. Bi(OCMe$_2$^{i}Pr)$_3$ proved to be a good ALD precursor. With Bi(OC^{i}Pr$_3$)$_3$, no growth was obtained. It seemed that Bi(OC^{i}Pr$_3$)$_3$ was decomposing already at the required evaporation temperature of 150 °C. Using Bi(thd)$_3$, Bi_2O_3 films could be deposited at 200 – 300 °C with a growth rate of approximately 0.1 Å/cycle, as also reported by Østreng et al.[212] and later by others too.[213] With Bi(O$_2$C^{t}Bu)$_3$ no film growth was observed at 250 °C, and at 300 °C Bi_2O_3 films grew but with very low growth rate of 0.06 Å/cycle. Bi(O$_2$C^{t}Bu)$_3$ is thermally durable, and decomposition at 300 °C is minor. Most likely the pivalate needs a stronger oxidizer than water for efficient growth.

More detailed ALD studies were done with Bi(OCMe$_2$^{i}Pr)$_3$, which was found to be the most suitable precursor among the alkoxides investigated. The process was the first well-controlled one for ALD of binary bismuth oxide films. Previously reproducible ALD growth was proven only for mixed oxides such as $BiTi_xO_y$ and $BiTa_xO_y$.[VI,208]

Beneficial properties combined in Bi(OCMe$_2$^{i}Pr)$_3$ are 1) reactivity with water, 2) liquid state at source temperature (in ASM F120 reactor 85 °C while the mp. is 40 °C), 3) large temperature window that can be used (150 – 250 °C), 4) pure films (TOF-ERDA: 0.3 ± 0.3 at-% carbon and 1.4 ± 0.4 at-% of hydrogen), 5) higher growth rate than with any previous or later process (0.38 Å/cycle), and 6) sufficiently good long term stability at source temperature.

4.2.2.2 Conclusions

Different bismuth compounds were synthesized and evaluated in respect of possible usage as ALD precursors. As expected, simple alkyl compounds were found to be highly volatile and reactive with oxygen but unreactive with water and potentially dangerous due to explosion risks. Simple alkylamides are highly volatile and reactive, but their thermal stability is low. In addition, their sensitivity to air and moisture is extreme, and they tend to be sensitive to light. The silylamide, $Bi(N(SiMe_3)_2)_3$, has better thermal stability and not so extreme but still sufficient reactivity. Volatility and thermal stability of this compound allowed ALD of $SrBi_2Ta_2O_9$ and $BiTaO_4$ in a narrow temperature window of 10 – 15 °C around 190 °C when H_2O was used as the oxygen precursor. Deposition of Bi_2O_3 reliably, however, proved impossible. Simple tertiary alkoxides were found to have proper volatility and thermal stability. Volatility decreases with increasing molecular weight and enlarging the steric bulk of the alkoxo ligand further from $^iPrMe_2CO$ decreases the thermal stability. $Bi(OCMe_2{}^iPr)_3$ seems to have the best thermal stability among the studied alkoxides. ALD of Bi_2O_3 and other bismuth-containing oxide materials was proved within a broad temperature window at 150 – 250 °C. The growth rate of Bi_2O_3 was the highest observed so far (0.38 Å/cycle). The β-diketonate $Bi(thd)_3$ was found volatile and highly reactive against H_2O. These properties allowed ALD of bismuth oxide at 200 – 300 °C but the growth rate was rather low (0.1 Å/cycle) and the compound is, unlike $Bi(OCMe_2{}^iPr)_3$, a solid at the evaporation temperature. Among the studied compounds $Bi(O_2C{}^tBu)_3$ is thermally the most stable one, and it also has sufficient volatility. However, $Bi(O_2C{}^tBu)_3$ is a solid, and the growth experiments suggested low growth rates with H_2O. Apparently, the reactivity of $Bi(O_2C{}^tBu)_3$ with water and surface OH groups is not high enough.

To date, it seems that $Bi(OCMe_2{}^iPr)_3$ is still the best precursor choice for depositing Bi_2O_3 when H_2O is used as the co-precursor. Films of Bi_2O_3 can be deposited in a well-controlled and repeatable manner.

4.3 Silver

Silver is used in electrical conductors, highly reflective mirrors, decorative coatings, and antimicrobial coatings.[245] It has been suggested that silver could be used in future IC interconnects.[246] Silver nanostructures are used as substrate materials in surface-enhanced Raman spectroscopy (SERS).[247]

Silver is a noble metal residing between Cu and Au in Group 11. The most common oxidation state of Ag is +I. The moderate electronegativity of Ag (1.9) [73] predicts the bonds between Ag and various ligands to be only mildly polar. Ionicities of Ag – O, Ag – P, Ag – N, and Ag – C bonds are 43.4, 1.7, 26.5, and 9.2%, respectively, when calculated using the Pauling's equation.[74] The charge to radius ratio of Ag^+ ion (CN=2) is as large as 1.49, which means that AgL compounds are keen to increase their coordination number through oligomerization and adduct formation. Because Ag^+ is a soft Lewis acid, it forms the strongest bonds with soft Lewis bases, e.g., sulfur and phosphorus donor ligands. Because silver is a transition metal d-electrons are available for bonding. This makes some of the silver compounds with adduct forming ligands quite stable, especially those capable of π-back bonding.

Our interest to silver precursors originated in addition to general curiosity from the desire to deposit silver for surface-enhanced Raman scattering (SERS) substrates.

4.3.1 Precursors and other volatile compounds

Considering ALD of silver, the main issues are finding a silver precursor with sufficient thermal stability and finding a suitable co-precursor which converts the silver precursor to a silver film. Most of the volatile silver compounds known are thermally quite unstable. In the ALD of the platinum group metals (Ru, Os, Rh, Ir, Pd, Pt) the usage of O_2, O_3, and $O_3 + H_2$ as co-precursors has been found to result in good quality metal films from many kinds of noble metal precursors.[248] These combustion-type processes rely on the corresponding oxides being thermally unstable at deposition temperatures. For silver, this approach has not been used, and to date, the ALD of silver films has relied on the usage of a reducing agent.

In CVD, the mostly used silver precursors have been β-diketonates and carboxylates with and without adduct forming ligands [249]. As typical, the volatility of the compounds is enhanced by adducting and by using bulky and fluorinated ligands. Majority of the silver precursor compounds used in CVD have relatively low thermal stability, and in fact, in most cases, thermal stability has not even been aimed. However, it has been noticed that adduct forming ligands and their type have a crucial effect on the thermal stability and volatility of Ag complexes. Electronic properties, i.e., the π-acceptor strengths of the adduct forming ligands, seem to be especially important. Out of the neutral ligands introduced to silver complexes (alkene,[250] alkyne,[251] methylisocyanide,[252] polyamines,[253] polyethers,[254,255] and phosphines [249]) phosphines seem to form the strongest bonds with silver as indicated by the thermal stability. The adduct forming ligand also affects the Ag to charged ligand bond stability and among the phosphine adducts the Ag – O bond stability increases in the order: $PMe_3 < PEt_3 < PPh_3$, following the π-acceptor strength of the ligands. However, PPh_3 is not a good ligand considering the volatility.

At the time doing the precursor studies for this thesis, there was at first none and then three reports, including the studies in papers VIII and IX.[256] At the moment there are a total of eleven processes reported for ALD of silver. Six of the processes reported are plasma-enhanced processes utilizing H_2/Ar, H_2/N_2, H_2 or NH_3 plasma or radicals formed with the aid of the plasma. In one process $Ag(O_2C^tBu)(PEt_3)$ is used as the silver precursor.[VIII] In four of the processes $Ag(fod)(PEt_3)$ is the Ag precursor.[IX,257–259] In the most recent report (NHC)Ag(btsa) (NHC = 1,3-di-tertbutyl-imidazolin-2-ylidene) is used in atmospheric hydrogen plasma enhanced spatial ALD process.[260] Silver precursors used in thermal ALD processes are Ag(hfac)(1,5-COD),[61,256,261] $Ag(hfac)(PMe_3)$,[262] and $Ag(fod)(PEt_3)$.[263] Processes utilizing Ag(hfac)(1,5-COD) are liquid injection ALD processes where the precursor is dissolved in toluene and injected as demanded to a heated evaporator. Thus, thermal decomposition of the relatively unstable precursor over time in a heated source is circumvented. Reducing agents in these processes have been 1-propanol and tert-butylhydrazine ($^tBuHNNH_2$). With 1-propanol non-conductive films of nanoparticles were formed, and with $^tBuHNNH_2$ the films were more continuous. In the processes utilizing $Ag(hfac)(PMe_3)$ [262] the reducing co-precursors have been formalin solution and TMA. With TMA, an additional H_2O pulse was used. Deposition temperatures have been quite high (170 –

200 °C) considering the expected decomposition temperature of the silver precursor. In addition, ALD behavior of these processes have not been proven, and the deposits have been Ag nanoparticles. Ag(fod)(PEt_3) has been combined with dimethylamine borane $BH_3(NHMe_2)$ by us.[263] The growth was self-limiting (i.e., ALD type) but the resulting films were particulate and therefore non-conducting.

4.3.2 Precursors for silver [I, VIII, IX]

Different silver compounds with and without adduct forming phosphine ligands were synthesized and studied in respect of volatility and thermal stability. The aim was to find a compound with sufficient volatility and as high as possible thermal stability combined. At the time beginning the studies, there were no ALD processes reported for silver. Though most of the compounds were known, they had to be synthesized and studied in order to evaluate their suitability to ALD.

4.3.2.1 Compounds studied: synthesis and properties

The compounds synthesized that were amidinates, carboxylates, and β-diketonates are listed in Table 5. The amidinate was synthesized using the common route employing a metathesis reaction between lithium amidinate and silver chloride.[264] The carboxylates were synthesized by reacting potassium salts of the appropriate ligands with $AgNO_3$ in a water solution. The β-diketonates were synthesized reacting Ag_2O with the appropriate β-diketone in toluene. Phosphine adducts were synthesized by adding the phosphine into a toluene solution of the appropriate Ag compound.

Table 5 *Silver compounds synthesized. Oligomerization degree, melting point temperatures, and sublimation temperatures.*

Compound	Oligomerization degree	mp [°C]	T(subl) [°C/mbar]
Ag(^{i}PrNCMeNC^{i}Pr)	2-3 [264]	95	80/0.04torr vp [264]
[Ag(iPrNCMeNiPr)]$_2$(PEt_3)	2	104	-
Ag(S_2CNEt_2)	polymeric [265]	170	decomposes
Ag(O_2CMe)	likely polymeric	-	decomposes
Ag(O_2CCF_3)	likely polymeric	258	decomposes
Ag(O_2C^tBu)	polymeric [266]	-	decomposes
Ag(O_2C^tBu)(PEt_3)	3	59	140-160/0.5mbar
Ag(O_2C^tBu)(PBu_3)	2 [267]	90	140-160/0.5
Ag(fod)	likely polymeric	-	-
Ag(hfac)(PMe_3)	1 [268]	143	80-100/0.05 mmHg
Ag(thd)(PEt_3)	2	28	80-100/0.5
Ag(fod)(PEt_3)	2	28	80-100/0.5

Structures of the compounds [Ag(^{i}PrNCMeCN^{i}Pr)]$_2$(PEt$_3$), Ag(O$_2$C^{t}Bu)(PEt$_3$), Ag(thd)(PEt$_3$) and Ag(fod)(PEt$_3$) were solved while the structures of Ag(^{i}PrNCMeCC^{i}Pr),[264] Ag(O$_2$C^{t}Bu),[266] Ag(O$_2$C^{t}Bu)(PBu$_3$),[267] and Ag(hfac)(PMe$_3$) [268] were already known in the literature. The new structures are presented in Figures 20 and 21. It was found that the oligomerization degree of the compounds is lowered when the adduct forming ligand is coordinated, but still, most of the adducts are dimeric. However, the interactions between the monomeric units differ in different compounds. In [Ag(^{i}PrNCMeCN^{i}Pr)]$_2$(PEt$_3$) (Figure 20a) the N atoms of both amidinato ligands bond to different Ag atoms and there is also Ag – Ag interaction (2.720 Å). In the trimeric [Ag(O$_2$C^{t}Bu)(PEt$_3$)]$_3$ the O atoms of the pivaloyl ligand of the monomeric unit in the middle interact with the Ag atoms of the neighbouring units (Figure 20b) while in the dimeric Ag(thd)(PEt$_3$) there is an interaction between the two Ag atoms (2.948 Å) (Figure 21a). In the dimeric Ag(fod)(PEt$_3$) there are several interactions between the two monomeric units Ag – O (2.684 Å) and Ag – F (3.111 Å) but no Ag – Ag interaction (3.490 Å) (Figure 21b).

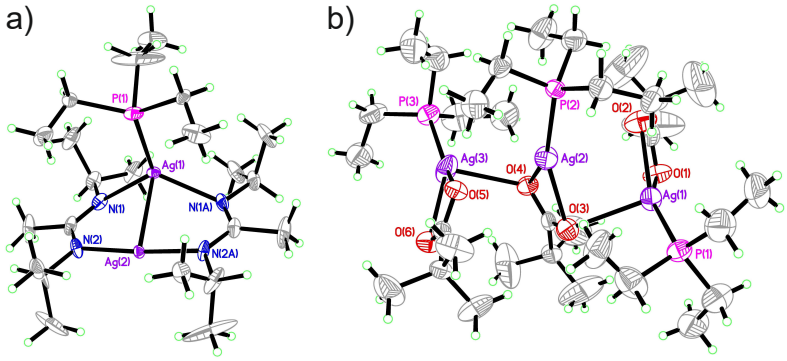


Figure 20 *Molecular structures of a) [Ag(^{i}PrNCMeN^{i}Pr)]$_2$(PEt$_3$) (dimer) and b) [Ag(O$_2$C^{t}Bu)(PEt$_3$)]$_3$ (trimer).[VIII] Thermal ellipsoids are drawn in 30% probability level. Ag1 – Ag2 distance in [Ag(^{i}PrNCMeN^{i}Pr)]$_2$(PEt$_3$) is 2.720 Å. Ag3 – O4 and Ag1 – O3 distances in [Ag(O$_2$C^{t}Bu)(PEt$_3$)]$_3$ are 2.639 and 2.543 Å, respectively.*

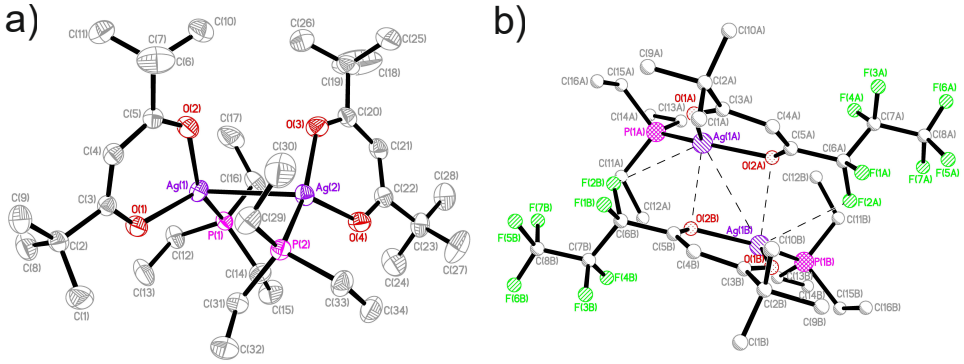


Figure 21 *Molecular structure of a) Ag(thd)(PEt$_3$) and b) Ag(fod)(PEt$_3$).[IX] Dimeric structures. Thermal ellipsoids are drawn in 30% probability level, in Ag(thd)(PEt$_3$) as anisotropic and in Ag(fod)(PEt$_3$) as isotropic. Hydrogen atoms are omitted for clarity. Ag1 – Ag2 distance in Ag(thd)(PEt$_3$) is 2.948 Å.*

TG measurements revealed that all the prepared compounds except Ag(fod)(PEt_3) left residues which were larger or approximately equal to the theoretical amount of silver in the compounds, i.e., the compounds decomposed (Figure 22). In contrast, Ag(fod)(PEt_3) left only a 6 % residue while the Ag content is 22.7 %, which proves that most of the compound evaporated. Though the carboxylates seem to have higher thermal stability than any of the β-diketonates, including Ag(fod)(PEt_3), their volatility is so low that evaporation does not take place at 1 atm pressure before thermal decomposition. At lowered pressures, the phosphine adducts Ag(O_2C^tBu)(PEt_3) and Ag(O_2C^tBu)(P^nBu_3), however, do evaporate: both compounds sublime almost quantitatively at 140 – 160 °C/0.5 mbar, while the pure unadducted carboxylates require higher sublimation temperatures where they show substantial decomposition as also reported in the literature.[267] While TGA suggests that Ag(O_2C^tBu)(PEt_3) could be thermally stable at least up to ~230 °C, CVD growth from this precursor, indicating decomposition, has been reported to take place already at 170 °C.[269] Thus ALD was considered to be possible at 160 °C at the highest. Likely, the compound is less stable in the gas phase and when adsorbed on a surface.

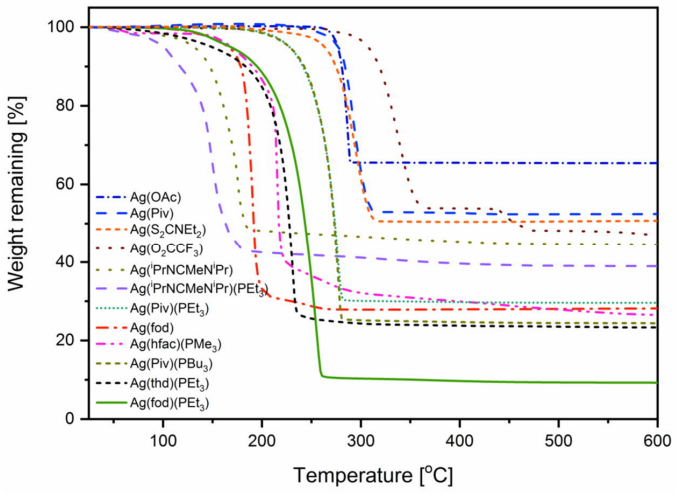


Figure 22 *TG curves of different silver compounds prepared. Measured in flowing N_2 atmosphere.*

Clearly, for all the other silver compounds studied except Ag(fod)(PEt_3), the temperature of efficient evaporation at 1 atm is higher than the onset temperature of decomposition. It seems evident that in Ag(fod)(PEt_3) the volatility and thermal stability are in an optimal balance.

In addition to Ag(fod)(PEt_3), literature reports some other silver compounds which show evaporation before decomposition in TGA. These include Ag(thd)(P^nBu_3),[270] Ag(fod)(PMe_3),[268] and Ag(hfac)($^-C\equiv^+NMe$).[252] However, being a better σ-donor and π-acceptor ligand than PMe_3 or methyl isocyanide, ($^-C\equiv^+NMe$), PEt_3 should form more stable compounds. PEt_3 and P^nBu_3 are expected to be quite similar. Comparing thd and fod, fod should be a weaker electron donor causing the Ag atom to be more acidic and thereby enhancing the bond strength between the adduct forming ligand and Ag. The lower thermal stability of Ag(thd)(PEt_3) may also be connected with the structural feature of a short Ag – Ag distance (Figure 21a). In general, it appears that Ag – Ag interaction might lower the thermal stability.

Otherwise, it seems difficult to make any straight conclusions concerning the thermal stabilities of the compounds based on their crystal structures. Concerning the volatility, polymeric compounds are less volatile than the monomeric or dimeric compounds.

Three of the compounds $Ag(O_2C^tBu)(PEt_3)$, $Ag(O_2C^tBu)(PBu_3)$, and $Ag(fod)(PEt_3)$ were tested in ALD depositions.[VIII,IX] Adducts of silver pivalate, $Ag(O_2C^tBu)(PEt_3)$ and $Ag(O_2C^tBu)(PBu_3)$, were combined with hydrogen radicals produced with a remote plasma source (radical-enhanced ALD).[VIII] Molecular H_2 did not yield any films while H radicals did. The silver precursors started to decompose at temperatures above 160 °C. As the precursors needed to be heated to 125 °C to volatilize them, the ALD window was limited to 140 – 160 °C. With $Ag(O_2C^tBu)(PEt_3)$ saturative growth behavior characteristic to ALD was confirmed, and conformal mirror-like and conducting films could be grown. With $Ag(O_2C^tBu)(PBu_3)$ films grew slowly, the resistivities were high, and the appearance of the films was dark. The worse results were assumed to be due to slower reaction kinetics or the PBu_3 ligands leaving more impurities in the films. Later on, upscaling the $Ag(O_2C^tBu)(PEt_3) – H_2$ plasma process was tried on 200 mm Si wafers, but no uniform films could be deposited over the whole substrate. To overcome this limitation, $Ag(fod)(PEt_3)$ was introduced as a new precursor.

$Ag(fod)(PEt_3)$ was used with plasma-activated hydrogen (PEALD).[IX] Again, mirror-like continuous films were deposited on silicon and glass substrates. Using this process, the films were uniform on substrates with a diameter of 200 mm. ALD window for the process was found at 120 – 140 °C. At 120 °C the growth rate was 0.30 Å/cycle and at 140 °C, where some signs of decomposition were already seen, 0.38 Å/cycle. The much lower growth rate compared to that observed for the $Ag(O_2C^tBu)(PEt_3) – H$ radical process (1.2 Å/cycle) was attributed to the larger fod ligand. The deposited films were polycrystalline, and the resistivity of a 22 nm film was 6 – 8 μΩ·cm. The films contained considerably fewer impurities than the films deposited with the $Ag(O_2C^tBu)(PEt_3) – H$ radicals process. These differences, however, may have been affected by the different reactor configurations too. Anyhow, a clear advantage of $Ag(fod)(PEt_3)$ over $Ag(O_2C^tBu)(PEt_3)$, as tested in the same reactor, is the ability to deposit uniform films over large area substrates. Later on, we developed a thermal ALD process where $Ag(fod)(PEt_3)$ was combined with $BH_3(NHMe_2)$ acting as a reducing agent.[263] This process showed self-limiting growth characteristics, but the resulting films were particulate and non-conducting. The $Ag(fod)(PEt_3) – H_2$ plasma process has been used to make SERS substrates which have been tested and found functioning.[15]

4.3.2.2 Conclusions

In the quest of finding suitable ALD precursors for silver, the main issue was to find a compound that has good volatility combined with sufficient thermal stability. Adding ancillary Lewis base ligands to silver(I) complexes is an efficient way to enhance the volatility of simple and otherwise low volatility compounds. Adducting lowers the aggregation degree of the unadducted compounds and decreases interactions between molecules, and thus enhances the volatility. The most suitable adduct forming ligands for Ag are ligands capable of π-back bonding interactions, e.g., alkyl phosphines.

Silver pivalate with triethyl phosphine, $Ag(O_2C^tBu)(PEt_3)$, was found to have adequate volatility and thermal stability to allow deposition of Ag films using hydrogen radicals as the

reducing agents. However, the temperature window for ALD was narrow and scaling up the process to larger substrates proved impossible. Better thermal stability and volatility were pursued by using chelating β-diketonato ligands. Fluorination of the ligand further enhances the volatility of the complex and also gives the Ag center higher Lewis acidity which makes the adduct forming Lewis base ligands to bond more strongly, which in turn makes the complexes thermally more stable. Ag(fod)(PEt_3) was found to be a precursor that can be used to deposit conducting and continuous Ag films in an ALD manner using plasma activated H_2 as the other precursor. Later on, it was found that this precursor also allows thermal ALD of silver films when combined with $BH_3(NHMe_2)$ as a reducing agent.[263] However, the films deposited using this method are particulate and non-conducting. Fortunately, fluorine was not found in any of the silver films deposited.

While Ag(fod)(PEt_3) is the state-of-the-art silver precursor combining sufficient volatility and thermal stability, still a volatile compound with better stability is desired. Unlike many other noble metals, silver has not been deposited using O_2 or O_3 as precursors. An O_3 process is, however, a distant dream. A volatile silver compound that is thermally stable above the Ag_2O decomposition temperature, which is > 350 °C, should be found.

4.4 Heavier Group 15 and 16 elements As, Sb, Bi, Se, and Te

Many selenides and tellurides are materials of great importance in modern thin film technology, e.g., germanium antimony telluride (GST) as a phase change memory (PCRAM) material,[271,272] $CuInSe_2$ and $CuIn_xGa_{(1-x)}Se$ (CIGS) as solar cell absorbers,[273] Sb_2Te_3 and Bi_2Te_3 as thermoelectric materials,[274] and ZnSe, CdSe, and CdTe as optoelectronic materials.[275]

Out of the compounds of arsenic, GaAs has surely been the material of the greatest interest. GaAs is an important direct bandgap semiconductor material which is used in, for example, various transistors,[276] high-efficiency solar cells,[277] laser diodes,[278] and LEDs to directly convert electricity into light.[279] Antimony is a constituent of the GST phase change material. Out of binary antimonides, Ge–Sb alloys are possible alternative tellurium free phase change materials,[280] and the III–V semiconductors AlSb, GaSb, InSb, and their mixtures are used in bipolar transistors, field-effect transistors, lasers, and IR detectors.[281,282]

Out of the pnictogens and chalcogens studied As, Sb and Te are classified as semimetals while Se is a nonmetal. While chalcogens make compounds with oxidation states from +6 to -2 and pnictogens from +5 to -3, all the materials of interest mentioned above are chalcogenides and pnictides in which the formal oxidation states are -2 and -3, respectively (as an exception in Sb_2Te_3 Sb is +3). Considering this, it is sensible to look for precursors where these elements are at the same formal oxidation state as they are in the films to be deposited. For this reason, cationic Bi precursors were examined in section 4.2 while the anionic Bi precursors are presented here.

The main issue considering the quest for finding precursors for chalcogens Se and Te, and pnictogens As, Sb, and Bi, is to find compounds that have suitable reactivity with the chosen co-precursors. Volatility and thermal stability are generally not issues because of the high electronegativity of the elements (As: 2.18, Sb: 2.05, Bi, 2.02, Se: 2.55, Te; 2.10) which causes

their compounds with typical ligands to be mostly covalent and hence volatile and thermally stable. Because the electronegativities of As, Sb, Bi, Se, and Te are higher than those of the O, N, and C (3.44, 3.04, 2.55, respectively), in the compounds with ligands having O, N, or C as the bonding atoms there is a decreased electron density, i.e., positive charge, on the pnictogen or chalcogen atom. On the other hand, silicon has an electronegativity of 1.90, and thus in the compounds of the pnictogen or chalcogen elements with ligands having Si as the bonding atom, there is a negative charge on the pnictogen or chalcogen atom.

4.4.1 Precursors used in ALD and other volatile compounds

CVD of chalcogenides has been done by combining a separate chalcogen precursor and a metal precursor, and by using single-source precursors. The first chalcogen precursors in CVD were hydrides H_2S and H_2Se, but they were found usually to react with the metal precursors already in the gas phase causing deposition of films with non-uniform morphology.[42] Less reactive alkyl compounds used as CVD precursors have been, e.g., MeSeH, Et_2Se, ^tBuSeH, $^tBu_2Se$, Me_2Te, Et_2Te, and $^iPr_2Te$.[283] To enable deposition of the chalcogenides at lower temperatures, compounds which have lower thermal stability have been introduced. Most of these compounds have been organometallic selenides and tellurides with larger alkyl, allyl or aromatic groups. Several single-source precursors of different metal-chalcogen combinations have been synthesized and studied during the last decades.[42] However, the single-source approach is not usually considered applicable to ALD. Obviously, the differences in designing and choosing selenium and tellurium precursors for CVD and ALD are pronounced here. In the articles by Groshens et al., deviating from the general trends of metal chalcogenide CVD, deposition of Sb_2Te_3 and Bi_2Te_3 using alkylsilyl compound of tellurium, $(Me_3Si)_2Te$, with $Sb(NMe_2)_3$ and $Bi(NMe_2)_3$ at temperatures from 24 to 150 °C and pressures of 0.25 – 100 Torr, have been reported.[284, 285]

For the CVD of arsenides, AsH_3 has been the most common precursor. To avoid the usage of this highly toxic gas and to lower the deposition temperature, monoalkyl and dialkylarsines have been introduced.[275] Trialkylarsine adducts and other single source precursors are also common.[42]

Selenium precursors used in ALD are elemental Se, H_2Se, Et_2Se, Et_2Se_2, and alkylsilyl compounds $(R_3Si)_2Se$ (R = Me, Et). Tellurium precursors have been elemental Te, Et_2Te, $^iPr_2Te$, Me(allyl)Te, and alkylsilyl compounds $(R_3Si)_2Te$.[28] MgTe, ZnTe, ZnSe, and CdSe have been deposited by ALD using elemental Se and Te as precursors.[28] The elemental forms have been evaporated at quite high temperatures of 300 and 400 °C under approximately 10 mbar pressure. Vapor pressures of the elements at these temperatures are only 0.225 [286] and 0.046 [287] mbar, respectively.

Dihydrogenselenide, H_2Se, has been used together with Zn, $ZnCl_2$, $ZnMe_2$, $ZnEt_2$, and $Zn(N(SiMe_3)_2)_2$ to deposit ZnSe, and together with $CdMe_2$ to deposit CdSe.[28] H_2Se is a fairly good ALD precursor, but its extreme toxicity makes it somewhat unattractive. For tellurium, the usage of H_2Te is not an option because of the low stability of the compound.[288]

Alkyl compounds of selenium and tellurium which are thermally quite stable and volatile have been combined with Zn, $ZnMe_2$, $ZnEt_2$, $CdMe_2$, and $HgMe_2$ to deposit ZnSe, ZnTe, CdTe, and HgTe.[28,289–296] These results might give an impression that the alkyl compounds are

generally suitable precursors for ALD, but that is not the case. The alkyl compounds are not particularly reactive with metal precursors. In most of the processes, the precursors are either partially decomposing or somehow activated to enhance the reactivity, or the materials deposited act as catalysts which enhance the reactions. Besides, H_2 has been used as the carrier gas in all these processes. Attempts to deposit GST using $^{i}Pr_2Te$ and $^{n}Bu_2Te$ as the tellurium precursor have been reported.[297–299] In these attempts, the approach was to deposit each element in its own cycle using hydrogen plasma as the reducing precursor. However, it seems that these processes did not result in real ALD type of growth. Later on, a similar plasma approach where di-n-butylditelluride $Te_2(n\text{-}C_4H_9)_2$, $Ge(NMe_2)_4$ and $Sb(cyclo\text{-}NC_2H_4)_3$ were used as precursors was presented.[300,301]

The alkylsilyl compounds of selenium and tellurium which are volatile, thermally stable, and reactive especially against metal halides, were introduced to ALD by us.[X] Afterward, these alkylsilyl compounds have been used to deposit a range of selenium and tellurium containing thin films as listed in Table 6. An analogous alkylgermanide compound $(Me_3Ge)_2Te$ has been used together with $Sb(NMe_2)_3$ to deposit Sb_2Te_3.[302]

Precursors used for arsenide films in ALD are elemental As, AsH_3, alkyl derivatives $EtAsH_2$ and $^{t}BuAsH_2$, $As(NMe_2)_3$, and the alkylsilyl compound $(Et_3Si)_3As$.[21,28] Despite the extreme toxicity, AsH_3 has been used extensively in the deposition of GaAs, AlAs, and InAs. The alkylarsines are liquids and slightly less hazardous than AsH_3.[275] Deposition temperatures in processes using arsine and alkylarsines have usually been quite high (300 – 580 °C). Elemental As, in turn, has a low vapor pressure. However, it has been evaporated at 400 °C [303] where it has a vapor pressure as high as 1.66 mbar.[304] 0.1 mbar is reached at 335 °C. $As(NMe_2)_3$ has been used at such high temperatures (~300 – 495 °C) that the compound is likely decomposing at least partly (decomposes at >300 °C [305] to As). However, growth has been reported to be self-limiting.[306,307]

The antimony precursors used in ALD have been Sb, $SbCl_3$, $SbCl_5$, $Sb(OEt)_3$, $Sb(NMe_2)_3$, $(Me_3Si)_3Sb$ and $(Et_3Si)_3Sb$.[28,308–310] However, only the alkylsilyl compounds $(Me_3Si)_3Sb$ and $(Et_3Si)_3Sb$, and elemental Sb have been used to deposit antimonides – others have been precursors for antimony oxide, sulfide, selenide, telluride, and elemental antimony. Though the vapor pressure of elemental antimony is low (e.g., 0.0025 mbar at 500 °C) [311] it has been used for ALD of InSb in high vacuum MBE system.[312,313] Bismuthides have not been deposited. Bismuth precursors used for the other bismuth-containing materials were reviewed in chapter 4.2.1.

Table 6 *Reported ALD processes utilizing alkylsilyl compounds of chalcogen and pnictogen elements.*

Chalcogen or pnictogen precursor	Metal/other precursors	Material	Reference
$(Me_3Si)_2Te$	$Te(OEt)_4$	Te	314,315
	$HGeCl_3$	GeTe	315,316
	$HGeCl_3$, Sb(OEt)3	Ge-Sb-Te	316
	$Ge(btsa)_2$, MeOH	GeTe	317
	$SbCl_3$	Sb-Te	318,319
	$Sb(OEt)_3$, $(Me_3Si)_3Sb$	Sb-Te	309
	$Ge(OMe)_4$ or $Ge(OEt)_4$, $Sb(OEt)_3$	Ge-Sb-Te	320,321
	$Ge(OEt)_4$, $Sb(OEt)_3$, $(Me_3Si)_3Sb$	Ge-Sb-Te	310
	$BiCl_3$, $SbCl_3$	Bi-Te/Sb-Te	322,323,324
	$Ge(OEt)_4$, $Sb(OEt)_3$, $(Me_3Si)_2Se$	Ge-Sb-Se-Te	325
$(Et_3Si)_2Te$	$SbCl_3$	Sb_2Te_3	X,308,326,327
	$SbCl_3$, $(Et_3Si)Sb$	Sb–Te	308
	$GeCl_2$·dioxane	GeTe	X,17,326
	$ZnCl_2$	ZnTe	X
	$BiCl_3$	Bi_2Te_3	X,19
	$Pb(thd)_2$	PbTe	328, 329,330
$(Me_3Si)_2Se$	$Ge(OEt)_4$, $Sb(OEt)_3$, $(Me_3Si)_2Te$	Ge-Sb-Se-Te	325
	$Te(^tBu)_2$, $Sb(NMe_2)_3$	Sb-Te-Se	331
	$HGeCl_3$	GeSe	332
	$Mo(CO)_6$	$MoSe_2$	333
	$MoCl_5$	$MoSe_2$	333
	$Pb(thd)_2$	PbSe	328
$(Et_3Si)_2Se$	CuCl	CuSe	X
	$Cu(O_2C^tBu)_2$	CuxSe	X
	$ZnCl_2$	ZnSe	X
	$InCl_3$	In_2Se_3	X
	$BiCl_3$	Bi_2Se_3	X,20
	$SbCl_3$	Sb_2Se_3	327
$(Me_3Si)_3Sb$	$Sb(OEt)_3$	Sb	309
	$Ge(OEt)_2$, $Sb(OEt)_2$, $(Me_3Si)_2Te$	Ge-Sb-Te	310
$(Et_3Si)_3Sb$	$SbCl_3$	Sb	308
	$AlCl_3$	AlSb	308
	$GaCl_3$	GaSb	308
	$GeCl_2$· dioxane	GeSb	308
	$SbCl_3$, $(Et_3Si)_2Te$	Sb–Te	308
$(Et_3Si)_3As$	$GaCl_3$	GaAs	21

4.4.2 Alkylsilyl compounds of As, Sb, Bi, Se and Te [I, X]

Our interest in studying precursors for the Group 15 and 16 elements initially originated from the need of an ALD process for germanium antimony telluride (GST) based materials for making phase-change random access memories (PCRAM). When the right chemistry for the purpose was found, the studies were immediately expanded to other chalcogenide and pnictide materials, whose deposition was also enabled by the new ALD chemistry.

From the beginning, a thermal process was desired, and also depositing each element in its own deposition cycle, like in the earlier approaches,[297,298] seemed unnecessary. While the previous attempts seemed to approach GST as a ternary alloy material, we saw it as a mixture of the stoichiometric binary components of GeTe and Sb_2Te_3.

We were not keen to use the gaseous and extremely toxic hydrides AsH_3 (arsine), SbH_3 (stibine), H_2Se, and H_2Te as precursors. It was also realized very soon that the problems using the common CVD precursors in ALD were due to reactivity issues: alkyl tellurides do not react efficiently with the common metal precursors. Thus we were to find a more reactive precursor for tellurium or more reactive precursor combinations for GST.

While making a literature search, articles about alkylsilyl compounds of tellurium, selenium, and antimony, especially the two articles on low temperature (24 – 150 °C) CVD of Sb_2Te_3 and Bi_2Te_3 where $(Me_3Si)_2Te$ was used together with $Sb(NMe_2)_3$ and $Bi(NMe_2)_3$, were found.[284,285] The reactivity between $(Me_3Si)_2Te$ and the amines mentioned in the articles immediately seemed something that was exactly looked for.

The alkylsilyls of the Group 15 and 16 elements were known compounds, and they had been suggested and tested as CVD precursors. The reactivity of the alkylsilyl compounds towards different metal compounds, especially metal chlorides (dehalosilylation reaction) was also known already at the 1980s. Materials such as GaAs, InAs, and GaSb had been synthesized in solution by mixing appropriate halides and alkylsilyl compounds.[284,334–344]

4.4.2.1 Compounds studied: synthesis and properties

Alkylsilyl compounds with the ligands trimethylsilyl, tert-butyldimethylsilyl, and triethylsilyl were synthesized (Table 7) using literature methods [345,346] with slight modifications. At first (Eq. 1) Group 15 or 16 element was reacted with 3 or 2 equivalents of alkali metal (Li or Na) in ether (Et_2O or DME) to form the appropriate alkali metal compound A_xE (A = Na or Li, E = As, Sb, Se, Te).[345] Naphthalene was used to catalyze the reaction which took, depending on the element, from some hours to several days to proceed under reflux. In the second phase (Eq. 2) the appropriate alkylsilyl ligand was added in the form of the alkylsilyl chloride.[314,347]

(1) $$E + n\,A \xrightarrow[\text{refluxing}]{\text{naphthalene}} A_nE$$

(2) $$A_nE + n\,R^1R^2R^3SiCl \longrightarrow (R^1R^2R^3Si)_nE + n\,ACl$$

The compounds prepared are listed in Table 7. The products were identified using ^{1}H and ^{13}C NMR spectroscopy and MS, and for the known compounds, the results were in agreement with those reported in the literature.

Table 7 *Alkylsilyl compounds synthesized. Yields, melting temperatures, boiling point temperatures, and molecular weights.*

Compound	Yield	mp [°C]	bp [°C/mbar]	Reference
$(Et_3Si)_3As$	44	liquid	137/1	-
$(Me_3Si)_3Sb$	78	6	88/2.7	348,349
$(Et_3Si)_3Sb$	78	liquid	148-153 / 1.3	350
$(Et_3Si)_3Bi$	22	liquid	113/1	351
$(Et_3Si)_2Se$	83	liquid	116-118/5.3;280	352,353
$(^tBuMe_2Si)_2Se$	69	44	66/1	351
$(Me_3Si)_2Te$	56	Liquid, 13.5	49-51/2.5; 74/1.7; 40-42/0.33	346,354,355
$(Et_3Si)_3Te$	77	liquid	97-99/1; 289.5	351,352,353
$(^tBuMe_2Si)_2Te$	80	44	90-95/5.5; 105/4.5	346,356

Yields of the synthesis were reasonably good (56 – 83%) for the group 16 elements and Sb (78%). For the Group 15 elements As and Bi, the yields were lower (44 and 22%). The low yields were due to slowness and inefficient formation of the alkali metal compounds of the elements in question. The reactions were far from complete even after refluxing the reaction mixtures up to one week. $Et_3SiSiEt_3$ was seen as an impurity in the synthesis products, and this was most likely because of the incomplete formation of the alkali metal compounds: the reaction mixture contained some unreacted alkali metals when Et_3SiCl was added, and this caused $Et_3SiSiEt_3$ to form through Wurz reaction. $Et_3SiSiEt_3$ was removed from the targeted synthesis product by distillation. The compounds with the $^tBuMe_2Si$ ligand were low melting point solids (Table 7) while those with the Me_3Si and Et_3Si ligands were liquids. While the molecular weights of Et_3Si and $^tBuMe_2Si$ are the same, Et_3Si ligand has more degrees of freedom than $^tBuMe_2Si$, which may explain this difference.

Crystal structures of $(^tBuMe_2Si)_2Se$ and $(^tBuMe_2Si)_2Te$ were solved, and the structures are shown in Figure 23. Both structures consist of monomeric molecules. As expected, the molecules are bent due to the two lone electron pairs taking their space.

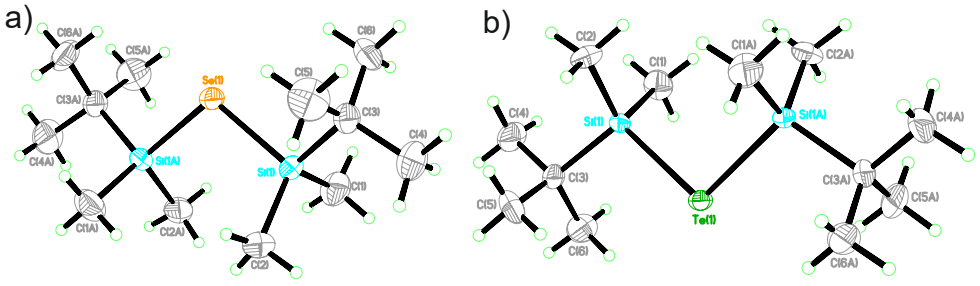


Figure 23 *Molecular structures of a) $(^tBuMe_2Si)_2Se$ and b) $(^tBuMe_2Si)_2Te$.[351,X] Thermal ellipsoids are drawn at 50% probability level.*

While $(Et_3Si)_3Bi$ is a liquid compound, crystals were found from an impure product. The crystals were of an intermediate product $[(Et_3Si)_2BiNa(DME)]_n$ (Figure 24) although the amount of Et_3SiCl used in the synthesis was five times the amount of Bi. This indicates that also the reaction between R_3SiCl and $BiNa_3$ is not that fast or that the formation of $(Et_3Si)_3Bi$ is not thermodynamically strongly favored over the formation of $[(Et_3Si)_2BiNa(DME)]_n$. However, based on the literature data all pure alkylsilyl compounds of the Group 15 and 16 elements appear to be monomeric as, e.g. $(Me_3Si)_2Te$ [357] and $(Me_3Si)_3Sb$ [358] with the smallest alkylsilyl ligand are monomeric in the solid state.

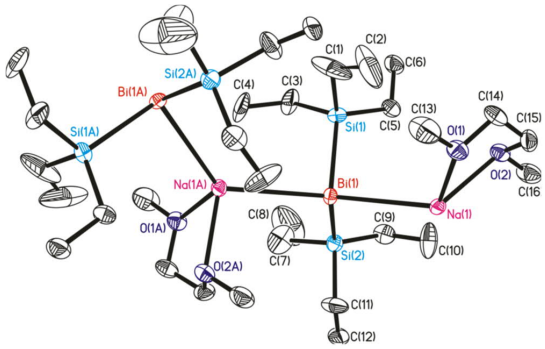


Figure 24 *After standing for some time, crystals were found from the otherwise liquid $(Et_3Si)_3Bi$ synthesis product. The compound is $[(Et_3Si)_2BiNa(DME)]_n$, i.e., an intermediate product of the synthesis. Chain structure. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.*

TG measurements revealed that all the compounds of the Group 16 elements (S, Se, Te) are volatile and exhibit pure evaporation behavior which also confirms the thermal stability of the compounds up to the temperatures where evaporation was complete (Figure 25). The volatility of the compounds depends strongly on their molecular weight. The compounds of the Group 15 elements (As, Sb, Bi) were found to lose weight at higher temperatures compared to the analogous Group 16 compounds. Only part of the samples was evaporated before decomposition of the compounds set in as indicated by the residues seen. The residues got larger in the order of As < Sb < Bi. DTA (not shown) also revealed that the single weight loss step was accompanied by heat release (exotherm) which indicates decomposition. However, $(Et_3Si)_3As$ leaves practically no residue apparently because the decomposition products are volatile too. It may be estimated from the TGA results that at least as bulk materials $(Et_3Si)_3E$ (E = As, Sb, Bi) start to show thermal decomposition at temperatures above about 260 °C. The curve measured for $(Me_3Si)_3Sb$ also seems untypical for simple evaporation though there is near zero residue at the end of the measurement. Like $(Et_3Si)_3As$, $(Me_3Si)_3Sb$ probably decomposes, but all the decomposition products are volatile. The change starts to take place around 190 – 200 °C. In an early publication by Vyazankin et al.[350] it was said that $(Et_3Si)_3Sb$ and $(Et_3Si)_2Bi$ should be stable up to 300 and 290 °C, respectively, which is in some contrast with the TGA data.

The reason for the choice of using ligands other than the most simple and small Me_3Si, i.e., larger ligands $^tBuMe_2Si$ and Et_3Si, was that vapor pressures of the trimethylsilyl compounds of Se and Te were thought to be unnecessarily high considering the safe handling of the

compounds. Also, the compounds with larger alkylsilyl ligands were found to be less sensitive to light, air, and moisture.

The high thermal stability of the Group 16 compounds suggested by TGA was confirmed by ALD experiments of ZnSe and ZnTe which were grown using $(Et_3Si)_2Se$ + $ZnCl_2$ and $(Et_3Si)_2Te$ + $ZnCl_2$ at 400 °C without any observed decomposition.[X]

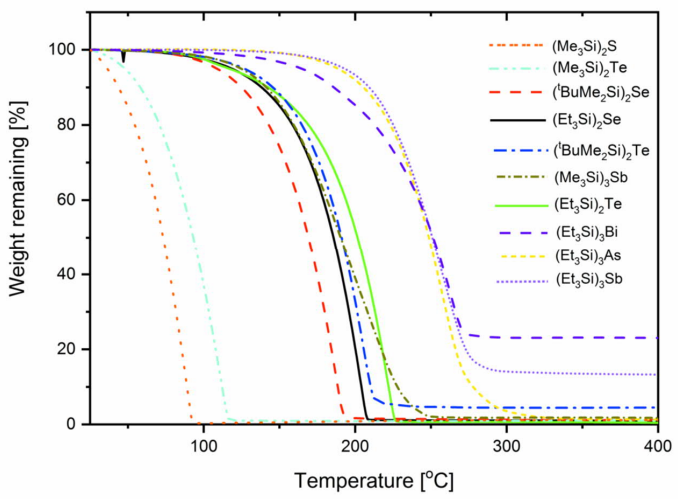


Figure 25 *TG curves measured for different alkylsilyl compounds of As, Sb, Bi, S, Se, and Te. Curve measured for $(Me_3Si)_2S$ is for a commercial sample. Heating rate 10 °C/min, flowing N_2 atmosphere, 1 atm pressure.*

Reactivities of $(Et_3Si)_2Se$, $(Et_3Si)_2Te$, $(^tBuMe_2Si)_2Te$, and alkyl tellurides were preliminarily studied by mixing the compounds with different metal precursors in solution at room temperature.[351] Selected results of the tests are collected in Table 8. As mentioned above, different materials had been synthesized by reactions between alkylsilyl compounds and various metal compounds in solution before our work, but information on the rate of the reactions was absent or inadequate in most cases.

It was found that the alkylsilyl compounds are reactive with many metal halides and other metal compounds while alkyl tellurides do not react with the same metal compounds at all (Figure 26). This can be understood in the light of formal oxidation state of tellurium in these compounds: in the alkylsilyl compounds tellurium is at a formal oxidation state -2 while in the alkyl compounds it is +2. The positive tellurium will hardly react with the positive metal centers. Also, the hard-soft acid-base, i.e., the HSAB principle, was found useful rationalizing the reactivity [48]. In $(R_3Si)_3Se$ and $(R_3Si)_2Te$ silicon, a hard Lewis acid is unfavorably coordinated to a soft Lewis base (Se, Te). Upon exchange reaction with metal chlorides, for example, silicon becomes bonded to the harder base:

(3) $$MCl_x + x\ (Et_3Si)_2Te \longrightarrow MTe_x + x\ Et_3SiCl$$

Further, if the metal in the metal chloride is a 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).

Table 8 *Results from the reactivity tests in solution. Compositions of the solid products formed were measured with EDS.[351]*

Reaction	Observations	Caomposition by EDS[1]
$SbCl_3$ + $(^tBuMe_2Si)_2Te$	Immediate formation of a black solid and reflective film	Sb 38%, Te 57%, Cl 5% XRD: Sb_2Te_3
$Sb(NMe_2)_3$ + $(Et_3Si)_2Te$	Slow darkening of the solution, eventually after days black solid + reflective film	-
$Sb(OEt)_3$ + $(Et_3Si)_2Te$	A dark solution in less than a minute, in a few minutes a black solid	Sb 46%, Te 54%
$GeBr_2$ + $(Et_3Si)_2Te$	Darkening in less than a minute, a brown solid in a few minutes	Ge 38%, Te 8%, Br 55%[2]
$GeCl_2$·dioxane + $(Et_3Si)_2Te$	Almost immediate formation of a black solid	Ge 40%, Te 52%, Cl 8%
$GeCl_4$ + $(^tBuMe_2Si)_2Te$	Immediate formation of a black solid and reflective film	Ge 32%, Te 60%, Cl 7%
$Ge(NMe_2)_4$ + $(^tBuMe_2Si)_2Te$	Slow darkening of the solution, a black solid in 3 days	-
$Cu(O_2C^tBu)_2$ + $(Et_3Si)_2Se$	A black solid in a few minutes	Cu 51%, Se 49%

[1] Carbon and oxygen were also detected in all samples.

[2] High bromine content suggests a substantial amount of unreacted $GeBr_2$ in the product.

Alkylsilyl compounds of tellurium and selenium reacted with metal chlorides in seconds while the reactions with metal alkylamides proceeded slowly. For example, $SbCl_3$ + $(Et_3Si)_2Te$ resulted in an immediate formation of a black solid and reflective film of Sb_2Te_3 (composition confirmed with EDS) while the reaction between $Sb(NMe_2)_3$ and $(Et_3Si)_2Te$ proceeded slowly so that in hours only slight darkening of the yellow color of the solution was observable. After one day there was some black deposit, and the solution looked black. After three days, a reflective film was observed (Figure 26). In the case of $GeBr_2$, the reaction proceeded but with EDS large amounts of Br was found in the solid even after several days. This can be explained by the fact that Br^- is a soft base and thus the reaction with the alkylsilyl compounds is less favorable.

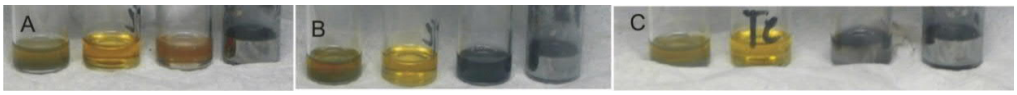


Figure 26 *Reactivity of $(C_6H_{13})_2Te$ and $(Et_3Si)_2Te$ with $Sb(NMe_2)_3$ and $SbCl_3$. The photos show four bottles, from left to right, containing $(C_6H_{13})_2Te$ + $Sb(NMe_2)_3$, $(C_6H_{13})_2Te$ + $SbCl_3$, $(Et_3Si)_2Te$ + $Sb(NMe_2)_3$ and $(Et_3Si)_2Te$ + $SbCl_3$. A: immediately after mixing, B: after one day, C: after three days.*

Tests conducted with $(Et_3Si)_3Sb$, $(Et_3Si)_3As$ and $(Et_3Si)_3Bi$ (Figures 27 and 28) revealed a similar trend with that observed with the Se and Te compounds: metal chlorides showed immediate reaction while amides, alkoxides, and alkyl compounds reacted slowly. The reaction of $(Et_3Si)_3As$ with $GaCl_3$ did not result in GaAs but some orange solid that might have been, e.g., $Et_3SiAsGaCl$, $Ga(As(SiEt_3)_2)_3$, or $Ga_2(As(SiEt_3))_3$.

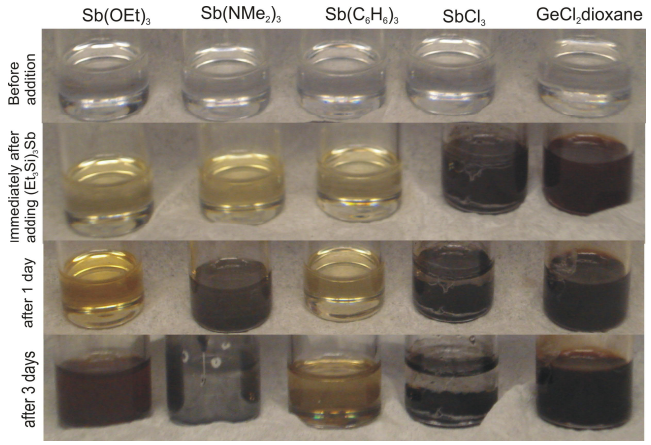


Figure 27 *Reactivity of $(Et_3Si)_3Sb$ with different co precursors in toluene solution. Immediate reaction with $SbCl_3$ and $GeCl_2$·dioxane is observed. Slow reaction with $Sb(NMe_2)_3$ and $Sb(OEt)_3$ and no reaction with $Sb(Ph)_3$.*

Judging from the above examples, it seemed evident that the reactions between alkylamides of antimony and alkylsilyl compounds of tellurium may be too slow to be used in ALD. Indeed, in the ALD experiments, we observed hardly any growth from the alkylamide $Sb(NMe_2)_3$ and $(Et_3Si)_2Te$, i.e., the reaction that had been used in CVD.[284,285] In general, this kind of solution tests were found useful in planning new ALD processes.

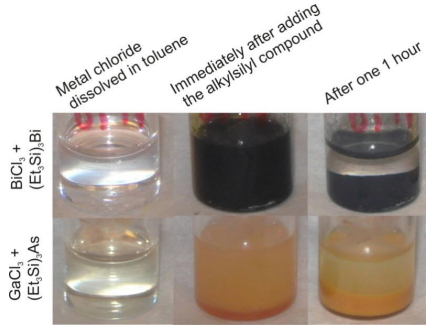


Figure 28 *Reactivity of $(Et_3Si)_3Bi$ and $(Et_3Si)_3As$ with $BiCl_3$ and $GaCl_3$, respectively. Toluene was used as the solvent.*

ALD using the alkylsilyl compounds of the Group 15 and 16 elements proved to be successful when combined with metal chlorides (see Table 6). Deposition of several materials that had not been deposited by ALD before was realized. In addition to the deposition of binary and ternary materials, an ALD process for elemental antimony utilizing comproportionation reaction between $(Et_3Si)_3Sb$ and $SbCl_3$ was developed.[308] Out of the prepared compounds, only the alkylsilyl compound of bismuth was not tested, though it is likely to work as well. The initial main goal of finding suitable precursors and a process for the deposition of the Ge – Sb – Te phase change materials was achieved.

All the processes studied were found to be true ALD processes in the sense that the growth rates more or less saturated with respect to the precursor pulse lengths. The processes also showed a linear relationship between the number of deposition cycles and film thickness. Atypical for ALD some of the processes (Bi_2Te_3, Bi_2Se_3, GST with alkoxides) seem to be somewhat sensitive to the purge lengths, possibly due to desorption, physisorption, or rearrangement processes. A typical peculiarity of most of the processes, e.g., GeTe, Sb_2Te_3, Bi_2Te_3, Bi_2Se_3, Sb, and GaAs, is the strong temperature dependence of the growth rate. These processes do not have the classic temperature window of constant growth rate, but instead, the growth rate decreases rapidly with increasing growth temperature. This feature, however, is not due to the processes or the alkylsilyl precursors but rather because of the materials themselves. The temperature has been found to have similar effects on sputtering and MBE of the corresponding tellurides.[359,360] Conformality of several processes was studied and found as good as can be expected for a good thermal ALD process. While most of the processes studied were found to work best at low temperatures, some processes like those for ZnSe and ZnTe worked at 400 °C without any signs of precursor decomposition.[X] In-situ mechanism studies for GeTe, Sb_2Te_3, and Sb processes, utilizing $(Et_3Si)_2Te$, $(Et_3Si)_3Sb$ and metal chlorides, proved that the only byproduct formed in the processes was alkylsilyl chloride Et_3SiCl and that the films were formed through ligand exchange reactions.[308,326] Most of the Et_3SiCl was released during the metal chloride pulse.

The ternary material GST could be deposited by combining processes of GeTe, Sb_2Te_3, and Sb. By adjusting the cycle ratios, the compositions of the films could be controlled. In Figure 29a, there is a GST phase diagram showing the compositions reached using the metal chloride – alkylsilyl tellurium/antimony based ALD processes.[I] The ability of the alkylsilyl chemistry to produce conformal films on high aspect ratio structures and to fill sub-100 nm holes in actual PCRAM device structure was confirmed in all the cases tested. As an example, Figure 29b shows a TEM image of a GeTe film filling a 31 nm × 84 nm via.[17] Scalability of the alkylsilyl processes has been demonstrated, e.g., by depositing GST films with less than 3% 1σ thickness nonuniformity on 200 mm wafers.[361]

In our studies, metal precursors other than chlorides were only sparsely tested with the alkylsilyl compounds. When combining $(Et_3Si)_2Te$ with $Sb(OEt)_3$ and $GeBr_2$ films were produced while no growth was observed with $Sb(NMe_2)_3$, $Ge(N(SiMe_3)_2)_2$, $Ge(O^tBu)_2$ $GeCl_4$, and $GeBr_4$. $(Et_3Si)_2Se$ combined with $Cu(O_2C^tBu)_2$ produced CuSe films. In general, metal chlorides seem to have good reactivity with the alkylsilyls while metalorganic compounds have varying reactivity.

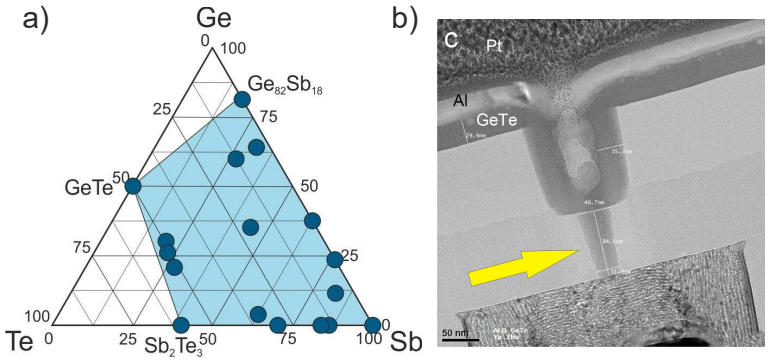


Figure 29 *a) Ge-Sb-Te phase diagram showing compositions reached with the metal chloride - alkylsilyl tellurium/antimony based ALD processes. Reprinted from [I] with permission from Elsevier, Copyright (2013). b) Transmission electron microscopy image of a GeTe film filing a 31 × 84 nm via indicated by the arrow. Reproduced with permission from [17] with permission from The Electrochemical Society Copyright (2011).*

Phase change properties of the GeTe and GST films deposited were tested and found similar to those of the sputtered films.[17,18] Thermoelectric properties of Bi_2Se_3 and Bi_2Te_3 deposited by us have also been studied and concluded to be appropriate for the usage in thermoelectric devices.[19,20]

4.4.2.2 Conclusions

A new class of precursors for the ALD of chalcogenides and pnictides was found. Various alkylsilyl compounds of selenium, tellurium, arsenic, antimony, and bismuth were synthesized, characterized, and studied as potential ALD precursors for selenides, tellurides, arsenides, and antimonides. It was found that these compounds exhibit high volatility and thermal stability. Preliminary reactivity studies in solution proved that the alkylsilyl compounds are reactive against many metal compounds such as alkoxides, amides, carboxylates, and most importantly very highly reactive against metal chlorides. These results were corroborated by the ALD deposition experiments where the alkylsilyl compounds were found good ALD precursors when combined with metal chlorides. It was shown that the alkylsilyl compounds of the Group 16 and 15 elements enable ALD processes for a large selection of materials, e.g., GST, Sb_2Te_3, GeTe, Bi_2Se_3, Bi_2Te_3, CuSe, Cu_2Se, In_2Se_3, ZnSe, ZnTe, GaAs, Sb, Ge–Sb, AlSb, and GaSb, with all the benefits of ALD like conformality on demanding 3D structures. Since inventing the processes utilizing alkylsilyl compounds, they have been studied and used by many research groups, and they are still the state-of-the-art precursors for selenides, tellurides, and antimonides.

5 Conclusions and Outlook

The success of ALD is built on chemistry. To deposit a thin film material of interest with all the advantageous features of ALD, one must find the right set of precursors. In general, the ALD precursors have to have sufficient volatility and thermal stability. In addition, the precursors have to be reactive against the co-precursors so that the desired solid material is formed. The properties of the material deposited may be affected by choice of precursors and other deposition parameters. Factors driving the precursor development are in one hand the need to deposit new materials and on the other hand, the need to improve or to make the materials more suitable for certain applications. Applications may also require, e.g., processes working at lower temperatures. To push the process development forward new precursors for all, i.e., metals, nonmetals, and, e.g., reduction and ligand scavenging, are needed. In general, a search for new precursors is not a separate task but an integral part of the process development. From the beginning, one must consider the whole process, and based on that, choose the line of precursors to be developed. The combination of precursors makes a good process, not a single precursor alone. However, very few processes are ideal, and usually one has to compromise between different "flaws". In this work, potential precursor compounds were invented, synthesized and studied, and precursor-based process development for different materials was done.

β-diketonates of alkaline earth metals are kind of first-generation precursors that are very good for CVD but lack some desired properties needed in ALD, like reactivity with H_2O. For depositing sulfides with H_2S, the β-diketonates are suitable. β-diketonates had suffered from inconsistent quality resulting in different evaporation and growth behaviors. To get first-hand knowledge and insight on β-diketonates of alkaline earth metals, they were taken into study. Especially $Mg(thd)_2$ and its adducts were studied. It was found that adducts with consistent quality may be synthesized without exclusion of air and moisture as long as multidentate Lewis bases with a sufficient number of donor atoms coordinating strongly enough are used so that coordination of H_2O and other possibly reactive small molecules is hindered. Adducting may be used to render the oligomers into monomers and to enhance the volatility, but at elevated temperatures, below those typically needed for the ALD growth, the adducts of the Mg, Ca, Sr, and Ba thd β-diketonates tend to dissociate.

As an answer to the request and need to deposit oxides of alkaline earth metals, especially strontium and barium, cyclopentadienyl compounds were developed and tested. In the prior art, β-diketonates had been found unreactive towards water and to deposit carbonates with stronger oxidants like O_3. Thus, more reactive precursors were needed. The best cyclopentadienyl compounds for the purpose were found to be those with sufficiently bulky cyclopentadienyl ligands, i.e., $Sr(^tBu_3C_5H_2)_2$ and $Ba(^tBu_3C_5H_2)_2$. With the bulky ligands, volatile monomeric compounds with no or with minor interactions with surroundings, having the intrinsic high thermal stability of metallocenes, still retaining their high reactivity against small molecules like H_2O and H_2S, were realized. Making adducts of the Cp compounds and using donor-functionalized Cp ligands were found inferior strategies for making good ALD precursors as compared with the strategy of using bulky Cp ligands. Cp compounds enabled ALD of alkaline earth oxides containing films, in particular, $SrTiO_3$, $BaTiO_3$, and $(Ba,Sr)TiO_3$, that have been of interest as possible high permittivity dielectric materials for DRAM capacitors. To date, Cp compounds are still the state-of-the-art alkaline earth metal precursors for ALD.

Motivation to study bismuth precursors originated from the need to deposit bismuth-containing ternary oxides. Drawbacks of bismuth precursors $BiCl_3$, $BiPh_3$ and $Bi(mmp)_3$, i.e., tendency to deposit oxyhalides, lack of reactivity with H_2O and long term thermal instability, respectively, were to be tackled. Different bismuth compounds were synthesized, and the most suitable one for the oxide processes was found to be a bismuth alkoxide $Bi(OCMe_2{}^iPr)_3$ with tertiary alkoxy ligands. With this low melting, volatile and thermally stable compound, and H_2O sufficiently pure good quality films could be deposited reliably in a wide temperature range.

Precursors for silver were taken into study due to a general curiosity and the possible application of ALD silver films as SERS substrates. At the beginning of the studies, there were no ALD silver processes reported. The most promising compounds found were $Ag(O_2C{}^tBu)(PEt_3)$ and $Ag(fod)(PEt_3)$, both containing an anionic bidentate oxygen donor ligand and a neutral phosphine adduct ligand. Adducting enhances the volatility, and the use of a π acceptor, like the phosphine, as the adduct forming ligand is essential for thermal stability. Both silver precursors combined with H_2 radicals or plasma were shown to deposit silver in the ALD mode. With $Ag(fod)(PEt_3)$ uniform silver thin films have been deposited on 200 mm wafers.

Studies on the Group 15 and 16 elements were initiated by a need to deposit germanium antimony telluride films for phase change memory applications. The key was to find a suitable tellurium precursor and combining that with right germanium and antimony precursors. For this purpose, alkylsilyl compounds were found the most suitable. They were found out to react efficiently with metal chlorides like $GeCl_2 \cdot$dioxane and $SbCl_3$ depositing the desired tellurides. Immediately it was also realized that the chemistry could be expanded to other Group 16 elements and also Group 15 elements. After the introduction of this chemistry, a large selection of chalcogenide and pnictide materials new for ALD have been deposited with it.

Considering the impact of the work, the articles that are included in this thesis have found some interest. Altogether, the ten articles have been cited 453 times in 373 articles. The least cited article V has 19 citations, and the most cited X has 95 citations. Out of the precursors introduced in the articles cyclopentadienyl compounds of alkaline earth metals, $Bi(OCMe_2{}^iPr)_3$, $Ag(fod)(PEt_3)$, and many alkylsilyl compounds of chalcogenides and pnictides have become commercially available afterward.

The ALD precursor chemistry has been and will be crucial in developing new ALD processes and thereby bringing the whole ALD technology forward. Challenges exist still in finding precursors and precursor combinations for depositing new materials and materials whose deposition need improvement. Also tuning the precursor properties in order to fulfill the requirements of different applications will always be needed. There is a large set of known ligands that can be used in designing and synthesizing metal precursors, but there is still also space to tune the ligands further by substitution and to synthesize completely new types of ligands. In this work, heteroleptic compounds other than adducts were not studied, but they have been getting more common all the time and will most likely do so also in the future. It should also be kept in mind that at the same time as entirely new compounds are studied as precursors there are also many known compounds synthesized for some other purpose that only wait to be found for the ALD purpose. While most of the efforts in the ALD precursor chemistry are targeted on the metal precursors, developing and finding non-metal precursors, reducing agents, and other co-reactants will also be most important.

References

[1] A. C. Jones, P. R. Chalker, *J. Appl. Phys.* **36** (2003) R80.

[2] M. Ritala, M. Leskelä, *Atomic Layer Deposition*. In H. S. Nalwa (Ed.), *Handbook of Thin Film Materials, Volume 1: Deposition and Processing of Thin Films*, Chapter 2, pages103–159, Academic Press, (2002).

[3] A. Pakkala, M. Putkonen, *Atomic Layer Deposition.* In P. M. Martin (Ed.), *Handbook of Deposition Technologies for Films and Coatings, Science, Application and Technology*, 3rd edition, Chapter 8, pages 364–388, Elsevier, (2010).

[4] J. Ihanus, T. Hänninen, T. Hatanpää, T. Aaltonen, I. Mutikainen, T. Sajavaara, J. Keinonen, M. Ritala, M. Leskelä, *Chem. Mater.* **14** (2002) 1937.

[5] J. Ihanus, T. Hänninen, T. Hatanpää, M. Ritala, M. Leskelä, *J. Electrochem. Soc.* **151** (2004) H221.

[6] M. Vehkamäki, T. Hatanpää, T. Hänninen, M. Ritala, M. Leskelä, *Electrochem. Solid-State Lett.* **2** (1999) 504.

[7] M. Vehkamäki, T. Hänninen, M. Ritala, M. Leskelä, T. Sajavaara, E. Rauhala, J. Keinonen, *Chem. Vapor Depos.* **7** (2001) 75.

[8] M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, S. Väyrynen, E. Rauhala, *Chem. Vapor Depos.* **13** (2007) 239.

[9] M. Vehkamäki (**2007**), *Atomic Layer Deposition of Multicomponent Oxide Materials.* Academic dissertation, University of Helsinki, http://ethesis.helsinki.fi/.

[10] M. Tyunina, M. Plekh, J. Levoska, M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, *Integr. Ferroelectr.* **102** (2008) 29.

[11] M. Vehkamäki, T. Hatanpää, M. Kemell, M. Ritala, M. Leskelä, *Chem. Mater.* **18** (2006) 3883.

[12] M. Puttaswamy, M. Vehkamäki, K. Kukli, M. C. Dimri, M. Kemell, R. Stern, M. Leskelä, *Thin Solid Films* **611** (2016) 78.

[13] P. Jalkanen, V. Tuboltsev, B. Marchand, A. Savin, M. Puttaswamy, M. Vehkamäki, K. Mizohata, M. Kemell, T. Hatanpää, V. Rogozin, J. Räisänen, M. Ritala, M. Leskelä, *J. Phys. Chem. Lett.* **5** (2014) 4319.

[14] S. M. Prokes, O. J. Glembocki, E. Cleveland, J. D. Caldwell, E. Foos, J. Niinistö, M. Ritala, *Appl. Phys. Lett.* **100** (2012) 053106.

[15] J. D. Caldwell, O. J. Glembocki, F. J. Bezares, M. I. Kariniemi, J. T. Niinistö, T. T. Hatanpää, R. W. Rendell, M. Ukaegbu, M. K. Ritala, S. M. Prokes, C. M. Hosten, M. A. Leskelä, R. Kasica, *Opt. Express* **19** (2011) 26056.

[16] A. Radtke, T. Jedrzejewski, W. Kozak, B. Sadowska, M. Wieckowska-Szakiel, E. Talik, M. Mäkelä, P. Piszczek, *Nanomaterials* **7** (2017) 193.

[17] T. Sarnet, V. Pore, T. Hatanpää, M. Ritala, M. Leskelä, A. Schrott, Y. Zhu, S. Raoux, H.Y. Cheng, *J. Electrochem. Soc*. **158** (2011) D694.

[18] M. Ritala, V. Pore, T. Hatanpää, M. Heikkilä, M. Leskelä, K. Mizohata, A. Schrott, S. Raoux, S. M. Rossnagel, *Microelectron. Eng.* **86** (2009) 1946.

[19] T. Sarnet, T. Hatanpää, E. Puukilainen, M. Mattinen, M. Vehkamäki, K. Mizohata, M. Ritala, M. Leskelä, *J. Phys. Chem. A* **119** (2015) 2298.

[20] T. Sarnet, T. Hatanpää, M. Vehkamäki, T. Flyktman, J. Ahopelto, K. Mizohata, M. Ritala, M. Leskelä, *J. Mater. Chem. C* **3** (2015) 4820.

[21] T. Sarnet, T. Hatanpää, M. Laitinen, T. Sajavaara, K. Mizohata, M. Ritala, M. Leskelä, *J. Mater. Chem. C* **4** (2016) 449.

[22] H. O. Pierson, *Handbook of Chemical Vapor Deposition, Principles, Technology and Applications*, 2nd Edition, Noyes Publications, (1999).

[23] J. O. Carlsson, *Chemical Vapor Deposition.* In R. F. Bunshah (Ed.), *Handbook of Deposition Technologies for Films and Coatings. Science, Technologies and Applications*, 2nd edition, pages 274–433, Noyes Publications**, (**1994).

[24] J. E. Mahan, *Physical Vapor Deposition of Thin Films,* Wiley Interscience, (2000).

[25] M. Leskelä, M. Ritala, *Angew. Chem. Int. ed.* **42** (2003) 5548.

[26] S. M. George, *Chem. Rev.* **110** (2010) 111.

[27] P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Rozeboom, G. Sundaram, A. Vermeer, *J. Vac. Sci. Technol. A* **30 (2012)** 010802.

[28] V. Miikkulainen, M. Leskelä, M. Ritala, R. L. Puurunen, *J. Appl. Phys.* **113** (2013) 021301.

[29] A. C. Jones, H. C. Aspinall, P. R. Chalker, *Chemical Vapour Deposition of Metal Oxides for Microelectronics Applications*. In A. C. Jones, M. L. Hitchman (Eds.), *Chemical Vapour Deposition, Precursors, Processes, and Applications*, Chapter 8, pages 357–412, RSC Publishing, (2009).

[30] W. A. Wojtczak, P. F. Fleig, M. J. Hampden-Smith, *A review of Group 2 (Ca, Sr, Ba) Metal-Organic Compounds as Precursors for Chemical Vapor Deposition.* In F. G. A. Stone, R. West (Eds.) *Advances in Organometallic Chemistry*, Volume 40, pages 215–340, Academic Press, San Diego, (1996).
[31] W. A. Herrmann, N. W. Huber, O. Runte, *Angew. Chem. Int. Ed. Engl.* **34** (1995) 2187.
[32] S. R. Drake, S. A. S. Miller, M. B. Hursthouse, K. M. A. Malik, *Polyhedron* **12** (1993) 1621.
[33] A. Drozdov, S. Troyanov, *J. Chem. Soc. Chem. Commun.* (1993) 1619.
[34] S. I. Troyanov, N. P. Kuzmina, I. E. Soboleva, N. V. Chugarov, *Proc. Electrochem. Soc.* **97** (1997) 886.
[35] S. E. Koponen, P. G. Gordon, S. T. Barry, *Polyhedron* **108** (2016) 59.
[36] L. G. Hubert-Pfalzgraf, H. Guillon, *Appl. Organomet. Chem.* **12** (1998) 221.
[37] A. C. Jones, *J. Mater. Chem.* **12** (2002) 2576.
[38] I. Lhermitte-Sebire, R. Colmet, R. Naslain, C. Bernard, *J. Less-Common Metals* **118** (1986) 83.
[39] S. T. Barry, *Coord. Chem. Rev.* **257** (2013) 3192.
[40] H. A. Stecher, A. Sen, A. L. Rheingold, *Inorg. Chem.* **28** (1989) 3280.
[41] G. Fang, L. Xu, Y. Cao, A. Li, *Coord. Chem. Rev.* **322** (2016) 94.
[42] M. A. Malik, P. O'Brien, *Basic Chemistry of CVD and ALD Precursors*. In A. C. Jones, M. L. Hitchman (Eds.), *Chemical Vapor Deposition, Precursors, Processes, and Applications*, Chapter 5, pages 207–271, RSC Publishing, (2009).
[43] D. H. Ripin, D. A. Evans*, Chem 206 Advanced organic Chemistry, pKa Tables 1-3*, http://evans.rc.fas.harvard.edu/pdf/evans_pKa_table.pdf accessed 21st of Dec., (2018).
[44] G. Fang, L. Xu, Y. Cao, A. Li, *Coord. Chem. Rev.* **322** (2016) 94.
[45] I. Kazadojev, D. J. Otway, S. D. Elliott, *Chem. Vapor Depos.* **19** (2013) 117.
[46] S. D. Elliott, *Semicond. Sci. Technol.* **27** (2012) 074008.
[47] S. D. Elliott, *Surf. Coat. Tech.* **201** (2007) 9076.
[48] R. G. Pearson, *Chemical Hardness - Applications From Molecules to Solids*, Wiley-VCH, Weinheim, (1997).
[49] R. K. Kanjolia, J. Anthis, R. Odedra, P. Williams, P. N. Heys, *ECS Trans.* **16** (2008) 79.
[50] A. Roine, *Outokumpu HSC Chemistry, Version 5.11*., Outokumpu Research Oy, Pori Finland, 2002.
[51] D. M. Price, *Thermochimica Acta* **367-368** (2001) 253.
[52] A. Niskanen, T. Hatanpää, M. Ritala, M. Leskelä, *J. Thermal Anal. Calorim.* **64** (2000) 955.
[53] G. V. Kunte, S. A. Shivashankar, A. M. Umarji, *Meas. Sci. Technol.* **19** (2008) 025704.
[54] S.A. Rushworth, L.M. Smith, A.J. Kingsley, R. Odedra, R. Nickson, P. Hughes, *Microelectron. Reliab.* **45** (2005) 1000.
[55] O. Nilsen, H. Fjellvåg, A. Kjekshus, *Thermochim. Acta* **404** (2003) 187.
[56] A. E. Turgambaeva, I. K. Igumenov, *J. Phys. IV France* **11** (2001) Pr3-621.
[57] T. Pilvi, T. Hatanpää, E. Puukilainen, K. Arstila, M. Bischoff, U. Kaiser, N. Kaiser, M. Leskelä, M. Ritala, *J. Mater. Chem.* **17** (2007) 5077.
[58] T. Pilvi, M. Ritala, M. Leskelä, M. Bischoff, U. Kaiser, N. Kaiser, *Appl. Opt.* **47** (2008) C271.
[59] T. Pilvi, E. Puukilainen, U. Kreissig, M. Leskelä, M. Ritala, *Chem. Mater.* **2** (2008) 5023.
[60] M. Ritala, K. Kukli, A. Rahtu, P. I. Räisänen, M. Leskelä, T. Sajavaara, J. Keinonen, *Science* **288** (2000) 319.
[61] Z. Golrokhi, P. A. Marshall, S. Romani, S. Rushworth, P. R. Chalker, R. Potter, *Appl. Surf. Sci.* **399** (2017) 123.
[62] L. C. Kalutarage, S. B. Clendenning, C. H. Winter, *Chem. Mater.* **26** (2014) 3731.
[63] T. J. Knisley, T. C. Ariyasena, T. Sajavaara, M. J. Saly, C. H. Winter, *Chem. Mater.* **23** (2011) 4417.
[64] J. P. Klesko, C. M. Thrush, C. H. Winter, *Chem. Mater.* **27** (2015) 4918.
[65] K. Nashimoto, D. K. Fork, T. H. Geballe, *Appl. Phys. Lett.* **60** (1992) 1199.
[66] A. N. Basit, H. K. Kim, J. Blachere, *Appl. Phys. Lett.* **73** (1998) 3941.
[67] C. Pithan, D. Hennings, R. Waser, *Int. J. Appl. Ceram. Technol.* **2** (2005) 1.
[68] C. A. Paz de Araujo, J. D. Cuchiaro, K. D. McMillan, M. C. Scott, J. F. Scott, *Nature* **374** (1995) 627.
[69] W.-M. Li, M. Ritala, M. Leskelä, R. Lappalainen, J. Jokinen, E. Soininen, B. Huttl, E. Nykänen, L. Niinistö, *J. Appl. Phys.* **84** (1998) 1029.
[70] M. Tammenmaa, H. Antson, M. Asplund, L. Hiltunen, M. Leskelä, L. Niinistö, E. Ristolainen*, J. Cryst. Growth* **84** (1987) 151.
[71] M. Friz, F. Waibel, *Optical Coatings*. In N. Kaiser, H. K. Pulker (Eds.), *Springer Series in Optical Sciences*, Vol. 88, pages 105 – 130, Springer, Berlin, (2003).
[72] R. D. Shannon, *Acta. Crystallogr., Sect. A* **32** (1976) 751.
[73] J. E. Huheey, *Inorganic Chemistry: Priciples of Structure and reactivity (4th Ed.)*, pages 187–190, HarperCollins, New York, (1993).
[74] L. Pauling, *The Nature of The Chemical Bond and the Structure of Molecules and Crystals (3rd Ed.)*, Chapter 3, p. 98, Cornell University Press, Ithaca, New York, (1960).

[75] J. M. Hartmann, J. Cibert, F. Kany, H. Mariette, M. Charleux, P. Alleysson, R. Langer, G. Feuillet, *J. Appl. Phys.* **80** (1996) 6257.
[76] J. M. Hartmann, M. Charleux, H. Mariette, J. L. Rouviere, *Appl. Surf. Sci.* **112** (1997) 142.
[77] R. Huang, A. H. Kitai, *J. Electron. Mater.* **22** (1993) 215.
[78] R. Huang, A. H. Kitai, *Appl. Phys. Lett.* **61** (1992) 1450.
[79] R. Huang, A. H. Kitai, *J. Mater. Sci. Lett.* **12** (1993) 1444.
[80] M. Ylilammi, T. Ranta-Aho*, J. Electrochem. Soc.* **141** (1994) 1278.
[81] P. Soininen, E. Nykänen, L. Niinistö, M. Leskelä, *Chem. Vapor Depos.* **2** (1996) 69.
[82] V. Saanila, J. Ihanus, M. Ritala, M. Leskelä, *Chem. Vapor Depos.* **4** (1998) 227.
[83] M. Leskelä, L. Niinistö, E. Nykänen, P. Soininen, M. Tiitta, *Mat. Res. Soc. Symp. Proc.* **222** (1991) 315.
[84] P. Soininen, L. Niinistö, E. Nykänen, M. Leskelä, *Appl. Surf. Sci.* **75** (1994) 99.
[85] M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, M. Tammenmaa, *Chemtronics* **3** (1988) 113.
[86] J. Rautanen, L. Niinistö, E. Nykänen, P. Soininen, M. Leskelä, *Appl. Surf. Sci.* **82/83** (1994) 553.
[87] T. Hänninen, I. Mutikainen, V. Saanila, M. Ritala, M. Leskelä, J. C. Hanson, *Chem.Mater.* **9** (1997) 1234.
[88] M. Tiitta, L. Niinistö, *Chem. Vapor Depos.* **3** (1997) 167.
[89] W.-C. Shin, S.-O. Ryu, I.-K. You, B.-G. Yu, W.-J. Lee, K.-J. Choi, S.-G. Yoon, *J. Electrochem. Soc.* **151** (2004) C292.
[90] R. J. Potter, P. A. Marshall, J. L. Roberts, A. C. Jones, P. R. Chalker, M. Vehkamäki, M. Ritala, M. Leskelä, P. A. Williams, H. O. Davies, N. L. Tobin, L. M. Smith, *Mater. Res. Soc. Symp. Proc.* **784** (2004) 97.
[91] M. Vehkamäki, M. Ritala, M. Leskelä, A.C. Jones, H.O. Davies, T. Sajavaara, E. Rauhala*, J. Electrochem. Soc.* **151** (2004) F69.
[92] W.-J. Lee, I.-K. You, S.-O. Ryu, B.-G. Yu, K. I. Cho, S.-G. Yoon, C.-S. Lee*, Jpn. J. Appl. Phys. Part 1* **40** (2001) 6941.
[93] S. Acharya, J. Torgersen, Y. Kim, J. Park, P. Schindler, A. L. Dadlani, M. Winterkorn, S. Xu, S. P. Walch, T. Usui, C. Schildknechte, F. B. Prinz, *J. Mater. Chem. C* **4** (2016) 1945.
[94] X. Lou, H. Zhou, S. B. Kim, S. Alghamdi, X. Gong, J. Feng, X. Wang, P. D. Ye, R. G. Gordon, *Nano Letters* **16** (2016) 7650.
[95] M. J. Saly, F. Munnik, C. H. Winter, *J. Mater. Chem.* **20** (2010) 9995.
[96] M. J. Saly, F. Munnik, C. H. Winter, *Chem. Vapor Depos.* **17** (2011) 128.
[97] J. A. T. Norman, M. Perez, M. S. Kim, X. Lei, S. Ivanov, A. Derecskei-Kovacs, L. Matz, I. Buchanan, A. L. Rheingold, *Inorg. Chem.* **50** (2011) 12396.
[98] O. Nilsen, H. Fjellvåg, A. Kjekshus, *Thin Solid Films* **450** (2004) 240.
[99] A. Kosola, M. Putkonen, L. S. Johansson, L. Niinistö, *Appl. Surf. Sci.* **211** (2003) 102.
[100] Y. D.-S. Kil, J.-M. Lee, J.-S. Roh, *Chem. Vapor Depos.* **8** (2002) 195.
[101] J. H. Lee, Y. J. Cho, Y. S. Min, D. Kim, S. W. Rhee, *J. Vac. Sci. Technol. A* **20** (2002) 1828.
[102] S. M. George, B. K. Park, C. G. Kim, T.-M. Chung, *Bull. Korean Chem. Soc.* **34** (2013) 967.
[103] S. M. George, B. K. Park, C. G. Kim, T.-M. Chung, *Eur. J. Inorg. Chem.* (2014) 2002.
[104] W. Lee, W. Jeon, C. H. An, M. J. Chung, H. J. Kim, T. Eom, S. M. George, B. K. Park, J. H. Han, C. G. Kim, T.-M. Chung, S. W. Lee, C. S. Hwang, *Chem. Mater.* **27** (2015) 3881.
[105] M. J. Chung, W. Jeon, C. H. An, S. H. Kim, Y. K. Lee, W. Lee, C. S. Hwang, *ACS Appl. Mater. Interfaces* **10** (2018) 8836.
[106] M. Li, J. Zou, H. Tao, L. Wang, Z. Zhou, J. Peng, *Nanotechnology* **27** (2016) 494003.
[107] H. Wang, K. Fu, *J. Vac. Sci. Technol. A* **31** (2013) 06F101.
[108] E. Kim, Y. Han, W. Kim, K. C. Choi, H.-G. Im, B.-S. Bae, *Organic Electronics* **14** (2013) 1737.
[109] Y. Lee, H. Sun, M. J. Young, S. M. George, *Chem. Mater.* **28** (2016) 2022.
[110] J. Hennessy, A. D. Jewell, F. Greer, M. C. Lee, S. Nikzad, *J. Vac. Sci. Technol. A* **33** (2015) 01A125.
[111] E. Ahvenniemi, M. Karppinen, *Chem. Mater.* **28** (2016) 6260.
[112] J. Holopainen, K. Kauppinen, K. Mizohata, E. Santala, E. Mikkola, M. Heikkilä, H. Kokkonen, M. Leskelä, P. Lehenkari, J. Tuukkanen, M. Ritala, *Biointerphases* **9** (2014) 031008.
[113] H. H. Sønsteby, E. Østreng, H. Fjellvåg, O. Nilsen, *Chem. Vapor Depos.* **20** (2014) 269.
[114] S. B. Kim, C. Yang, T. Powers, L. M. Davis, X. Lou, R. G. Gordon, *Angew. Chem. Int. Ed.* **55** (2016) 10228.
[115] E. Ahvenniemi, M. Matvejeff, M. Karppinen, *Appl. surf. Sci.* **320** (2014) 838.
[116] H. Wang, X. Jiang, K. Fu, B. G. Willis, *J. Phys. Chem.* C **117** (2013) 11578.
[117] H. J. Choi, S. W. Park, G. D. Han, J. Na, G.-T. Kim, J. H. Shim, *Appl. Phys. Lett.* **104** (2014) 242105
[118] S. Rentrop, T. Moebus, B. Abendroth, R. Strohmeyer, A. Schmid, T. Weling, J. Hanzig, F. Hanzig, H. Stöcker, D. C. Meyer, *Thin Solid Films* **550** (2014) 53.
[119] S. Rentrop, B. Abendrotha, J. Walter, J. Rensbergb, W. Münchgesang, R. Strohmeyer, H. Stöcker, C. Ronning, S. Gemming, D. C. Meyer, *Thin Solid Films* **577** (2015) 134.

[120] M. D. McDaniel, A. Posadas, T. Q. Ngo, A. Dhamdhere, D. J. Smith, A. Demkov. J. G. Ekerdt, *J. Vac. Sci. Technol. A* **31** (2013) 01A136.
[121] W. Lee, J. H. Han, W. Jeon, Y. W. Yoo, S. W. Lee, S. K. Kim, C.-H. Ko, C. Lansalot-Matras, C. S. Hwang, *Chem. Mater.* **25** (2013) 953.
[122] S. H. Kim, W. Lee, C. H. An, D. S. Kwon, D.-G. Kim, S. H. Cha, S. T. Cho, C. S. Hwang, *ACS Appl. Mater. Interfaces* **10** (2018) 41544.
[123] S. H. Kim, W. Lee, C. H. An, D.-G. Kim, D. S. Kwon, S. T. Cho, S. H. Cha, J. I. Lim, C. S. Hwang, *Phys. Status Solidi RRL* (2019) 1800557-1.
[124] M. D. McDaniel, A. Posadas, T. Q. Ngo, C. M. Karako, J. Bruley, M. M. Frank, V. Narayanan, A. A. Demkov, J. G. Ekerdt, *J. Appl. Phys.* **115** (2014) 224108.
[125] J. H. Han, C. S. Hwang, *ECS Trans.* **58** (2013) 171.
[126] V. Longo, M. A. Verheijen, F. Rozeboom, W. M. M. Kessels, *ECS J. Solid State Sci. Technol.* **2** (2013) N120.
[127] V. Longo, F. Rozebom, W. M. M. kessels, M. Verheijen, *ECS Trans.* **58** (2013) 153.
[128] N. Aslam, V. Longo, W. Keuning, F. Rozeboom, W. M. M. Kessels, R. Waser, S. Hoffmann-Eifert, *Physica Status Solidi A* **211** (2014) 389.
[129] N. Aslam, V. Longo, C. Rodenbücher, F. Roozeboom, W. M. M. Kessels, K. Szot, R. Waser, S. Hoffmann-Eifert, *J. Appl. Phys.* **116** (2014) 064503.
[130] E. O. Filatova, I. V. Kozhevnikov, A. A. Sokolov, A. S. Konashuk, F. Schaefers, M. Popovici, V. V. Afanas'ev, *J. Electron Spectrosc.* **196** (2014) 110.
[131] P. J. King, M. Vehkamäki, M. Mattinen, M. J. Heikkilä, K. Mizohata, W. Noh, M. Leskelä, M. Ritala, *J. Vac. Sci. Technol. A* **37** (2019) 020602-1.
[132] T. Q. Ngo, A. B. Posadas, M. D. McDaniel, C. Hu, j. Bruley, E. T. Yu, A. A. Demkov, J. G. Ekerdt, *Appl. Phys. Lett.* **104** (2014) 082910.
[133] E. L. Lin, A. B. Posadas, H. W. Wu, D. J. Smith, A. A. Demkov, J. G. Ekerdt, *J. Cryst. Growth* **476** (2017) 6.
[134] P. Schindler, Y. Kim, D. Thian, J. An, F. B. Prinz, *Scripta materialia* **111** (2016) 106.
[135] R. C. Mehrotra, R. Bohra, D. P. Gaur, *Metal β-diketonates and Allied Derivatives*, Academic Press, (1978).
[136] D. J. Otway, W. S. Rees Jr, *Coord. Chem. Rev.* **210** (2000) 279.
[137] E. Weiss, J. Kopf, T. Gardein, S. Corbelin, U. Shümann, M. Kirilov, G. Petrov, *Chem. Ber.* **118** (1985) 3529.
[138] V.-C. Arunasalam, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, S. A. S. Miller, D. M. P. Mingos, *Dalton Trans.* (1996) 2435.
[139] J. Brooks, H. O. Davies, T. J. Leedham, A. C. Jones, A. Steiner, *Chem. Vapor Depos.* **6** (2000) 66.
[140] A. A. Drozdov, S. I. Troyanov, *Polyhedron* **11** (1992) 2877.
[141] S. R. Drake, M. B. Hursthouse, K. M. A. Malik, D. J. Otway, *Dalton Trans.* (1993) 2883.
[142] A. Gleizes, A. A. Drozdov, S. I. Troyanov, *Koord. Chim.* **20** (1994) 922.
[143] L. Huang, S. B. Turnipseed, R. C. Haltiwanger, R. M. Barkley, R. E. Sievers, *Inorg. Chem.* **33** (1994) 249.
[144] A. Drozdov, S. Troyanov, *Polyhedron* **15** (1996) 1747.
[145] N. Hovnanian, J. Galloy, P. Miele, *Polyhedron* **14** (1995) 297.
[146] A. A. Drozdov, S. I. Troyanov, A. P. Pisarevsky, Yu. T. Struchkov, *Polyhedron* **13** (1994) 1445.
[147] M. Putkonen, A. Szeghalmi, E. Pippel, M. Knez, *J. Mater. Chem.* **21** (2011) 14461.
[148] S. H. Shamilian, M. L. Hitchman, S. L. Cook, B. C. Richards, *J. Mater. Chem.* **4** (1994) 81.
[149] G. Malandrino, I. L. Fragala, D. A. Neumayer, C. L. Stern, G. J. Hinds, T. J. Marks, *J. Mater. Chem.* **4** (1994) 1061.
[150] W. S. Rees Jr, C. R. Caballero, W. Hesse, *Angew. Chem. Int. Ed. Engl.* **31** (1992) 735.
[151] J. A. P. Nash, S. C. Thompson, D. F. Foster, D. Cole-Hamilton, J. C. Barnes, *J. Chem. Soc., Dalton Trans.* (1995) 269.
[152] J .H .Lee, S .W .Rhee, *J. Mater. Res.* **14** (1999) 3988.
[153] Y .S .Min, Y .J .Cho, D .Kim, J .H .Lee, B .M .Kim, S .K .Lim, I .M . Lee, W .I .Lee, *Chem Vapor Depos.* **7** (2001) 146.
[154] Y.-S. Min, Y. J. Cho, J.-H. Lee, D. Kim, I. Yoon, K.-M. Park, S. S. Lee, B. R. Cho, *Chem. Vapor Depos.* **9** (2003) 241.
[155] D. L. Schulz, B. J. Hinds, C. L. Stern, T. J. Marks, *Inorg. Chem.* **32** (1993) 249.
[156] D. L. Schulz, B. J. Hinds, D. A. Neumayer, C. L. Stern, T. J. Marks, *Chem. Mater.* **5** (1993) 1605.
[157] D. B. Studebaker, D. A. Neumayer, B. J. Hinds, C. L. Stern, T. J. Marks, *Inorg. Chem.* **39** (2000) 3148.
[158] J. E. Scwarberg, R. E. Sievers, R. W. Moshier, *Anal. Chem.* **42** (1970) 1828.
[159] G. Malandrino, F. Castelli, I. L. Fragala, *Inorg. Chim. Acta* **224** (1994) 203.
[160] S. B. Turnipseed, R. M. Bakley, R. E. Sievers, *Inorg. Chem.* **30** (1991) 1164.

[161] A. A. Drozdov, S. I. Troyanov, A. P. Pisarevsky, Yu. T. Struchkov, *Polyhedron* **13** (1994) 2459.
[162] R. Sato, K. Takahashi, M. Yoshino, H. Kato, S. Ohshima, *Jpn. J. Appl. Phys.* **32** (1993) 1590.
[163] M. Putkonen, L.-S. Johansson, E. Rauhala, L. Niinistö, *J. Mater. Chem.* **9** (1999) 2449.
[164] T. Kuech, P. J. Wang, M. A. Tischler, R. Potemski, G. J. Scilla, F. Cardone, *J. Cryst. Growth* **93** (1988) 624.
[165] P. Hacke, H. Nakayama, T. Detchprohm, K. Hiramatsu, N. Sawaki, *Appl. Phys. Lett.* **68** (1996) 1362.
[166] M. Suzuki, J. Nishio, M. Onomura, C. Hongo, *J. Cryst. Growth* **189/190** (1998) 511.
[167] J.-Y. Leem, C.-R. Lee, J.-I. Lee, S. K. Noh, Y.-S. Kwon, Y.-H. Ryu, S.-J. Son, *J. Cryst. Growth.* **193** (1998) 491.
[168] T. Kimura, H. Yamauchi, M. Nakabayashi, *Jpn. Kokai Tokkyo Koho* (1995), JP 07249616 A 19950926.
[169] T. Kimura, H. Yamauchi, *Jpn. Kokai Tokkyo Koho* (1995), JP 07201739 A 19950804.
[170] Y. Yamada, T. Morimoto, *Jpn. Kokai Tokkyo Koho* (1990), JP 02225317 A 19900907.
[171] K. Mizutani, M. Katayama, N. Ito, T. Hatsutori, *Jpn. Kokai Tokkyo Koho* (1995), JP 07065954 A 19950310.
[172] M. J. Benac, A. H. Cowley, R. A. Jones, A. F. Tasch, *Chem. Mater.* **1** (1989) 289.
[173] Y. Tasaki, R. Sakamoto,Y. Ogawa, S. Yoshizawa, J. Ishiai, S. Akase, *Jpn. J. Appl. Phys.* **33** (1994) 5400.
[174] I. Hung, C. L. B.Macdonald, R. W. Schurko, *Chem. Eur. J.* **10** (2004) 5923.
[175] A. Xia, J. E. Knox, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Organometallics* **22** (2003) 4060.
[176] A. Jaenschke, J. Paap, U. Behrens, *Z. Anorg. Allg. Chem.* **634** (2008) 461.
[177] S. Harder, M. Lutz, A. W. G. Straub, *Organometallics* **16** (1997) 107.
[178] F. Feil, S. Harder, *Eur. J. Inorg. Chem.* (2003) 3401.
[179] K. Fichtel, K. Hofmann, U. Behrens, *Organometallics* **23** (2004) 4166.
[180] R. Zerger, G. Stucky, *J. Organomet. Chem.* **80** (1974) 7.
[181] W. Bunder, E. Weiss *J. Organomet. Chem.* **92** (1975) 1.
[182] T. P. Hanusa, *Organometallics* **21** (2002) 2559.
[183] D. J. Burkey, T. P. Hanusa, J. C. Huffman, *Adv. Mater. Opt. El.* **4** (1994) 1.
[184] T. P. Hanusa, *Chem. Rev.* **93** (1993) 1023.
[185] E. O. Fischer, G. Stölzle, *Chem. Ber.* **94** (1961) 2187.
[186] M. L. Hays, T. P. Hanusa, T. A. Nile, *J. Organomet. Chem.* **514** (1996) 73.
[187] P. Juzi, J. Dahlhaus, M. O. Kristen, *J. Organomet. Chem.* **450** (1993) C1.
[188] H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert, J. Demtschuk, *J. Organomet. Chem.* **617-618** (2001) 588.
[189] C. J. Burns, R. A. Andersen, *J. Organomet. Chem.* **325** (1987) 31.
[190] T. K. Hollis, J. K. Burdett, B. Bosnich, *Organometallics* **12** (1993) 3385.
[191] T. V. Timofeeva, J.-H. Lii, N. L. Allinger, *J. Am. Chem. Soc.* **117** (1995) 7452.
[192] M. J. Harvey, K. T. Quisenberry, T. P. Hanusa, V. G. Young Jr., *Eur. J. Inorg. Chem.* (2003) 3383.
[193] R. A. Williams, K. F. Tesh, T. P. Hanusa, *J. Am. Chem. Soc.* **113** (1991) 4843.
[194] H. Sitzmann, T. Dezember, M. Ruck, *Angew. Chem., Int. Ed.* **37** (1998) 3114.
[195] M. Ritala, K. Kukli, M. Vehkamäki, T. Hänninen, T. Hatanpää, P. I. Räisänen, M. Leskelä, *Proc. Electrochem. Soc* **2000-13** (2000) 597.
[196] R. Matero, A. Rahtu, S. Haukka, M. Tuominen, M. Vehkamäki, T. Hatanpää, M. Ritala, M. Leskelä, *ECS Trans.* **1** (2006) 137.
[197] A. Rahtu (**2002**), *Atomic Layer Deposition of High Permittivity Oxides: Film Growth and In situ Studies*. Academic dissertation, University of Helsinki.
[198] A. Rahtu, T. Hänninen, M. Ritala, *J. Phys. IV France* **11** (2001) Pr3-923.
[199] R. Katamreddy, Z. Wang, V. Omarjee, P. V. Rao, C. Dussarrat, N. Blasco, *ECS Trans.* **25** (2009) 217.
[200] H. Wang, X. Jiang, K. Fu, B. G. Willis*, J. Phys. Chem. C* **117** (2013) 11578.
[201] M. Popovici, K. Tomida, J. Swerts, P. Favia, A. Delabie, H. Bender, C. Adelmann, H. Tielens, B. Brijs, B. Kaczer, M. A. Pawlak, M.-S. Kim, L. Altimime, S. Van Elshocht, J. A. Kittl, *Phys. Status Solidi A* **208** (2011) 1920.
[202] M. Mehring, *Coord. Chem. Rev.* **251** (2007) 974.
[203] P. Shuk, H. D. Wiemhöfer, U. Guth, W. Göopel, M. Greenblatt, *Solid State Ionics* **89** (1996) 179
[204] N. M. Sammes, G. A. Tompsett, H. Näfe, F. Aldinger, *J. Eur. Ceram. Soc.* (1999) 1801.
[205] A. Cabot, A. Marsal, J. Arbiol, J. R. Morante, *Sens. Actuator B Chem.* **99** (2004) 74.
[206] R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, *Nature* **413** (2001) 597.
[207] M. Vehkamäki, unpublished results.
[208] M. Schuisky, K. Kukli, M. Ritala, A. Hårsta, M. Leskelä, *Chem. Vapor Depos.* **6** (2000) 139.
[209] J. Harjuoja, S. Väyrynen, M. Putkonen, L. Niinistö, E. Rauhala*, J. Cryst. Growth* **285** (2006) 376.
[210] W. C. Shin, S. O. Ryu, I. K. You, S. M. Yoon, S. M. Cho, N. Y. Lee, K. D. Kim, B. G. Yu, W. J. Lee, K. J. Choi, S. G. Yoon, *Electrochem. Solid State Lett.* **7** (2004) F31.

[211] J. Harjuoja, T. Hatanpää, M. Vehkamäki, S. Väyrynen, M. Putkonen, L. Niinistö, M. Ritala, M. Leskelä, E. Rauhala, *Chem. Vapor Depos.* **11** (2005) 362.
[212] E. Østreng, K.B. Gandrud, O. Nilsen, H. Fjellvag, *BALD2009, Book of abstracts*,Uppsala, Sweden (2009).
[213] Y. D. Shen, Y. W. Li, W. M. Li, J. Z. Zhang, Z. G. Hu, J. H. Chu, *J. Phys. Chem. C* **116 (**2012) 3449.
[214] Y. J. Cho, Y.-S. Min, J.-H. Lee, B.-S. Seo, J. K. Lee, Y. S. Park, *Integr. Ferroelectr.* **59** (2003) 1483.
[215] G. W. Hwang, W. D. Kim, Y.-S. Min, Y. J. Cho, C. S. Hwang, *J. Electrochem. Soc.***153** (2006) F20.
[216] G. W. Hwang, W. D. Kim, C. S. Hwang, Y.-S. Min, Y. J. Cho, *J. Electrochem. Soc.* **154** (2007) H915.
[217] Y.-S. Min, Y. J. Cho, I. P. Asanov, J. H. Han, W. D. Kim, C. S. Hwang, *Chem. Vapor Depos.* **11** (2005) 38.
[218] Y.-S. Min, I. P. Asanov, C. S. Hwang, *Electrochem. Solid State Lett.* **9** (2006) G231.
[219] M. Rusek, T. Komossa, G. Bendt, S. Schulz, *J. Cryst. Growth* **470** (2017) 128.
[220] Y.-T. Liu, C.-S. Ku, S.-J. Chiu, H.-Y. Lee, S.-Y. Chen, *ACS Appl. Mater. Inter.* **6** (2014) 443.
[221] Q. Qiao, Y. W. Li, J. Z. Zhang, Z. G. Hua, J. H. Chu, *Thin Solid Films* **622** (2017) 65.
[222] Y. W. Li, Q. Qiao, Z. Dong, J. Z. Zhang, Z. G. Hu, J. H. Chu*, J. Non-Cryst. Solids* **443** (2016) 17.
[223] M. Stefik, *ChemSusChem* **9** (2016) 1727.
[224] B. Lamm, A. Sarkar, M. Stefik, *J. Mater. Chem. A* **5** (2017) 6060.
[225] A. V. Plokhikh, M. Falmbigl, I. S. Golovina, A. R. Akbashev, I. A. Karateev, M. Y. Presnyakov, A. L. Vasiliev, J. E. Spanier*, ChemPhysChem* **18** (2017) 1966.
[226] D. Z. Austin, D. Allman, D. Price, S. Hose, M. Saly, J. F. Conley Jr., *J. Vac. Sci. Technol. A* **32** (2014) 01A113.
[227] F. Zhang, G. Sun, W. Zhao, L. Wang, L. Zheng, S. Liu, B. Liu, L. Dong, X. Liu, G. Yan, L. Tian, Y. Zeng, *J. Phys. Chem. C* **117** (2013) 24579.
[228] J. Wena, J, Wang, Y, Dong, N, Chen, Y, Luo, G.-d. Peng,F. Pang, Z. Chen, T. Wang, *Appl. Surf. Sci.* **349** (2015) 287.
[229] C. D. Pham, J. Chang, M. A. Zurbuchen, J. P. Chang, *Chem. Mater.* **27** (2015) 7282.
[230] N. Mahuli, D. Saha, S. K. Sarkar, *J. Phys. Chem. C* **121** (2017) 8136.
[231] M. Schuisky, *Acta. Univ. Uppsa. Abstr. Uppsala Diss. Sci.* **594** (2000).
[232] C. Bedoya, G. G. Condorelli, G. Anastasi, A. Baeri, F. Scerra, I. L. Fragala, J. G. Lisoni, D. Wouters*, Chem. Mater.* **16** (2004) 3176.
[233] F. Ando, T. Hayashi, K. Ohashi, J. Koketsu, *J. Inorg. Nucl. Chem.* **37** (1975) 2011.
[234] H. Suzuki, Y. Matano in H. Suzuki, Y. Matano (Eds.), *Organobismuth Chemistry*, Elsevier, Amsterdam, (2001).
[235] M.-C. Massiani, R. Papiernik, L.G. Hubert-Pfalzgraf, J.-C. Daran, *Polyhedron* **10** (1991) 437.
[236] W. J. Evans, J. H. Hain Jr., J. W. Ziller, *J. Chem. Soc., Chem. Commun.* (1989) 1628.
[237] A. P. Pisarevskii, L. I. Martynenko, N.G. Dzyubenko, *Russ. J. Inorg. Chem.* **37** (1992) 38.
[238] S. I. Troyanov, A. P. Pisarevsky, *Koord. Khim.* **17** (1991) 909.
[239] A. P. Pisarevskii, L. I. Martynenko, N. G. Dzyubenko, *Russ. J. Inorg. Chem.* **35** (1990) 843.
[240] G. K. Fukin, A. P. Pisarevskii, A. I. Yanovskii, Yu. T. Struchkov, *Russ. J. Inorg. Chem.* **38** (1993) 1205.
[241] S. I. Troyanov, A. P. Pisarevsky, *J. Chem. Soc., Chem. Commun.* (1993) 335.
[242] J. A. Dean, *Lange's Handbook of Chemistry*, 15th edition, McGraw-hill Inc., (1999).
[243] W. A. Herrmann, N. W. Huber, R. Anwander, T. Priermeier, *Chem. Ber.* **126** (1993) 1127.
[244] S. I. Troyanov and A. P. Pisarevsky, *Koord. Khim.* **14 (**1991) 1011.
[245] A. P. Piedade, M. T. Vieira, A. Martins, F. Silva, *Nanotechnology* **18** (2007) 105103.
[246] International Technology Roadmap for Semiconductors, (2009).
[247] M. Moskovits, *Rev. Modern Phys.* **57** (1985) 783.
[248] J. Hämäläinen, M. Ritala, M. Leskelä *Chem. Mater.* **26** (2014) 786.
[249] A. Grodzicki, I. Lakomska, P. Piszczek, I. Szymanska, E. Szlyk, *Coord. Chem. Rev.* **249** (2005) 2232.
[250] K.-M. Chi, C.-T. Lin, S.-M. Peng, G.-H. Lee, *Organometallics* **15** (1996) 2660.
[251] C.-M. Chi, Y.-H. Lu, *Chem. Vapor Depos.* **7** (2001) 117.
[252] Z. Yuan, N. H. Dryden, X. Li, J. J. Vittal, R. J. Puddephatt, *J. Mater. Chem.* **5** (1995) 303.
[253] J. A. Darr, M. Poliakoff, W.-S. Li, A. J. Blake, *J. Chem. Soc., Dalton Trans.* (1997) 2869.
[254] M. E. Fragala, G. Malandrino, O. Puglisi, C. Benelli, *Chem. Mater.* **12** (2000) 290.
[255] J. A. Darr, M. Poliakoff, A. J. Blake, W.-S. Li, *Inorg. Chem.* **37** (1998) 5491.
[256] P. R. Chalker, S. Romani, P. A. Marshall, M. J. Rosseinsky, S. Rushworth, P. A. Williams, *Nanotechnology* **21** (2010) 405602.
[257] F. J. van den Bruele, M. Smets, A. Illiberi, Y. Creyghton, P. Buskens, F. Roozeboom, P. Poodt, *J. Vac. Sci. Technol. A* **33** (2015) 01A131.
[258] A. A. Amusan, B. Kalkofen, H. Gargouri, K. Wandel, C. Pinnow, M. Lisker, E. P. Burte, *J. Vac. Sci. Technol. A* **34** (2016) 01A126.

[259] M. M. Minjauw, E. Solano, S. P. Sree, R. Asapu, M. Van Daele, R. K. Ramachandran, G. Heremans, S. W. Verbruggen, S. Lenaerts, J. A. Martens, C. Detavernier, J. Dendooven, *Chem. Mater.* **29** (2017) 7114.
[260] N. Boysen, T. Hasselmann, S. Karle, D. Rogalla, D. Theirich, M. Winter, T. Riedl, A. Devi, *Angew. Chem. Int. Ed.* **57** (2018) 16224.
[261] Z. Golrokhi, S. Chalker, C. J. Sutcliffe, R. Potter, *Appl. Surf. Sci.* **364** (2016) 789.
[262] S. S. Masango, L. Peng, L. D. Marks, R. P. Van Duyne, P. C. Stair, *J. Phys.Chem. C.* **118** (2014) 17655.
[263] M. Mäkelä, T. Hatanpää, K. Mizohata, K. Meinander, J. Niinistö, J. Räisänen, M. Ritala, M. Leskelä. *Chem. Mater.* **29** (2017) 2040.
[264] B. S. Lim, A. Rahtu, J.-S. Park, R. G. Gordon, *Inorg. Chem.* **42** (2003) 7951.
[265] H. Anacker-Eickhoff, R. Hesse, P. Jennische, A. Wahlberg, *Acta Chem. Scand.* **36** (1982) 251.
[266] S. E. Paramonov, E. V. Mychlo, S. I. Troyanov, N. P. Kuz'mina, *Russ. J. Inorg. Chem.* **45** (2000) 1852.
[267] S.E. Paramonov, N.P. Kuzmina, S.I. Troyanov, *Polyhedron* **22** (2003) 837.
[268] Z. Yuan, N. H. Dryden, J. J. Vittal, R. J. Puddephatt, *Chem. Mater.* **7** (1995) 1696.
[269] P. Piszczek, E. Szlyk, M. Chaberski, C. Taeschner, A. Leonhard, W. Bala, K. Bartkiewicz, *Chem. Vapor Depos.* **11** (2005) 53.
[270] C. N. Silvana, K. K. Banger, P. J. Toscano, J. T. Welch, *Polyhedron* **21** (2002) 1289.
[271] S. Raoux, W. Welnic, D. Ielmini, *Chem. Rev.* **110** (2010) 240.
[272] P. Noé, C. Vallée, F. Hippert, F. Fillot, J.-Y. Raty, *Semicond. Sci. Technol.* **33** (2018) 013002.
[273] T. Kato, *Jpn. J. Appl. Phys.* **56** (2017) 04CA02.
[274] I. Cado, E. Miller, *Thermoelectric Materials and Devices,* Reinhold Publishing Corporation, New York, (1960).
[275] A. C. Jones, P. O'Brien, *CVD of Compound Semiconductors, Precursor Synthesis, Development and Applications*, VCH, (1997).
[276] D. Fisher, I. J. Bahl, *Gallium Arsenide IC Applications Handbook. 1*., p.61, Elsevier, (1995).
[277] X. Wang, M. R. Khan, J. L. Gray, M. A. Alam, M. S. Lundstrom, *IEEE J. Photovolt.* **3** (2013) 737.
[278] R. N. Hall, G. E. Fenner, J. D. Kingsley, T. J. Soltys, R. O. Carlson, *Phys. Rev. Lett.* **9** (1962) 366.
[279] J. Black, H. Lockwood, S. J. Mayburg, *Appl. Phys.* **34** (1963) 178. LED GaAs
[280] S. Raoux, C. Cabral, L. Krusin-Elbaum, J. L. Jordan-Sweet, K. Virwani, M. Hitzbleck, M. Salinga, A. Madan, T. L. Pinto, *J. Appl. Phys.* **105** (2009) 064918.
[281] P. S. Dutta, H. L. Bhat, V. J. Kumar, *Appl. Phys.* **81** (1997) 5821.
[282] D. R. Dupuis, *Science* **226** (1984) 623.
[283] M. Bochmann, *Chem. Vapor Depos.* **2** (1996) 85.
[284] T. J. Groshens, R. W. Gedridge, Jr., C. K. Lowe-Ma, *Chem. Mater.* **6** (1994) 727.
[285] T. J. Groshens, R. W. Gedridge Jr., R. Scheri, T. Cole, *15th International Conference on Thermoelectrics* (1996) 430.
[286] D. R. Stull, *Ind. Eng. Chem.* **39** (1947) 517.
[287] A. P. Ubelis, J. Eng. Phys. **42** (1982) 309.
[288] N. N. Greenwood, A. Earnshaw (Eds.) *Chemistry of the Elements, 2nd edition*, pages 766-767, Butterworth Heinemann, Oxford, (1997).
[289] R. Kimura, M. Konagai, K. Takahashi, *J. Cryst. Growth* **116** (1992) 283.
[290] H. Fujiwara, H. Kiryu, I. Shimizu, *J. Appl. Phys.* **77** (1995) 3927.
[291] W.-S. Wang, H. Ehsani, I. Bhat, *J. Electron. Mater.* **22** (1993) 873.
[292] I. Bhat, H. Ehsani, W. S. Wang, S. K. Ghandhi, N. H. Karam, *J. Vac. Sci. Technol. B* **10** (1992) 1376.
[293] W.-S. Wang, H. E. Ehsani, I. B. Bhat, *J. Cryst. Growth* **124** (1992) 670.
[294] N. H. Karam, R. G. Wolfson, I. B. Bhat, H. Ehsani, S. K. Gandhi, *Thin Solid Films* **225** (1993) 261.
[295] R. M. Emerson, J. L. Hoyt, J. F. Gibbons, *Appl. Phys. Lett.* **65** (1994) 1103.
[296] S. Dakshinamurthy, I. Bhat, *J. Electron. Mater.* **27** (1998) 521.
[297] B. J. Choi, S. Choi, Y. C. Shin, K. M.. Kim, C. S. Hwang, Y. J. Kim, Y. J. Son, S. K. Hong, *Chem. Mater.* **19** (2007) 4387.
[298] J. Lee, S. Choi, C. Lee, Y. Kang, D. Kim, *Appl. Surf. Sci.* **253** (2007) 3969.
[299] S. Song, D. Yao, Z. Song, L. Gao, Z. Zhang, L. Li, L. Shen, L. Wu, B. Liu, Y. Cheng, S. Feng, *Nanoscale Res. Lett.* **10** (2015) 89.
[300] M. Silinskas, B. Kalkofen, R. Balasubramanian, A. Batmanov, E. P. Burte, N. Harmgarth, F. Zörner, F. T. Edelmann, B. Garke, M. Lisker, *J. Vac. Sci. Technol. A* **36** (2018) 021510.
[301] N. Harmgarth, F. Zörner, P. Liebing, E. P. Burte, M. Silinskas, F. Engelhardt, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **643** (2017) 1150.
[302] B. Han, Y.-J. Kim, J.-M. Park, L. Yusup, H. Ishii, C. Lansalot-Matras, W.-J. Lee, *J. Nanosci. Nanotechnol.* **16** (2016) 4924.
[303] C. Sasaoka, M. Yoshida, A. Usui*, Jpn. J. Appl. Phys., Part 2* **27** (1988) L490.
[304] R. Celmer, M. Yamamoto, J. M. Toguri, *Can. Metall. Quart.* **23** (1984) 169.

[305] K. Hamaoka, I. Suemune, K. Fujii, T. Koui, A. Kishimoto, M. Yamanishi, *Jpn. J. Appl. Phys.* **30** (1991) L1579.
[306] I. Suemune, *Appl. Surf. Sci.* **82/83** (1994) 149.
[307] M. Ozeki, T. Hataguchi, A. Fujita, *J. Cryst. Growth* **298** (2007) 90.
[308] V. Pore, K. Knapas, T. Hatanpää, T. Sarnet, M. Kemell, M. Ritala, M. Leskelä, K. Mizohata*, Chem. Mater.* **23** (2011) 247.
[309] T. Eom, T. Gwon, S. Yoo, B. J. Choi, M.-S. Kim, S. Ivanov, A. Adamczyk, I. Buchanan, M. Xiao, C. S. Hwang, *J. Mater. Chem.C* **3** (2015) 1365.
[310] T. Eom, T. Gwon, S. Yoo, B. J. Choi, M.-S. Kim, I. Buchanan, S. Ivanov, M. Xiao, C. S. Hwang, *Chem. Mater.* **27** (2015) 3707.
[311] A. T. Alred, J. N. Pratt, *J. Chem. Eng. Data* **8** (1963) 429.
[312] P. E. Thompson, J. L. Davis, J. Waterman, R. J. Wagner, D. Gammon, D. K. Gaskill, R. Stahlbush, *J. Appl. Phys.* **69** (1991) 7166.
[313] G. S. Lee P. E. Thompson, J. L. Davis, J. P. Omaggio, W. A. Schmidt, *Solid-State Electron.* **36** (1993) 387.
[314] G. Nowling, V. Adinolfi, V. Narasimhan, K. Littau, *ALD 2018, Book of Abstracts p. 48.*
[315] L. Cheng, V. Adinolfi, S. L. Weeks, S. V. Barabash, K. A. Littau, *J. Vac. Sci. Technol. A* **37** (2019) 020907.
[316] T. Gwon, T. Eom, S. Yoo, C. Yoo, E.-S. Park, S. Kim, M.-S. Kim, I. Buchanan, M. Xiao, S. Ivanov, C. S. Hwang, *Chem. Mater.* **29** (2017) 8065.
[317] T. Gwon, T. Eom, S. Yoo, H.-K. Lee, D.-Y. Cho, M.-S. Kim, I. Buchanan, M. Xiao, S. Ivanov, C. S. Hwang, *Chem. Mater.* **28** (2016) 7158.
[318] L. Zheng, X. Cheng, D. Cao, Q. Wang, Z. Wang, C. Xia, L. Shen, Y. Yu, D. Shen, *RSC Adv.* **5** (2015) 40007.
[319] D. Gu, D. Nminibapiel, H. Baumgart, H. Robinson, V. Kochergin, *ECS Trans.* **41** (2011) 255.
[320] T. Eom, S. Choi, B. J. Choi, M. H. Lee, T. Gwon, S. H. Rha, W. Lee, M.-S. Kim, M. Xiao, I. Buchanan, D.-Y. Cho, C. S. Hwang, *Chem. Mater.* **24** (2012) 2099.
[321] T. Eom, T. Gwon, S. Yoo, B. J. Choi, M.-S. Kim, I. Buchanan, M. Xiao, C. S. Hwang, *Chem. Mater.* **26** (2014) 1583.
[322] D. Nminibapiel, K. Zhang, M. Tangirala, H. Baumgart, V. S. K. Chakravadhanula, C. Kubel, V. Kochergin, *ECS J.Solid State Sci.Technol.* **3** (2014) P95.
[323] D. Nminibapiel, K. Zhang, M. Tangirala, H. Baumgart, V. S. K. Chakravadhanula, C. Kuebel, V. Kochergin, *ECS Trans.* **58** (2013) 59.
[324] K. Zhang, D. Nminibapiel, M. Tangirala, H. Baumgart, V. Kochergin, *ECS Trans.* **50** (2012) 3.
[325] S. Yoo, C. Yoo, E.-S. Park, W. Kim, Y. K. Lee, C. S. Hwang, *J. Mater. Chem. C* **6** (2018) 5025.
[326] K. Knapas, T. Hatanpää, M. Ritala, M. Leskelä, *Chem. Mater.* **22** (2010) 1386.
[327] C. W. Wiegand, R. Zierold, R. Faust, D. Pohl, A. Thomas, B. Rellinghaus, K. Nielsch, *Adv. Mater. Interfaces* **5** (2018) 1701155.
[328] K. Zhang, A. D. R. Pillai, K. Bollenbach, D. Nminibapiel, W. Cao, H. Baumgart, T. Scherer, V. S. K. Chakravadhanula, C. Kübel, V. Kochergin, *ECS J. Solid State Sci. Technol.* **3** (2014) P207.
[329] A. D. R. Pillai, K. Zhang, K. Bollenbach, D. Nminibapiel, W. Cao, H. Baumgart, V. S. K. Chakravadhanula, C. Kubel, V. Kochergin, *ECS Trans.* **58** (2013) 131.
[330] K. Zhang, A. D. R. Pillai, M. Tangirala, D. Nminibapiel, K. Bollenbach, W. Cao, H. Baumgart, V. S. K. Chakravadhanula, C. Kübel, V. Kochergin, *Phys. Status Solidi A* **221** (2014) 1329.
[331] J. H. Jeong, D. J. Choi, *Matwer. Sci. Semicond. Process.* **54** (2016) 42.
[332] W. Kim, S. Yoo, C. Yoo, E.-S. Park, J. Jeon, Y. J. Kwon, K. S. Woo, H. J. Kim, Y. K. Lee, C. S. Hwang, *Nanotechnology* **29** (2018) 365202..
[333] M. Krbal, J. Prikryl, R. Zazpe, F. Dvorak, F. Bures, J. M. Macak, *Phys. Status Solidi RRL* **12** (2018) 1800023.
[334] R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, R. B. Hallock, *Chem. Mater.* **1** (1989) 4.
[335] R. L. Wells, W. L. Gladfelter*, J. Cluster Sci.* **8** (1997) 217.
[336] S. M. Stuczynski, J. G. Brennan, M. L. Steigerwald, *Inorg. Chem.* **28** (1989) 4431.
[337] M. L. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglass, L. E. Brus, *J. Am. Chem. Soc.* **110** (1988) 3046.
[338] A. R. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. J. Carroll, L. E. Brus, *J. Am. Chem. Soc.*, **112** (1990) 132.
[339] E. A. Turner, H. Rosner, D. Fenske, Y. Huang, J. F. Corrigan, *J. Phys. Chem. B* **110** (2006) 16261.
[340] E. A. Turner, H. Rosner, Y. Huang, J. F. Corrigan, *J. Phys. Chem. C* **111** (2007) 7319.
[341] C. M. Evans, S. L. Castro, J. J. Worman, R. P. Raffaelle, *Chem. Mater.* **20** (2008) 5727.

[342] S. Adam, D. V. Talapin, H. Borchert, A. Lobo, C. McGinley, A. R. B. De Castro, M. Haase, H. Weller, T. Moeller, *J. Chem. Phys.* **123** (2005) 084706.
[343] S. Schulz, *Chem. Rev.* **215** (2001) 1.
[344] S. Schulz, L. Martinez, J. L. Ross, *Adv. Mater. Opt. Electr.* **6** (1996) 185.
[345] K. K. Bhasin, V. Gupta, R. P. Sharma, *Indian J. Chem.* **30A** (1991) 632.
[346] M. R. Detty, M. D. Seidler, *J. Org. Chem.* **47** (1982) 1354.
[347] G. Becker, M. Roessler, Z. Naturforsch. B **37** (1982) 91.
[348] H. J. Breunig, W. Fichtner, *J. Organomet. Chem.* **222** (1981) 97.
[349] H. Bürger, U. Goetze, *J. Organomet. Chem.* **12** (1968) 451.
[350] N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, G. S. Semchikova, *J. Organomet. Chem.* **6** (1966) 474.
[351] T. Hatanpää, V. Pore, M. Ritala, M. Leskelä, *ECS Transactions*, **25** (2009) 609.
[352] M. N. Bochkarev, A. I. Charov, N. S. Vyazankin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **20** (1971) 1881.
[353] G. N. Bortnikov, M. N. Bochkarev, V. S. Vyazankin, S. Kh. Ratushnaya, Ya. I. Yashin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **20** (1971) 766.
[354] K. A. Hooton, A. L. Allred, *Inorg. Chem.* **4** (1965**)** 671.
[355] H. Bürger, U. Goetze, W. Sawodny, *Spectrochim. Acta A* **24** (1968) 2003.
[356] E. K. V. Schultz, D. N. Harpp, *Synthesis* **8** (1998) 1137.
[357] J. P. Eussner, R. O. Kusche, S. Dehnen, *Chem. Eur. J.* **21** (2015) 12376.
[358] H. J. Breunig, M. Jonsson, R. Rosler, E. Lork, *J. Organomet. Chem.* **608** (2000) 60.
[359] W. Braun, R. Shayduk, T. Flissikowski, M. Ramsteiner, H. T. Grahn, H. Riechert, P. Fons, A. Kolobov, *Appl. Phys. Lett.* **94** (2009) 041902.
[360] T. Sarnet (**2015**), *Non-metal Alkylsilyl Compounds as Precursors in Atomic Layer Deposition of Chalcogenides and Pnictides*, Academic dissertation, University of Helsinki, http://ethesis.helsinki.fi.
[361] S. Maitrejean, S. Lhostis, S. Haukka, C. Jahan, E. Gourvest, R. Matero, T. Blomberg, A. Toffoli, A. Persico, C. Jayet, M. Veillerot, J.P. Barnes, F. Pierre, F. Fillot, L. Perniola, V. Sousa, H. Sprey, F. Boulanger, B. de Salvo, T. Billon, *2011 IEEE International Interconnect Technology Conference and 2011 Materials for Advanced Metallization (IITC/MAM)*, Dresden (2011), http://dx.doi.org/10.1109/IITC.2011.5940298