



Growth of rare-earth oxide thin films for electronic applications by atomic layer deposition

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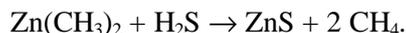
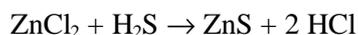
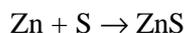
Rare earth oxides are emerging as very promising materials for electronic devices in silicon-based technologies because of their stability, high dielectric constant and buffer layer potential. Recently the novel gas-phase thin film processing technique, called Atomic Layer Epitaxy (ALE) or Atomic Layer Deposition (ALD), has successfully been applied for the controlled growth of RE oxide thin films at reasonably low temperatures.

Principle of ALE/ALD

Atomic Layer Epitaxy (ALE) was originally developed in the early 1970s by Dr. T. Suntola at Helsinki University of Technology and later at Instrumentarium Ltd to meet the needs of producing high-quality, large-area flat panel displays based on electroluminescence. First patent application dates back to 1974 and an industrial scale production of thin film electroluminescent (TFEL) displays utilizing ALE processes was initiated in Finland in the 1980s by Lohja Corporation which then entered a joint venture with Planar of Portland, USA to form Planar Systems, Inc. At the same time (1980s) in Japan and USA, ALE technology was explored for the deposition of II-VI and III-V compound semiconductors, e.g. GaAs.

The proceedings of the 1st International Symposium on Atomic Layer Epitaxy held in Espoo, Finland, give a good picture of the state-of-the art in 1990.¹

An ideal ALE/ALD growth proceeds by exposing the substrate surface alternately to different precursors separated by inert gas pulses. Thus, the deposition process is based on alternating chemisorption of the precursors, surface reaction and desorption. The precursors may be elements or compounds provided that they meet the volatility, stability and reactivity criteria necessary for an ALE/ALD growth. Zinc sulfide can be produced from the elements, from inorganic or organometallic compounds:



A representative example of II-VI compound thin film process is presented in Fig 1., which shows the formation cycle of ZnS from zinc chloride and hydrogen sulfide precursors. The scheme is somewhat idealized because mainly due to steric factors one monolayer (ML) of ZnS is not formed in each cycle but rather a distinct fraction thereof, in this case 1/3-1/2 monolayer per cycle

depending on the temperature. When starting with elements, viz. Zn and S, it is however possible to obtain a monolayer coverage in one cycle.

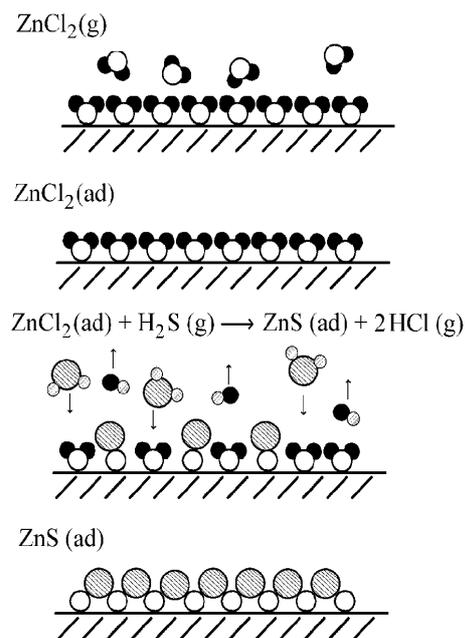


Figure 1. ALD reaction cycle leading to formation of zinc sulfide thin film from zinc chloride and water: $\text{ZnCl}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS} + 2 \text{HCl}$.⁸

Nevertheless, from the growth mechanism it follows that thickness control is straightforward because each deposition cycle produces a monolayer or a distinct fraction thereof. Figure 2 shows as an example the linear relationship between

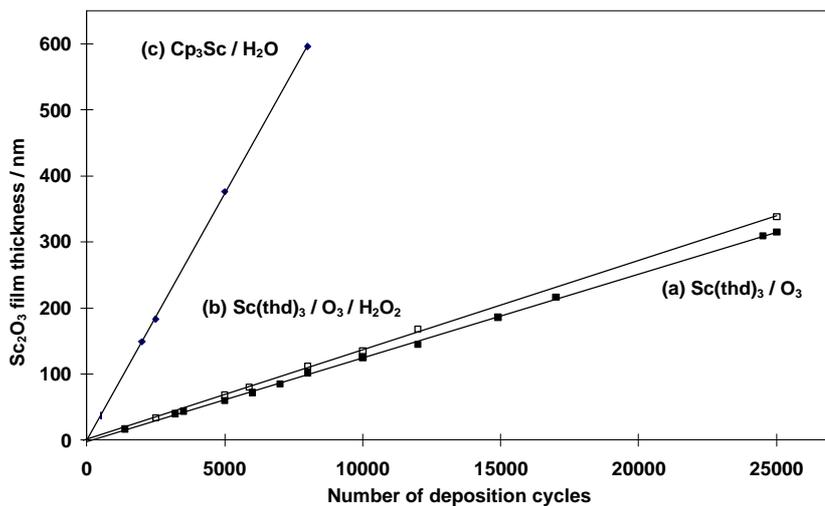


Figure 2. The linear relationship between film thickness and number of deposition cycles in the case of Sc_2O_3 deposited by ALD from different precursor combinations.²

film thickness and number of deposition cycles in the case of Sc_2O_3 .²

ALE or ALD?

T. Suntola originally coined the name *Atomic Layer Epitaxy* and the acronym *ALE* to describe the layer-by-layer growth mechanism and resulting epitaxial film. However, epitaxial growth can only be achieved on matching single crystal substrates. Growth on amorphous substrates, such as glass, leads to polycrystalline or amorphous films and the name *Atomic Layer Deposition (ALD)* should be preferred. Sometimes in the literature an ALE/ALD type growth is referred to as *layer-by-layer growth* or even *digital layer epitaxy (DLE)* because the number of deposition cycles can be used as the basis for thickness determination. The name *Atomic Layer Chemical Vapor Deposition (ALCVD)* emphasizes the relation to CVD.

Thin Films of Rare Earth Oxides by ALD for Electronic Applications

In silicon-based microelectronics the complementary metal-oxide-semiconductor (CMOS) integrated circuit technology developed very fast at the end of the last century, *i.e.* in the 1990s. Now, however, new gate dielectric materials are needed in

order to extend the device performance at a lower cost. This means in practice a higher density of transistors in a wafer. The dielectric currently used, *viz.* SiO_2 , cannot be scaled beyond 12-13 Å and therefore new materials with high permittivity (ϵ) (or dielectric constant k) are being searched for. These are called after their functional property as high- k gate dielectrics.³

Most of the high- k gate dielectric candidates considered are oxides (Si_3N_4 being an exception) and among them the RE oxides have recently gained considerable attention. While SiO_2 and Si_3N_4 have low dielectric constants 3.9 and 7, respectively, the

yttrium oxide has much higher constant of 15 and La_2O_3 twice that or 30.

RE oxides are refractive materials with several structure types and stoichiometries.⁴ Excluding the lower oxides, *e.g.* EuO and Eu_3O_4 , the main types are the sesquioxides RE_2O_3 which adopt three structures (A, B, C) and dioxides, most notably CeO_2 . The melting and boiling points are high for the sesquioxides (La-Lu) being in the range of 2200-2400°C and 3600-4100 °C, respectively. In the past, the RE_2O_3 thin films have usually been deposited by different physical methods such as electron-beam or pulsed-laser evaporation and vacuum evaporation. Oxidation of metallic overlayers has also been used to produce oxide films. Chemical gas phase methods occasionally considered include the spray pyrolysis and chemical vapor deposition (CVD) techniques.

ALE/ALD offers several practical advantages for thin film growth originating from the self-limiting and sequential operating mode briefly discussed above and in more detail in refs.5-8, for instance. A practical concept is so called 'ALE window' (Fig. 3) for determining the proper growth conditions, *i.e.* temperature range where the surface-controlled growth occurs giving in an ideal case

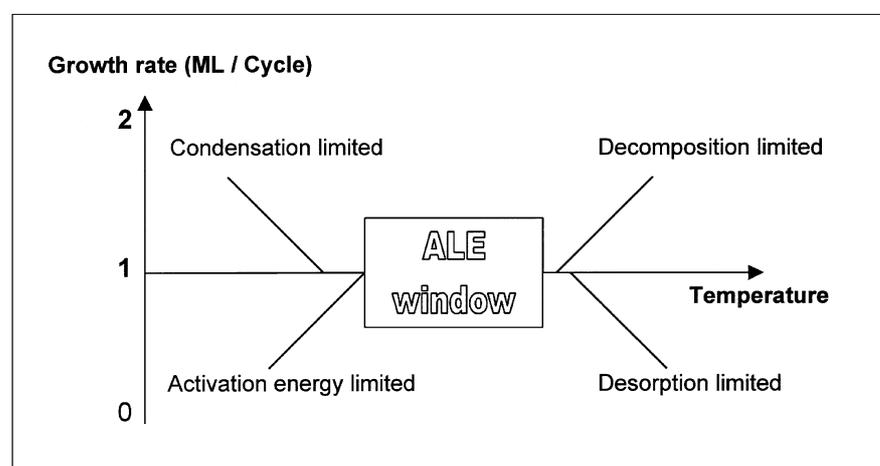


Figure 3. The concept of 'ALD window' or temperature region for surface-controlled growth yielding in an ideal case 1 monolayer (ML) per cycle.⁸

Table 1. Growth of binary rare earth oxide thin films by ALE/ALD on silicon substrates.

Oxide	Precursor	Growth temp. /°C	Applications	Ref.
Sc ₂ O ₃	Sc(thd) ₃ / O ₃ (C ₅ H ₅) ₃ Sc / H ₂ O	335-375 250-350	antireflection coatings, interface polarizers, constituent of ferroelectric films	2
Y ₂ O ₃	Y(thd) ₃ / O ₃	250-350	dielectric, refractory and buffer layers, constituent of YSZ (yttrium-stabilized zirconia)	9
La ₂ O ₃	La(thd) ₃ / O ₃	300-425	dielectric and protective layers, optical coatings	10

growth rate of 1 ML per cycle.

Quite recently ALE/ALD has systematically been exploited at the Helsinki University of Technology to grow thin films of binary RE oxides. The precursor combination has in most cases been a volatile RE β-diketonate complex and ozone, but true organometallics, viz. cyclopentadienyl compounds have also been used. Table 1 gives a summary of the recent work.^{2, 9, 10} A multitude of advanced analytical techniques including TOF-ERDA, RBS, FTIR, AFM and XRD has been used to characterize the thin films for structure and impurities and to develop improved processes to grow them.

Ternary and Other Oxides

Prompted by the successful growth of binary oxides, the deposition of ternary and other more complex oxides has investigated as well. Thus, LaAlO₃ and LaGaO₃ have been deposited.^{11,12} A material of high application potential is also the Y-stabilized zirconia (YSZ) which can be grown by ALD based on the experience gained from the deposition of zirconia thin films.¹³

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BOOKS

Handbook, Volume 31

The 31st volume of the *Handbook on the Physics and Chemistry of Rare Earths* is the second of a two-volume set of reviews devoted specifically to High-temperature Superconductors. It contains ten contributions: *Oxygen non-stoichiometry and lattice effects in Yba₂Cu₃O_x*, *Phase transitions, structural distortions and phase separation* (Emanuel Kaldis), *Flux Pinning* (H.W. Weber), *Magnetoresistance and Hall effect* (C.C. Almasan, M.B. Maple), *Neutron scattering studies of lanthanide magnetic ordering* (J.W. Lynn, S. Skanthakumar), *Heatcapacity* (P.M. Hallenspach, M.B. Maple), *Angle-resolved photoemission studies of untwined yttrium barium copper oxide* (M. Schabel, Z.-X. Shen), *Infrared properties of high-T_c superconductors: an experimental over-view* (D.N. Basov, T. Timusk), *Electronic and magnetic Raman scattering studies of the high-T_c cuprates* (S.L. Cooper), *Characterization of cuprate superconductors using tunneling spectra and scanning tunneling microscopy* (H. Sugawara, T. Hasegawa, K. Kitazawa).

Handbook on the Physics and Chemistry of Rare Earths, *High-Temperature Superconductors – II*, K.A. Gschneidner Jr., L. Eyring and B.M. Maple, eds, Elsevier Science Publishers, Amsterdam, 2001.

450 pages, 204 Euros (221 US \$), ISBN 0 444 50719 1.

EDITORIAL

This is a somewhat unusual issue in that we publish a scientific contribution from the Laboratory of Inorganic and Analytical Chemistry of the Helsinki University of Technology devoted to the growth of thin films. This is not the first time that ERES Newsletter is publishing a genuine research article, but the preceding ones were shorter notes. We thank Professor Lauri Niinistö and Dr Jani Päiväsaari for their outstanding contribution in this fast developing field of rare-earth science.

During the month of October, members will receive a letter describing their status within the association and a call for the payment of the association fees.

SOLIDARITY WITH THE US

At the time of completing this issue, we have learned about the tragedy suffered by the United States on September 11. The ERES committee express its sadness and dismay to see how a small group of people can destabilize an entire nation, if not the entire world. Its members express their warmest sympathy to the families of the victims and assure all their American colleagues and friends of their entire support.

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5TH ESTE

The 5th International Conference on Excited States of Transition Elements has been held in Wrocław-L'dek Zdój in Poland June 6-11, 2001. The organizers, Professors Janina Legendziwicz and W. Strêk from the Institute of Low Temperature and Structure Research (Polish Academy of Sciences) have come up with a very interesting scientific program a good deal of which was devoted to f-element luminescence. Altogether, 28 plenary lectures, 18 oral presentations and 89 posters were scheduled.

ERES has sponsored this events by providing 1600 Euros to help young scientists to attend the seminar. The following six persons, all under 35, received a stipend: Yanina Potapenok, Alexander Alexeenko, and Dimitry Kovalenko from Belarus, Irina Tsoltanova Bassieva and Galina Semkova from Russia, and Victor Trush from Ukraina.

INDUSTRY

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The most prestigious award given to a business in the United Kingdom, the Queen's Award, has been granted to Less-Common Metals Ltd, part of the Meldform Metals group of companies (www.meldform.com), and which supplies a wide range of rare earth alloys and master alloys on a global basis.

Congratulations !

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