NMP4-CT-2006-016172

REALISE

Rare earth oxide atomic layer deposition for innovations in electronics

Instrument: Specific targeted research or innovation project

Thematic Priority: IST-NMP

Publishable Final Activity Report

Covering the entire project duration

Start date of project: 01 Mar 2006

Project coordinator: Simon Elliott, Tyndall National Institute

Date of revision: 05 Mar 2010

Duration: 3 years 7 months

Revision 2

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

1 Executive Summary

The project 'Rare earth oxide atomic layer deposition by innovation in electronics' (REALISE) achieved the following aims: (i) deposition of high permittivity rare oxide based layers with sub-nanometer control and (ii) integration into innovative memory and communication devices.

The project partners were Tyndall National Institute (University College Cork), University of Helsinki, University of Liverpool, CNR-INFM-MDM, SAFC-Hitech, ASM Microchemistry, Numonyx, Qimonda Dresden, NXP Semiconductors Netherlands BV, CNRS-CEMES. The project started on 01 Mar 2006 and ended on 30 Sep 2009. It was funded by the European Commission and by the project partners under the Sixth Framework Programme, in response to a joint call of the IST and NMP thematic priorities. The contract number was NMP4-CT-2006-016172.

All tasks were successfully completed and all deliverables were successfully achieved. The main results of the project are:

- New precursors and materials;
- Precursor products;
- Precursor and process modelling;
- Deposition mechanism;
- High-*k* deposition & characterisation;
- Interface characterisation;
- Process scale-up;
- DRAM technology;
- NVM technology;
- RF decoupling capacitor technology.

Some of these results are being commercially exploited. In addition, 29 peer-reviewed journal papers have been published to date and 6 patents have been filed. The results have also been presented at international conferences, on the project website (http://www.tyndall.ie/realise) and in specific events organised by the consortium.

2 Overview of REALISE project

2.1 Project objectives

The project 'Rare earth oxide atomic layer deposition for innovation in electronics' (REALISE) aimed to (i) deposit high permittivity rare earth oxide layers with sub-nanometer control and (ii) integrate these into innovative memory and communications devices.

The process that is the subject of this project is atomic layer deposition (ALD), the leading technology for deposition of nanometre-scale films. Rare earth oxides were identified at the start of the project as showing promise as high-permittivity ("high-*k*") dielectrics in nano-electronic devices, and this has been borne out by the results obtained. However, prior to the project, no satisfactory ALD process existed for these oxides. The performance of nanoelectronic devices is strongly affected by the incorporation of impurities in the material, morphological instability and the quality of the interface to the substrate. The project therefore aimed to overcome these difficulties by developing a scalable and commercialisable ALD process, of demonstrated value to the semiconductor industry, through a vertically-integrated research collaboration. Individual goals were therefore:

- design, synthesis and scale-up of suitable precursors;
- optimisation of deposition parameters;
- high-resolution characterisation of film quality and interface to Si/Ge substrate;
- scale-up new ALD process to industrially-sized Si wafers;
- integrate dielectric layers into test capacitors for innovative memory (DRAM), embedded electronics (NVM) and wireless (RF) applications.

The emphasis is on materials integration for high-volume production of consumer electronics devices, consistent with the IST and NMP objectives of the European Framework programmes.

In this way, it is intended to strengthen high-tech industry in Europe and advance the position of European research teams as world-leaders. Both outcomes are important for the EU's Lisbon agenda, which aims to increase employment, social cohesion and economic activity through research and development.

2.2 Project partners

A wide spectrum of expertise was brought together within REALISE, including leading research groups in inorganic synthesis, materials science, process technology and electrical analysis. The collaboration spans two universities, three national research institutes, three major semiconductor companies, one research division of fabrication tool manufacturer and one fine chemicals company (Table 1).

Table 1: Overview of REALISE consortium.

Participant name	short name	country
Tyndall National Institute -University College Cork	Tyndall	Ireland
University of Helsinki	UHel	Finland

University of Liverpool	UnivLiv	UK
CNR-INFM-MDM	MDM	Italy
Epichem / SAFC-Hitech	SAFC-Hitech	UK
ASM Microchemistry	ASMM	Finland
ST Microelectronics / STMicroelectronics M6 Srl / Numonyx	ST	Italy
Infineon Technologies SC300 Dresden / Qimonda Dresden	Qimonda	Germany
Philips Electronics Nederland BV / Philips Research / NXP Semiconductors Netherlands BV	NXP	Netherlands
CNRS-CEMES	CEMES	France

2.3 Project management

The REALISE project was coordinated by Dr Simon Elliott, Tyndall, along with Tyndall's financial and legal support staff. The project Management Committee included all partners and met for a face-to-face meeting every six months (Table 2). Communication and cooperation between the partners was excellent. The project duration was extended to 43 months.

Table 2: Overview of project meetings.

Date	Location	Event
27 Mar 2006	Cork, IRL	Kickoff
14-15 Sep 2006	Bromborough, UK	2nd Meeting
6-7 Mar 2007	Helsinki, FIN	3rd Meeting
4-6 Sep 2007	Eindhoven, NL	Exploitation Seminar, 4th Meeting & Mid-term review
6-7 Mar 2008	Agrate, I	5th Meeting
18 Sep 2008	Dresden, D	6th Meeting & Workshop on lanthanum oxide
12-13 May 2009	Cork, IRL	7th Meeting
24 Sep 2009	Brussels, BE	Final Review

2.4 Work performed and final results

REALISE activity was divided into four technical workpackages (WP), along with management and exploitation workpackages (Figure 1). Precursor design (WP1) was the first step in both the $La_2O_3/LaZrO_x$ and $Er_2O_3/ErHfO_x$ phases of the project, along with subsequent scale-up of the synthetic route for the successful chemicals. The transition between WP1 and WP2 was marked by a change in emphasis to process optimisation and characterisation, with the objective of film quality. Interface quality on both Si and Ge substrates was addressed in WP3. The process from WP2 was applied to test structures in WP3 and WP4, where the electrical performance of the thin high-*k* layers was measured.

All tasks were successfully completed and all deliverables were successfully achieved (Table 3). The main results of the project are described in section 3:

1. New precursors and materials;

2. Precursor products;
3. Precursor and process modelling;
4. Deposition mechanism;
5. High-k deposition & characterisation;
6. Interface characterisation;
7. Process scale-up;
8. DRAM technology;
9. NVM technology;
10. RF decoupling capacitor technology.

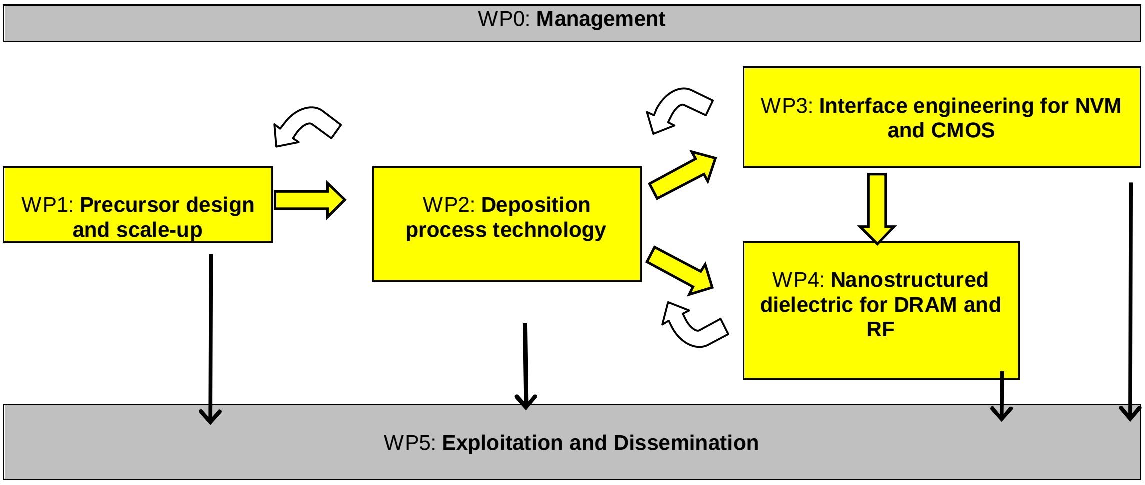


Figure 1: Diagram of workpackage interdependencies and information flow.

Table 3: List of deliverables (all achieved).

Del. no.	**Deliverable name**	**Ref.**
IAR1	Interim Activity Report 1	[1]
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
IAR2	Interim Activity Report 2	[3]
PAR1	Periodic Activity Report 1	[4]
D2	Optimised process for deposition of thin La_2O_3 films onto Si wafers using novel precursors	[5]
D3a	Physical properties of Si/La_2O_3 interface	[6]
D3b	Electrical properties of Si / La ternary interface	[7]
IAR3	Interim Activity Report 3	[8]
MTA	Mid-Term Assessment	[9]
DUP	Dissemination and Use Plan	[10]
D4	Assessment of electrical properties of La ternary NVM test structure	[11]
D5+D9	Optimised process for deposition of thin rare earth oxide films onto Ge wafers	[12]
D6	Assessment of electrical and physical properties of La ternary DRAM capacitor test structure	[13]
D7	Assessment of electrical properties of La ternary decoupling capacitor test structure	[14]
D8	Prototype synthetic route for production of novel La_2O_3 precursor	[15]
IAR4	Interim Activity Report 4	[16]
PAR2	Periodic Activity Report 2	[17]
D9	Structural and electrical properties of rare earth oxide / Ge interface (with D5)	[12]

D10	Final precursor selection for Ln_2O_3 atomic layer deposition	[18]
EHSA	Environmental, Health and Safety Assessment	[19]
D11	Optimised process for deposition of thin Ln_2O_3 or Ln ternary films onto Si wafers	[20]
IAR5	Interim Activity Report 5	[21]
D12	Structural and electrical properties of interface between Si and Ln_2O_3 or Ln ternary.	[22]
D13	Deposition of ternary oxide $LaMO_x$	[23]
D14	Prototype synthetic route for production of novel Ln_2O_3 precursor	[24]
D15	Assessment of electrical properties of Ln-based NVM test structure	[25]
D16	Assessment of electrical and physical properties of Ln-based DRAM capacitor test structure	[26]
D17	Assessment of electrical properties of Ln-based decoupling capacitor test structure	[27]
IAR6	Interim Activity Report 6	[28]
PAR3	Periodic Activity Report 3	[29]
IAR7	Interim Activity Report 7	[30]
PAR4	Periodic Activity Report 4	[31]
PDUK	Plan for Dissemination and Use of Knowledge	[32]
FR	Final Report	[33]

2.5 Exploitation and dissemination

A complete account of the plan and activity to date for exploitation of the REALISE results is given in the 'Plan for Dissemination and Use of Knowledge' [32]. A summary is given here:

- To date, 29 journal papers have been accepted by peer-review for publication and some more papers containing the final results are in preparation. 60% of the publications are joint papers within the consortium (Table 4).
- Six patents have been filed by NXP (Table 5).
- Project results have been presented in 52 conference presentations, 30% of them invited/plenary talks, and consortium members have been active in organising 15 conferences.
- Total visits to webpages and downloads from the project website http://www.tyndall.ie/realise averaged 930 hits/month over the last year of the project.
- The REALISE partners organised a public workshop on lanthanum oxide (Dresden, 19.09.2008) and three experts from outside the consortium were invited to attend.

Table 4: Peer-reviewed journal papers published or accepted for publication to date.

Partner(s)	**Title**	**Journal**	
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-κ films by liquid injection ALD*	Appl. Phys. Lett.	[34]
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-k films by liquid injection ALD and MOCVD*	Chem. Vap. Depos.	[35]
Tyndall	*Mechanism for zirconium oxide atomic layer deposition…*	Appl. Phys. Lett.	[36]
Tyndall & SAFC-Hitech	*An ab initio Evaluation of Cyclopentadienyl Precursors for the Atomic Layer Deposition of Hafnia and Zirconia*	Electrochem. Soc. Trans.	[37]
Tyndall	*Improving ALD growth rate via ligand basicity: quantum chemical calculations on lanthanum precursors*	Surf. Coat Techn.	[38]

MDM	*Vibrational and electrical properties of hexagonal La_2O_3 films*	Appl. Phys. Lett.	[39]
SAFC Hitech	*Thermal Stability Studies For Advanced Hafnium And Zirconium ALD Precursors*	Surf. Coat Techn.	[40]
NXP	*Remote plasma and thermal ALD of Al_2O_3 for trench capacitor applications*	Electrochem. Soc. Trans.	[41]
NXP	*ALD options for Si-integrated ultrahigh-density decoupling capacitors in pore and trench designs*	Electrochem. Soc. Trans.	[42]
NXP	*Growth Characteristics and Physical Properties of Remote Plasma and Thermal ALD of Al_2O_3 in a commercial 200mm ALD reactor*	J. Electrochem. Soc.	[43]
UHel	*In Situ Reaction Mechanism Studies on Atomic Layer Deposition of ZrO_2 from $(CpMe)_2Zr(OMe)Me$ and Water or Ozone*	Chem. Mater.	[44]
Univ. Liv., SAFC-Hitech & Tyndall	*Deposition of zirconium dioxide and hafnium dioxide thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors*	J. Mater. Chem.	[45]
CEMES & MDM	*Chemical/ Structural Nano-characterization And Electrical Properties of ALD-grown La_2O_3/Si Interfaces For Advanced Gate Stacks*	J. Electrochem. Soc.	[46]
CEMES & MDM	*ALD-grown Rare Earth Oxides for Advanced Gate Stacks*	Electrochem. Soc. Trans.	[47]
MDM & CEMES	*Infrared spectroscopy and X-ray diffraction studies on the crystallographic evolution of La_2O_3 films upon annealing*	Microelectr. Eng.	[48]
NXP & ASMM	*Spontaneous nanoclustering of ZrO_2 in atomic layer deposited $La_yZr_{1-y}O_x$ thin films*	Appl. Phys. Lett.	[49]
NXP & ASMM	*Enhanced electrical properties of atomic layer deposited La_2O_3 with embedded ZrO_2 nanoclusters*	Appl. Phys. Lett.	[50]
NXP & ASMM	*Silicon out-diffusion and aluminium in-diffusion in devices with atomic-layer deposited La_2O_3 thin films*	Appl. Phys. Lett.	[51]
MDM & CEMES	*Atomic layer deposition of $La_xZr_{1-x}O_{2-\delta}$ (x=0.25) high-κ dielectrics for advanced gate stacks*	Appl. Phys. Lett.	[52]
Tyndall, Qimonda & ASMM	*TiN/ZrO_2/Ti/Al Metal-Insulator-Metal Capacitors with sub-nm CET using ALD-deposited ZrO_2 for DRAM applications*	IEEE Electron Device Letters	[53]
Univ. Liv.	*Dielectric relaxation of lanthanum doped zirconium oxide*	J. Appl. Phys.	[54]
Numonyx & MDM	*Rare earth-based high-k materials for non-volatile memory applications*	Microelectr. Eng.	[55]
MDM	*Ab initio study of structural, vibrational and dielectric properties of high-k HfO_2 as a function of doping*	Mat. Sci. Eng.	[56]
Univ. Liv.	*Frequency dispersion and dielectric relaxation of $La_{0.5}Hf_{0.5}O_2$*	J. Vac. Sci. Technol.	[57]
NXP & ASMM	*Charge conduction mechanisms of atomic-layer-deposited Er_2O_3 thin films*	Appl. Phys. Lett.	[58]
NXP	*Maxwell-Wagner instability in bilayer dielectric stacks*	Appl. Phys. Lett.	[59]
NXP & ASMM	*Cubic phase stabilization and improved dielectric properties of atomic-layer-deposited $Er_yHf_{1-y}O_x$ thin films*	Appl. Phys. Lett.	[60]
MDM& CEMES	*Thermally-induced permittivity enhancement in La-doped ZrO_2 grown by atomic layer deposition on Ge(100)*	Appl. Phys. Lett.	[61]
MDM& CEMES	*Dielectric properties of Er-doped HfO_2 (Er ~15%) grown by atomic layer deposition for high-k gate stacks*	Appl. Phys. Lett.	[62]

Table 5: Patents connected with REALISE.

Assignee	Title	Inventors	Patent number	Date filed
NXP	*Ultrahigh-density Capacitor*	L. Guiraud, F. Le Cornec, F. Roozeboom, J. Klootwijk, D. Chevrie	PH005852EP1	2 May 2006
NXP	*Miniaturized DC:DC converter*	D. Reefman, F. Roozeboom, J. Klootwijk	PH005924EP1	15 May 2006
NXP	*Ultrahigh-density Capacitors*	J. Klootwijk, F. Roozeboom, J. Ruigrok, D. Reefman	PH007319EP1	Apr 2007
NXP	*Ultrahigh density capacitors*	K. B. Jinesh, F. Roozeboom, W. Dekkers, J. Klootwijk	8157896.5	9 Jun 2008
NXP	*Integrated Ultrahigh-Density devices with functional layer stacks on robust high-aspect ratio topography*	F. Roozeboom, M. Goossens, W. Besling, N. Verhaegh	81355227EP01	30 Sep 2008
NXP	*nanocluster-embedded dielectrics*	K. B. Jinesh, W. F. A. Besling, R. Wolters, J. Klootwijk, F. Roozeboom	81355857EP01	28 Apr 2008

3 Major Results

3.1 New precursors and materials based on rare earths

Screening, synthesis and exploratory deposition was carried out with novel complexes of the rare earths and of Zr and Hf. At UnivLiv, new La alkoxide precursors were synthesised and characterised. They showed promising volatility but insufficient thermal stability for ALD applications. Parallel studies at SAFC-Hitech identified $La(^{i}PrCp)_3$ as the most effective precursor for growth, while $La(thd)_3$ was most stable against decomposition. The ternary oxides $LaZrO_x$[1] and $LaHfO_x$ were deposited by liquid injection MOCVD and ALD, and were fully characterised, which was the first time that these oxides had been grown by CVD techniques. There is also a requirement in ALD for precursors with enhanced thermal stability. New *ansa*-metallocene complexes of Zr and Hf were synthesised, *e.g.* $(Cp_2CMe_2)Zr(Me)(OMe)$, and were shown to have higher thermal stability than the un-bridged analogues.

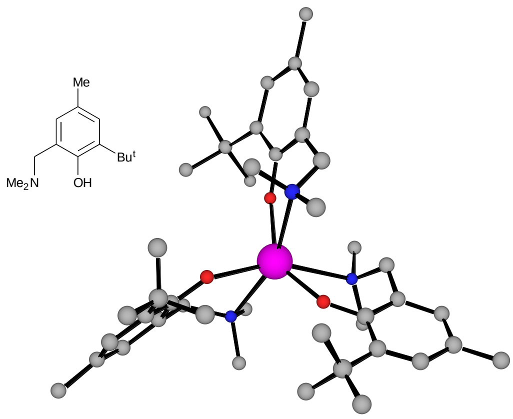


Figure 2: Crystal structure of the La alkoxide complex $[La(bammp)_3]$; inset shows bammpH ligand.

3.1.1 Activity

Task		Partners involved
WP1:	**Precursor design and scale-up**	
Task 1.1	Precursor reaction modelling	Tyndall
Task 1.2	Synthesis and characterisation of precursors	UnivLiv, SAFC Hitech
Task 1.3	MOCVD growth testing and film characterisation	UnivLiv
Task 1.4	ALD growth and film characterisation	UnivLiv, MDM
Task 1.5	Repeat synthesis of target precursor	UnivLiv, SAFC Hitech

3.1.2 Deliverables

Del. no.	Deliverable name	Ref.
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
D10	Final precursor selection for Ln_2O_3 atomic layer deposition	[18]

[1] The formula $LaZrO_x$ is used as a shorthand for the general formula for the La-Zr ternary oxide $Zr_{2-2x}La_{2x}O_{4-x}$, $0<x<1$ (or equivalently $La_{2-2y}Zr_{2y}O_{3+y}$, $0<y<1$). The same applies to the shorthand formula $ErHfO_x$.

3.1.3 Description of result

Based on ALD precursor design recommendations from Tyndall, the La alkoxide complexes, [La(mmp)$_3$] (mmp = 1-methoxy-2-methyl-2-propanolate), [La(dmop)$_3$] (dmop = 2-(4,4-dimethyloxazolinyl)-propanolate) and [La(bammp)$_3$] (bammp = 3-*tert*-butyl-5-dimethylamino-1-methyl-4-phenol) were investigated [2]. Precursor modelling studies at Tyndall (section 3.3) revealed that the La(bammp)$_3$ should react in ALD more readily than the other alkoxides. Deleterious decomposition by β-H elimination can occur for [La(mmp)$_3$], [La(dmop)$_3$] but not for [La(bammp)$_3$]. However, MOCVD and ALD studies showed that *all* the alkoxide complexes had insufficient thermal stability for ALD applications [2]. The previously-known precursor La(thd)$_3$ was found to be most stable against decomposition, but required O_3 as co-reagent for ALD. Parallel investigations at SAFC Hitech identified the La metallocene [(^{i}PrCp)$_3$La] as the preferred precursor for H_2O-based ALD of La_2O_3 and La-containing ternary oxides [2], thus achieving a specific project objective.

Replacement of the [MeCp] ligands in complexes of the type [(MeCp)$_2$MMe(OMe)] and [(MeCp)$_2$MMe$_2$] with the bidentate *ansa*-metallocene ligand [Cp$_2$CMe$_2$] was expected to lead to complexes with higher thermal stabilities due to the chelating effect of the [Cp$_2$CMe$_2$] ligand. This offers the potential for ALD at higher temperatures resulting in improved purity oxide films and better step-coverage. Synthesis routes were therefore developed to the monomeric *ansa*-metallocene complexes [(Cp$_2$CMe$_2$)MMe$_2$] and [(Cp$_2$CMe$_2$)MMe(OMe)] (M = Zr, Hf) (see Figure 3) [16].

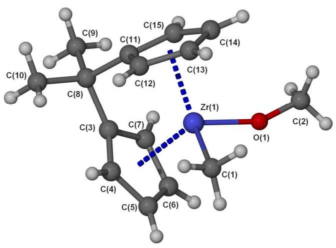


Figure 3: Crystal structure of [(Cp$_2$CMe$_2$)ZrMe(OMe)].

Deposition of ZrO_2 and HfO_2 films by liquid injection MOCVD and ALD using [(Cp$_2$CMe$_2$)MMe$_2$] and [(Cp$_2$CMe$_2$)MMe(OMe)] confirmed their high thermal stability [16]. Deposition rates were constant up to at least 350^{o}C and the complexes were shown to be more thermally stable than the analogous un-bridged metallocene complexes [45]. The use of thermally stable *ansa*-metallocene complexes may prove to be a fruitful direction for future ALD precursor development.

La_2O_3 is unstable in air, rapidly converting to La-carbonate and La-hydroxide. However, the La-containing ternary oxides LaZrO$_x$ and LaHfO$_x$ are air-stable and certain compositions potentially have significantly higher permittivities than the binary oxides ZrO_2, HfO_2 and La_2O_3. LaZrO$_x$ thin films were grown by liquid injection MOCVD and ALD using [(^{i}PrCp)$_3$La] and [(MeCp)$_2$ZrMe(OMe)] (H_2O was used as the oxygen source in the ALD studies) [8, 34, 35]. X-ray diffraction analysis of the films showed that all the LaZrO$_x$ films were amorphous as-grown. On annealing in air, films with lower La content crystallised into the cubic or tetragonal phase of ZrO_2 at 700°C, while higher La content films required an annealing temperature of 900^{o}C for crystallisation. The aim of obtaining La-containing oxide films with significantly enhanced permittivities was achieved by annealing a La=9% film at high temperature in N_2. The film crystallised into the cubic or tetragonal phase of ZrO_2 and had κ values as high as ~ 38 (at 50 Hz) and ~ 35 (at 1 KHz) [21].

Medium energy ion scattering (MEIS) data for annealed $LaZrO_x$ films on Si(100) and TiN substrates showed a significant level of interaction between the films and substrates [16]. In contrast, MEIS data showed that there was no significant interaction between annealed $LaHfO_x$ films and the Si substrate [16]. This is the first time that $LaZrO_x$ and $LaHfO_x$ have been deposited by ALD and the "state-of-the-art" film characterisation data obtained in this project may have a considerable impact on the high-*k* dielectric research sector.

3.1.4 Peer-reviewed papers published

Partner(s)	**Title**	**Journal**	
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-κ films by liquid injection ALD*	Appl. Phys. Lett.	[34]
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-k films by liquid injection ALD and MOCVD*	Chem. Vap. Depos.	[35]
Univ. Liv., SAFC-Hitech & Tyndall	*Deposition of zirconium dioxide and hafnium dioxide thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors*	J. Mater. Chem.	[45]
Univ. Liv.	*Dielectric relaxation of lanthanum doped zirconium oxide*	J. Appl. Phys	[54]
Univ. Liv.	*Frequency dispersion and dielectric relaxation of* $La_{0.5}Hf_{0.5}O_2$	J. Vac. Sci. Technol.	[57]

3.2 Precursor products

A new range of precursors was identified and the protocols to isolate high purity samples were developed. Reproducible lots on increased scale were prepared and towards the end of the project offered commercially.

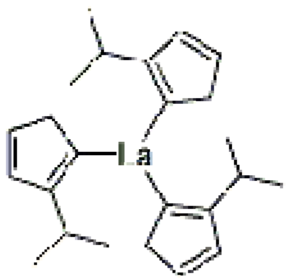


Figure 4: New product range introduced: $Ln(^{i}PrCp)_3$ for Ln_2O_3 / $LnMO_x$ deposition (the example Ln=La is illustrated).

3.2.1 Activity

Task		**Partners involved**
Task 1.2	Synthesis and characterisation of precursors	UnivLiv, SAFC Hitech
Task 1.6	Correlation of performance against analysis data	SAFC Hitech
Task 1.7	Definition of target specification	SAFC Hitech
Task 1.8	Larger scale synthesis of target precursors	SAFC Hitech

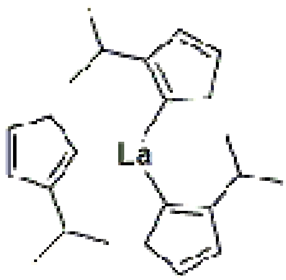
3.2.2 Deliverables

Del. no.	Deliverable name	
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
D8	Prototype synthetic route for production of novel La_2O_3 precursor	[15]
D10	Final precursor selection for Ln_2O_3 atomic layer deposition	[18]
EHSA	Environmental, Health and Safety Assessment	[19]
D14	Prototype synthetic route for production of novel Ln_2O_3 precursor	[24]

3.2.3 Description of result

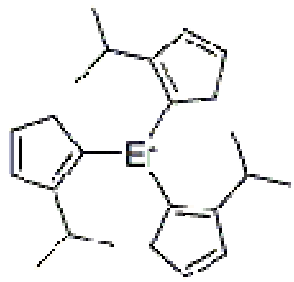
New compounds having been identified as well suited to ALD processes (section 3.1) [2, 18], the synthesis technologies were successfully developed to move from 5 g to 100 g batch size and beyond. Reproducible samples have been isolated at each stage of the process scale-up and uniform high performance achieved at all deposition sites. Quality correlation between in-house analysis data and deposited film characterisation results allowed a specification to be set for the final products [24]. Research samples were made available commercially towards the end of the project and further scale-up protocols were determined for implementation as demand increases.

In detail the isopropylcyclopentadienyl derivatives of La and Er (Figure 5) have been added to the SAFC portfolio as well-matched to existing Zr and Hf precursors for ALD of complex oxide high-*k* dielectric layers.



Mp: 34-35°C

VP: $\log_{10}P(\text{mTorr})=12.175-3568.2/T(\text{K})$



Mp: 64-65°C

VP: $\log_{10}P(\text{mTorr})=16.46-4697.9/T(\text{K})$

Figure 5: Chemical structures and physical characteristics of new products (isopropylcyclopentadienyl derivatives of La and Er).

The interest in precursors capable of yielding high-*k* films by ALD from research groups worldwide has been high and the addition of the new products enabling further development has been a significant advance in this field.

The ability to deposit state of the art mixed oxides such as ternaries in a controlled fashion will allow the development of integration schemes to include these advanced materials in next generation Si devices. As the market develops, precursor sales will rise and SAFC is ideally placed to achieve a dominant market position.

3.2.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-κ films by liquid injection ALD*	Appl. Phys. Lett.	[34]
Univ. Liv. & SAFC-Hitech	*Deposition of lanthanum zirconium oxide high-k films by liquid injection ALD and MOCVD*	Chem. Vap. Depos.	[35]

Tyndall & SAFC-Hitech	*An ab initio Evaluation of Cyclopentadienyl Precursors for the Atomic Layer Deposition of Hafnia and Zirconia*	Electrochem. Soc. Trans.	[37]
SAFC Hitech	*Thermal Stability Studies For Advanced Hafnium And Zirconium ALD Precursors*	Surf. Coat Techn.	[40]
Univ. Liv., SAFC-Hitech & Tyndall	*Deposition of zirconium dioxide and hafnium dioxide thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors*	J. Mater. Chem.	[45]

3.3 Precursor and process modelling

Three important aspects of the ALD process were modelled at the atomic-scale: precursor reactivity, precursor decomposition and oxide-specific surface chemistry. The first of these allows one-dimensional precursor screening, and ultimately precursor design, which was validated in collaboration with synthesis teams. The other aspects require more detailed computation on a case-by-case basis, yielding quantitative insights into process chemistry.

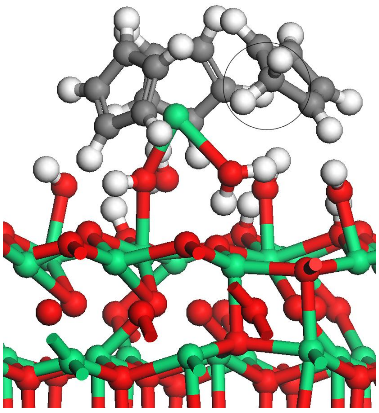


Figure 6: Computed structure of $ErCp_3$ adsorbed on the hydroxylated (001) surface of Er_2O_3. The acidity of the surface is illustrated by the spontaneous formation of CH_2 (circled) in one Cp ligand (green=Er, red=O, grey=C, white=H).

3.3.1 Activity

Task		**Partners involved**
Task 1.1	Precursor reaction modelling	Tyndall
Task 2.2	Atomic-scale modelling of film growth	Tyndall
Task 3.5	First principles modelling for interface	Tyndall

3.3.2 Deliverables

Del. no.	**Deliverable name**	
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
D2	Optimised process for deposition of thin La_2O_3 films onto Si wafers using novel precursors	[5]
D10	Final precursor selection for Ln_2O_3 atomic layer deposition	[18]
D11	Optimised process for deposition of thin Ln_2O_3 or Ln ternary films onto Si wafers	[20]

3.3.3 Description of result

The aim of the modelling work in REALISE is to apply the power of modern computational chemistry to achieve quantitative predictions for a processing technology as complex as atomic layer deposition, thereby explaining reaction mechanisms and designing new processes. The modelling was carried out at Tyndall guided by experimental data from UnivLiv, SAFC-Hitech, UHel, MDM and ASMM.

A descriptor was successfully proposed, computed and validated for the reactivity of precursor molecules with respect to the most important ALD reaction (ligand elimination) [2, 18, 38]. This descriptor was used in the computational screening of scores of metal-ligand combinations for the rare earths and explained the experimental findings for donor-functionalised alkoxides at UnivLiv (Figure 7 and section 3.1). By reducing experimental trial-and-error, the screening procedure promises to shorten development times for new chemicals.

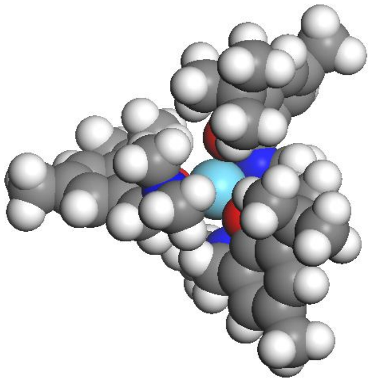


Figure 7: Computed structure of monomeric La(bammp)$_3$, predicted to be the most reactive of the donor-alkoxide La complexes. Good encapsulation of La may be correlated with the volatility of this compound (section 3.1) (grey=C, white=H, red=O, dark blue=N, light blue=La).

However, reactivity is only one necessary property of a good ALD precursor. Many of the compounds considered in REALISE were found to thermally decompose at common deposition temperatures. Finding the pathways for decomposition is a challenge for atomic scale calculations. Based on thermogravimetric data from SAFC-Hitech, Tyndall carried out a detailed theoretical analysis of the decomposition of $M(Cp)_2(CH_3)_2$ for M=Hf, Zr, Ti [37, 45, 63]. The most likely pathway was found to start with intramolecular α-H transfer to an alkylidene complex. Due to an increase in the electrophilicity of the metal, thermal stabilities were predicted to increase in the order Ti<Zr<Hf, which matches experiment. Replacing $-CH_3$ with $-OCH_3$ also increases the electrophilicity of the metal, which explains the success of the $M(MeCp)_2(CH_3)(OCH_3)$ precursors that have been used for ternary ALD in the project.

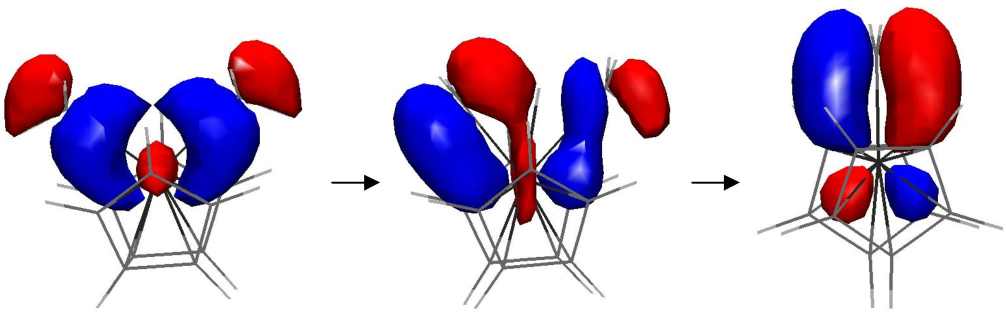


Figure 8. HOMO orbitals of reactant, transition state and product along the computed decomposition pathway of $Zr(Cp)_2(CH_3)_2$ to $Zr(Cp)_2(CH_2)$.

We have also carried out explicit modelling at the density functional level of molecule-surface reactions for Cp-based precursors of La and Er, the first time such large adsorbates have been computed on rare earth oxide surfaces [20, 64]. This is also the first time that the ALD reactions of two oxides have been computed at this level side-by-side. For La_2O_3 we find that non-ALD decomposition and desorption reactions are favoured, because the hygroscopicity of the oxide prevents ALD reactions. The crucial role of structural changes in the surface and sub-surface layers was identified. In contrast, the H-transfer reactions of standard ALD are computed to occur readily at the hydroxylated Er_2O_3 surface, so that Cp ligands eliminate to give a final surface of the type “surf-ErCp”. This is in good agreement with growth experiments at UHel, ASMM and MDM (section 3.4), and gives a deeper level of understanding than the simple descriptor of reactivity.

3.3.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
Tyndall	*Mechanism for zirconium oxide atomic layer deposition…*	Appl. Phys. Lett.	[36]
Tyndall & SAFC-Hitech	*An ab initio Evaluation of Cyclopentadienyl Precursors for the Atomic Layer Deposition of Hafnia and Zirconia*	Electrochem. Soc. Trans.	[37]
Tyndall	*Improving ALD growth rate via ligand basicity: quantum chemical calculations on lanthanum precursors*	Surf. Coat Techn.	[38]
Univ. Liv., SAFC-Hitech & Tyndall	*Deposition of zirconium dioxide and hafnium dioxide thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors*	J. Mater. Chem.	[45]

3.4 Deposition mechanism

Mechanisms of the ALD processes were studied with the unique QCM-QMS-ALD tool at University of Helsinki. Several metal precursors in combination with water and ozone were explored. The most conclusive results on the ALD mechanism were achieved on the $(CpMe)_2Zr(OMe)Me$ based processes, while the rare earth processes were more complicated because of various side reactions such as decomposition..

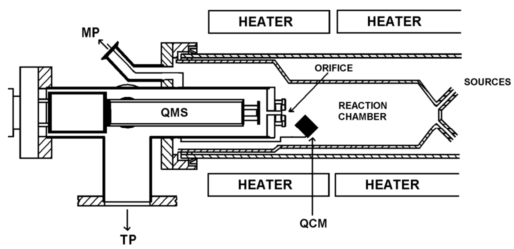


Figure 9: Schematics of the ALD-QCM-QMS setup. QCM monitors weight changes of the growing film while QMS samples the gas phase via an orifice.

3.4.1 Activity

Task		Partners involved
Task 2.1	Deposition in experimental ALD reactor	MDM
Task 2.2	Atomic-scale modelling of film growth	Tyndall
Task 2.3	In situ characterisation	UHel, MDM

3.4.2 Deliverables

Del. no.	Deliverable name	
D2	Optimised process for deposition of thin La_2O_3 films onto Si wafers using novel precursors	[2]
D11	Optimised process for deposition of thin Ln_2O_3 or Ln ternary films onto Si wafers	[11]

3.4.3 Description of result

Mechanisms of the ALD processes were studied with the unique experimental setup at University of Helsinki. This tool integrates a quadrupole mass spectrometer (QMS) and quartz crystal microbalance (QCM) to a flow-type ALD reactor with inert gas valved sources (Figure 9). Based on prior experience this setup is known to provide a great deal of mechanistic details about well-behaving ALD processes. On the other hand, in case of deviations from ideal ALD, the interpretation of the data becomes complicated.

In REALISE the following metal precursors were explored with both H_2O and O_3: $(Cp^iPr)_3La$, $La(thd)_3$, $(Cp^iPr)_3Er$, $(CpMe)_3Er$, $Er(thd)_3$, and $(CpMe)_2Zr(OMe)Me$ (ZrD-04). Unfortunately it turned out that only the $(CpMe)_2Zr(OMe)Me$ processes (both H_2O and O_3) truly behaved well and were thereby reasonably straightforward to study with the QCM-QMS setup.

Because there are three kinds of ligands in $(CpMe)_2Zr(OMe)Me$, the compound offers an interesting unique possibility to compare the reactivities of these ligands towards surface –OH groups upon adsorption. The reactivity order was found to be –Me > –CpMe > –OMe, in agreement with *ab initio* modelling of ligand reactivity at Tyndall (section 3.3) [36]. The $(CpMe)_2Zr(OMe)Me$ – O_3 process is the first ozone based process studied in detail with the QCM-QMS combination. As expected, assuming full combustion of the hydrocarbon ligands by ozone, the main byproducts were CO_2 and H_2O. Most interestingly, about 20% of both of these were released already during the $(CpMe)_2Zr(OMe)Me$ pulse and the rest during the O_3 pulse. To explain this observation, some active oxygen was concluded to be left on the surface after the O_3 pulse [44]. This was the first time ever the presence of active oxygen was suggested to play a role in the ozone based oxide ALD processes, although its chemical identity still remains to be determined. In later studies outside REALISE, active oxygen has been found also in ozone based hafnium oxide ALD, but not in growth of oxides of aluminium, titanium and erbium.

Lanthanum oxide processes were found to be highly complicated. This is attributed to several factors: precursor self-decomposition, formation of lanthanum carbonate species when ozone reacts with hydrocarbon ligands and the tendency to form lanthanum hydroxide when exposed to water. No conclusions about the growth mechanisms could therefore be worked out.

Erbium oxides shared some of the problems of the lanthanum oxide processes but hydroxide and carbonate formation occurred to notably smaller extent. This distinction was confirmed in simulations of the surface reactions (section 3.3). According to QCM traces, decomposition of $(^iPrCp)_3Er$ was notable in the water based process but not in the ozone based process. The slightly different precursor $(MeCp)_3Er$ gave inconsistent results with H_2O. In the $(MeCp)_3Er$ + O_3 process it seems that upon its adsorption $(MeCp)_3Er$ loses on average half of its ligands in reactions with surface hydroxyls to yield HCpMe, while the other half is combusted by ozone to CO_2 and H_2O.

3.4.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
UHel	*In Situ Reaction Mechanism Studies on Atomic Layer Deposition of ZrO_2 from $(CpMe)_2Zr(OMe)Me$ and Water or Ozone*	Chem. Mater.	[65]

3.5 High-k deposition & characterisation

ALD of La-based and Er-based high-k oxides on Si(100) and on Ge(100) was developed and investigated. Oxide properties and oxide/semiconductor interface details were thoroughly characterized. The effect of rare earth doping on the ZrO_2 and HfO_2 structural and dielectric properties was evaluated on Si and also on high mobility channel substrates for advanced memory and logic applications.

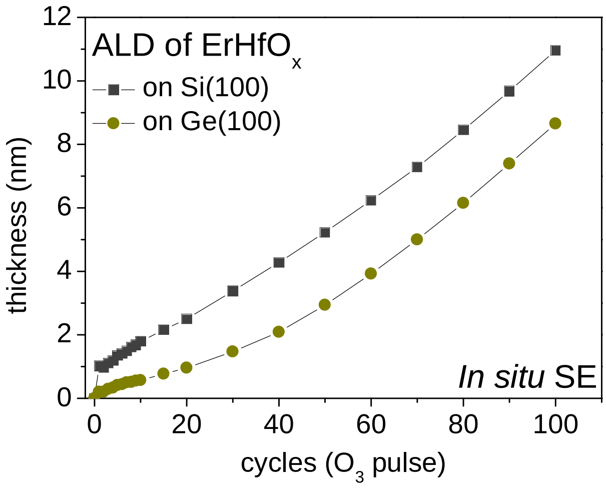


Figure 10: *In situ* SE monitoring of film thickness evolution during ALD of $ErHfO_x$ on Si(100) and on Ge(100).

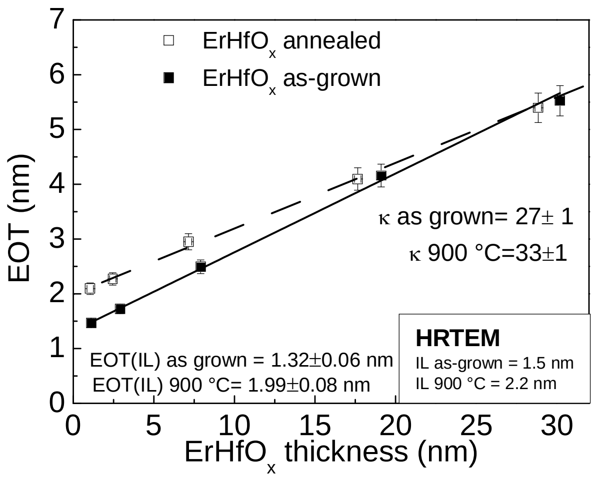


Figure 11: EOT vs high-*k* thickness for as-grown and annealed $ErHfO_x$ films grown by ALD on Si(100).

3.5.1 Activity

Task		**Partners involved**
Task 1.3	MOCVD growth testing and film characterisation	UnivLiv
Task 1.4	ALD growth and film characterisation	UnivLiv, MDM
Task 2.1	Deposition in experimental ALD reactor	MDM
Task 2.3	In situ characterisation	UHel, MDM
Task 2.5	Ex situ characterisation	MDM, CEMES
Task 2.6	Ternary oxides	ASMM, MDM
Task 3.1	Substrate preparation and ALD growth	ASMM
Task 3.2	Structural characterisation	MDM, CEMES
Task 3.3	Chemical characterisation	MDM, CEMES
Task 3.4	Electrical characterisation	MDM, CEMES, Tyndall

3.5.2 Deliverables

Del. no.	Deliverable name	
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
D2	Optimised process for deposition of thin La_2O_3 films onto Si wafers using novel precursors	[5]
D3a	Physical properties of Si/La_2O_3 interface	[6]
D3b	Electrical properties of Si / La ternary interface	[7]
D4	Assessment of electrical properties of La ternary NVM test structure	[11]
D5+D9	Optimised process for deposition of thin rare earth oxide films onto Ge wafers	[12]
D11	Optimised process for deposition of thin Ln_2O_3 or Ln ternary films onto Si wafers	[20]
D12	Structural and electrical properties of interface between Si and Ln_2O_3 or Ln ternary.	[22]
D13	Deposition of ternary oxide $LaMO_x$	[23]

3.5.3 Description of result

ALD of La and Er-based binary and ternary oxides was successfully developed on Si(100) wafers [5, 20] using novel precursors combinations [2, 18] and in accordance with project objectives. Spectroscopic ellipsometry *in situ* characterization gave insights on the early stages of ALD between different oxides and semiconductors [7, 22].

La_2O_3 was initially identified as a promising high-*k* oxide (*k*~27 [39]) although for this material major technological issues related to its hygroscopicity were determined [48], as reported elsewhere (sections 3.1.3 and 3.4.3). The family of La-Zr based oxides has then been considered with the aim to achieve high permittivity values together with an acceptable stability in air and in contact with Si. Morphological, structural and chemical properties of the stacks were thoroughly investigated at MDM combining experimental results on interface properties obtained at CEMES [6, 7, 46]. The electrical analysis of MOS structures evidenced the obtainment of high *k* (~30) value through the stabilization of tetragonal or cubic phase of ZrO_2 [11, 52].

As an alternative to La-Zr oxides, Er-Hf based compounds were developed and characterized together with CEMES as a function of the Er content. A correlation between the oxide stoichiometry and the material properties was proposed also considering the effects on the oxide/semiconductor interface details evidenced by TEM analysis (section 3.6). The best electrical performances, with *k* values even >30, were obtained for Er~15% and can be related to the stabilization of the cubic phase of HfO_2 [22].

Some selected materials such as La_2O_3, La-doped ZrO_2 and Er-doped HfO_2 were also grown and analyzed on Ge(100) for specific applications requiring stacks with high-*k* on high-mobility channels. Structural and electrical peculiarities, specifically related to the direct contact with Ge, were evidenced (section 3.6) [12, 61].

Those novel ALD processes and the related material characterization were communicated to the scientific community through peer-reviewed publications and presentations at international conferences affording a significant dissemination of new knowledge on the topic. The dielectrics were proposed to the academic and industrial research communities as novel promising candidates for both Si- and Ge-based advanced technology, while at the same time providing a deep understanding of the interface properties of these stacks. Reaching the objectives of the REALISE project in the framework of high-*k* deposition and characterization was peerless when compared to the state of the art, where the main rare-earth based ternary oxides are obtained by other, less conformal, deposition techniques.

Pursuing the integration of ALD processes for the deposition of rare earth-based dielectrics at an industrial level will provide the possibility of achieving advanced micro- and nano-electronic devices with improved performances on a very large scale. In parallel, the scientific research on the ALD of rare earth doped oxides and on the doping effects will certainly be pursued further in order to achieve a complete comprehension of the physical and chemical phenomena involved.

3.5.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
MDM	*Vibrational and electrical properties of hexagonal La_2O_3 films*	Appl. Phys. Lett.	[39]
CEMES & MDM	*Chemical/ Structural Nano-characterization And Electrical Properties of ALD-grown La_2O_3/Si Interfaces For Advanced Gate Stacks*	J. Electrochem. Soc.	[46]
CEMES & MDM	*ALD-grown Rare Earth Oxides for Advanced Gate Stacks*	Electrochem. Soc. Trans.	[47]
MDM & CEMES	*Infrared spectroscopy and X-ray diffraction studies on the crystallographic evolution of La_2O_3 films upon annealing*	Microelectr. Eng.	[48]
MDM & CEMES	*Atomic layer deposition of $La_xZr_{1-x}O_{2-\delta}$ (x=0.25) high-κ dielectrics for advanced gate stacks*	Appl. Phys. Lett.	[52]
Numonyx & MDM	*Rare earth-based high-k materials for non-volatile memory applications*	Microelectr. Eng.	[55]
MDM & CEMES	*Thermally-induced permittivity enhancement in La-doped ZrO_2 grown by ALD on Ge(100)*	Appl. Phys. Lett.	[61]
MDM	*Ab initio study of structural, vibrational and dielectric properties of high-k HfO_2 as a function of doping*	Mat. Sci. Eng.	[56]
MDM & CEMES	*Dielectric properties of Er-doped HfO_2 (Er ~15%) grown by atomic layer deposition for high-k gate stacks*	Appl. Phys. Lett.	[62]

3.6 *Interface characterisation*

The topographic, structural and chemical description of the interfaces between rare earth oxide based high-*k* dielectrics and semiconductor substrates was performed using transmission electron microscopy (TEM). The high-*k* dielectrics were binary (La-based) and ternary oxides ((La, Zr)-based and (Er, Hf)-based) deposited as thin films by ALD on Si(100) and on Ge(100). TEM yielded a complete description at the nanometric and atomic scale of the different layers in the stack and at the interface with the semiconductor substrate (Figure 12). Beyond this, the correlation of the corresponding results with electrical measurements was systematically considered in order to afford a more detailed investigation of the layers in terms of dielectric constants.

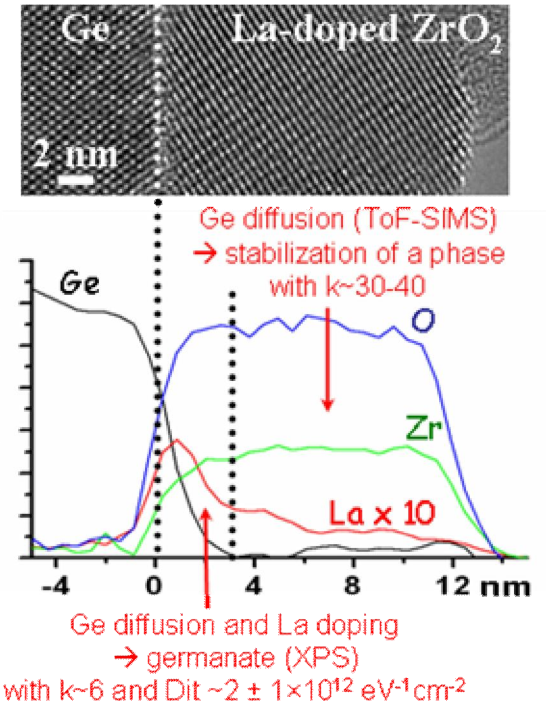


Figure 12: Atomic structure imaged with HRTEM (top) and associated elemental profiles determined by STEM-EELS (bottom) for a Ge/La-doped ZrO_2 high-k film with no amorphous interfacial layer (IL) like for Si substrate but a chemical IL (germanate).

3.6.1 Activity

Task		**Partners involved**
Task 2.5	Ex situ characterisation	MDM, CEMES
Task 2.6	Ternary oxides	ASMM, MDM
Task 3.2	Structural characterisation	MDM, CEMES
Task 3.3	Chemical characterisation	MDM, CEMES
Task 3.4	Electrical characterisation	MDM, CEMES, Tyndall

3.6.2 Deliverables

Del. no.	**Deliverable name**	
D3a	Physical properties of Si/La_2O_3 interface	[6]
D3b	Electrical properties of Si / La ternary interface	[7]
D5+D9	Optimised process for deposition of thin rare earth oxide films onto Ge wafers & Structural and electrical properties of rare earth oxide / Ge interface	[12]
D12	Structural and electrical properties of interface between Si and Ln_2O_3 or Ln ternary.	[22]

3.6.3 Description of result

High-resolution structural and chemical characterisation of film and interface to semiconductor has been systematically and successfully investigated at CEMES on representative stacks of rare earth based oxides deposited on Si(100) and on Ge(100). In combination with the electrical investigations and analyses performed at MDM, the complete dielectric description of the different layers present in the stack, defined either structurally and/or chemically, was determined therefore giving an insight of the quality of the stack to be integrated in innovative devices [6, 7, 12, 22].

Regardless of the choice of rare earth oxide (La-based, (La, Zr)-based and (Er, Hf)-based), the configuration of the IL is clearly differentiated by changing the nature of the substrate, being either Si(100) or Ge(100) (compare [6, 7] and [12] and also in [22]. Moreover, the different structural and chemical parameters of the interfaces and layers in the stacks are also dependent on the specific high-*k*. A detailed analysis of these parameters has been performed and, in particular, the chemical composition has been correlated to the *k* values of the different layers (section 3.5). A clear improvement in the quality of the stack has been observed going from binary A clear improvement in the quality of the stack has been observed going from binary systems (La-based) to ternary ones ((La, Zr)-based and (Er, Hf)-based) where the rare earth contribution is diluted in transition metal oxides that are more stable than La_2O_3 [6, 52]. Nanocharacterization performed on such films deposited on Ge(100) provided novel information on the quality of high-κ / high-mobility substrates interfaces [12, 22, 56].

The systematic correlation in the same experiment at CEMES of the atomic structure (HRTEM) to the elemental composition (STEM-EELS) across interfaces of series of stacks has proved to be a relevant way of investigation for a thorough qualification of rare earth oxide / semiconductor stacks. Moreover, a fruitful added value has been reached by the cross-correlation of the results of these investigations with results of other methods of characterisation, particularly electrical investigations, as performed at MDM. Such an approach is helpful for manufacturers and new to the scientific community. Several publications in regular journals and communications in international conferences have already been proposed to the community [46, 47, 48, 52].

TEM-based structural and analytical methods are today a necessary path to investigate future electronic devices with complicated morphologies including multilayers distributed at the nanometer and even subnanometer scale with materials of complex chemistry. An added value associated to TEM is the possibility to image the micrometric area of interest with an atomic resolution. Moreover, TEM is becoming more and more quantitative due to the recent development of new microscopes equipped with efficient computers.

3.6.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
CEMES & MDM	*Chemical/ Structural Nano-characterization And Electrical Properties of ALD-grown La_2O_3/Si Interfaces For Advanced Gate Stacks*	J. Electrochem. Soc.	[46]
CEMES & MDM	*ALD-grown Rare Earth Oxides for Advanced Gate Stacks*	Electrochem. Soc. Trans.	[47]
MDM & CEMES	*Infrared spectroscopy and X-ray diffraction studies on the crystallographic evolution of La_2O_3 films upon annealing*	Microelectr. Eng.	[48]
MDM & CEMES	*Atomic layer deposition of $La_xZr_{1-x}O_{2-\delta}$ (x=0.25) high-κ dielectrics for advanced gate stacks*	Appl. Phys. Lett.	[52]
MDM & CEMES	*Thermally-induced permittivity enhancement in La-doped ZrO_2 grown by ALD on Ge(100)*	Appl. Phys. Lett.	[61]
MDM & CEMES	*Dielectric properties of Er-doped HfO_2 (Er ~15%) grown by atomic layer deposition for high-k gate stacks*	Appl. Phys. Lett.	[62]

3.7 Process scale-up

At ASMM two lanthanum precursors $La(thd)_3$ and $(^iPrCp)_3La$ and two erbium precursors $Er(thd)_3$ and $(^iPrCp)_3Er$ were tested and scaled-up in F-450 ALCVD™ reactor on 200 mm wafer size as precursors for binary La_2O_3 and Er_2O_3 oxides. The preliminary test in F-450 reactor showed better thermal stability for $La(thd)_3$ and $Er(thd)_3$ than for $(^iPrCp)_3La$ and $(^iPrCp)_3Er$. Thus, β-diketonate precursors were tested as lanthanum and erbium precursors in Pulsar 2000® ALCVD™ reactor for ternary oxides, $LaZrO_x$ and $ErHfO_x$. It was demonstrated that both binary and ternary rare-earth oxide processes were suitable in semiconductor fabrication.

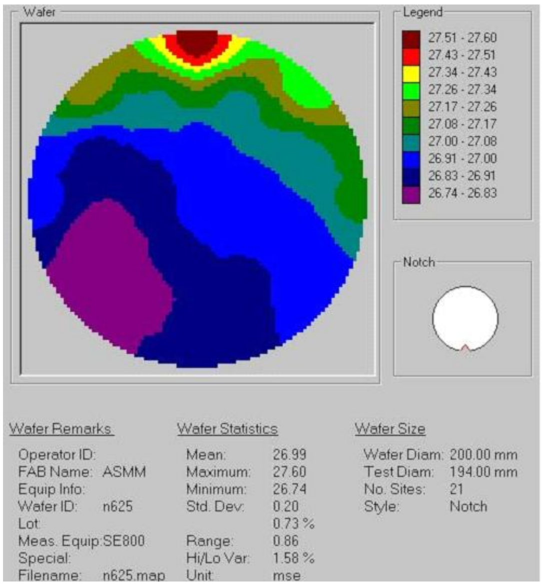


Figure 13: Wafer map of La_2O_3 film deposited on 200mm wafers in F-450 ALCVD™reactor using $La(^iPrCp)_3$ and ozone as precursors at reaction temperature 200°C.

3.7.1 Activity

Task		Partners involved
Task 2.4	ALD process scale-up of binary rare-earth oxide materials	ASMM
Task 2.6	ALD process scale-up of ternary rare-earth oxide materials	ASMM

3.7.2 Deliverables

Del. no.	Deliverable name	
D1	Precursor selection for La_2O_3 atomic layer deposition	[2]
D2	Optimised process for deposition of thin La_2O_3 films onto Si wafers using novel precursors	[5]
D11	Optimised process for deposition of thin Ln_2O_3 or Ln ternary films onto Si wafers	[20]
D13	Deposition of ternary oxide $LaMO_x$	[23]

3.7.3 Description of result

ALD processes for La_2O_3, $LaZrO_x$, Er_2O_3 and $ErHfO_x$ were investigated. All processes were successfully scaled-up on 200mm wafers. La, Zr, Er and Hf precursors showed good thermal stability and reasonably good volatility. ALD processes were repeatable and the film quality of binary and ternary rare earth oxide films was good; impurity content and particle count were low. ALD films were uniform, having a non-uniformity <5%, (1 σ). The reaction temperature affects the film uniformity. The optimum deposition temperature for ternary oxide was a compromise of the optimum deposition temperature for binary oxides, but the composition of the ternary rare earth oxide film was controllable and the properties of the films could easily be tailored by varying the pulse ratios in ALD growth.

It was shown that as little as ~5% of Er in $ErHfO_x$ films stabilizes the phase with the highest *k* value of HfO_2, which makes this material very interesting.

In this REALISE project La and Er based materials were tested for DRAM (section 3.8), RF decoupling (section 3.10) and NVM capacitor technology (section 3.9). Additionally, outside this project, these materials were tested for high-*k* gate stacks and for analog capacitors. Among its customers, ASM is continuously exploring for new possible applications for these new ALD processes.

In this project the target was to scale-up the processes on 200mm wafer size. Simultaneously La_2O_3 [$La(thd)_3 + O_3$ and $(^iPrCp)_3La + O_3$] processes were scaled-up to 300mm wafer size in a high volume manufacturing (HVM) Pulsar® 3000 reactor.

In this project two different rare-earth metals (La and Er) were studied. Based on this ALD process knowledge, processes for other metals that are generally considered rare earths could easily be implemented in a similar way ($HfYO_x$ and $HfScO_x$).

3.7.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
Tyndall, Qimonda, ASMM	*TiN/ZrO$_2$/Ti/Al Metal-Insulator-Metal Capacitors with sub-nm CET using ALD-deposited ZrO$_2$ for DRAM applications*	IEEE Electron Device Letters	[53]

3.8 DRAM technology

As test structures for DRAM, ZrO_2 MIM capacitors were fabricated and characterised structurally and electrically. The best capacitance equivalent thickness (CET) obtained for low leakage devices (J~1×10^{-9} A/cm^2 at V_g=1 V) was ~0.9 nm for a ZrO_2 physical thickness of ~7.5 nm. A *k*-value of ~31 was estimated. This was obtained for samples with a rapid thermal post-deposition (RTP) anneal in N_2 for 60s at 400°C (see Figure 14). Similar test structures using $LaZrO_x$ and $ErHfO_x$ were also fabricated and characterised. Little benefit in CET was obtained for higher leakage at the same physical thickness. Hence, the updated objective of CET<0.7 nm with $J<1\times10^{-8}$ A/cm^2 could not be achieved with these materials.

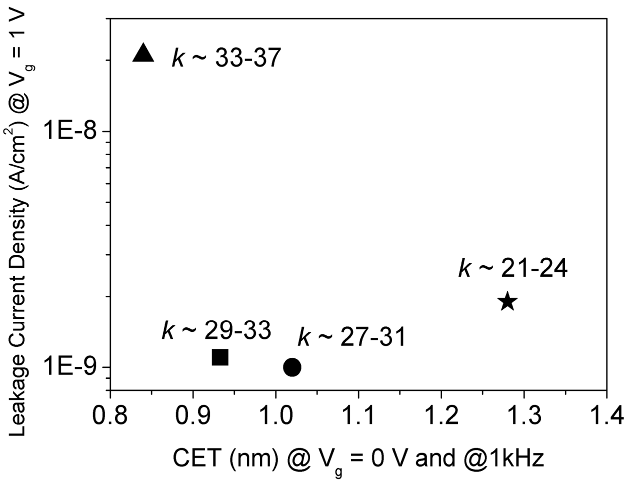


Figure 14: CET values extracted from 1 kHz C-V responses at V_g=0 V, plotted against leakage current densities at V_g=1 V. The calculated dielectric constants are also shown (star=as-deposited, square=400°C RTP, circle=500°C RTP, triangle=600°C RTP). The physical thickness of ZrO_2 is 7-8 nm in all cases.

3.8.1 Activity

Task		Partners involved
Task 3.4	Electrical characterisation	MDM, CEMES, Tyndall
Task 4.1	Patterning of Si test structure for DRAM capacitor	Qimonda
Task 4.2	ALD of Ln_2O_3 onto test structure for DRAM capacitor	ASMM
Task 4.3	Electrical testing and physical characterisation of DRAM capacitor test structure	Qimonda, Tyndall

3.8.2 Deliverables

Del. no.	Deliverable name	
D6	Assessment of electrical and physical properties of La ternary DRAM capacitor test structure	[13]
D16	Assessment of electrical and physical properties of Ln-based DRAM capacitor test structure	[26]

3.8.3 Description of result

This result is the product of collaboration between Qimonda, ASMM and Tyndall. 200 mm wafers of doped silicon substrates were prepared at Qimonda, where a bottom metal of TiN was deposited. These wafers were then sent to ASMM for the deposition of ZrO_2 or rare earth based high-*k* layers by ALD. Subsequently, the wafers were sent to Tyndall for annealing. The samples received top metal patterning and deposition by E-beam lithography at Tyndall or Qimonda. They were then electrically characterised at Tyndall and/or Qimonda, and physically characterised using XRD and TEM-EDX techniques at Qimonda.

The highlight was the development of MIM capacitors comprising doped-Si/TiN/ZrO_2/Ti/Al, the oxide formed by ALD with the new ZrD-04 precursor, which were investigated for the first time in this work [13, 53]. The best result post-RTP is a CET of ~0.9 nm with leakage of $\sim 1\times10^{-9}$ A/cm^2 (Figure 14, Figure 15). Conduction mechanisms were also investigated, and while leakage increases with temperature, the Schottky emission mechanism at V_g=1 V remains the same (Figure 15). As the leakage current density values obtained at 1 V are superior to the target of $<1\times10^{-8}$ A/cm^2, there remains scope for further slight reductions in CET with ZrO_2 MIM structures formed by ALD with the new ZrD-04 precursor.

Similar MIM structures were also developed using $LaZrO_x$ or $ErHfO_x$ layers [26]. Variations in process conditions and ternary concentrations gave no significant improvement in leakage or CET.

The structural and electrical properties of La-doped ZrO_2 films were assessed in planar capacitor DRAM test structures. The main results are [13]:

- Doping of ZrO_2 with only approx. 1% of La increases the crystallization temperature of ZrO_2 to values of approx. 400°C, thus, suppressing crystallization during growth and potentially reducing leakage.
- Both La-doped and non-doped ZrO_2 films crystallize in the tetragonal/cubic phase, which might present a high *k* value of approx. 40.

- MIM $LaZrO_x$ films annealed at temperatures of 400°C and 500°C with a La concentration of approx. 1% show best CET values of ~0.75 nm at 1×10^{-7} A/cm² and CET~0.9 nm at 1×10^{-8} A/cm², respectively. These results do not meet the updated targets of a CET<0.7 nm and $J<1\times10^{-8}$ A/cm². Further annealing to 600°C strongly increases the leakage current density.

In terms of CET vs. *J* data, La-doped ZrO_2 dielectric films show similar properties to Al-doped ZrO_2, which is already used in DRAM products. As no significant advantage has been observed, it seems unlikely that La-doped ZrO_2 will substitute the Al-doped ZrO_2 dielectrics in DRAM capacitors.

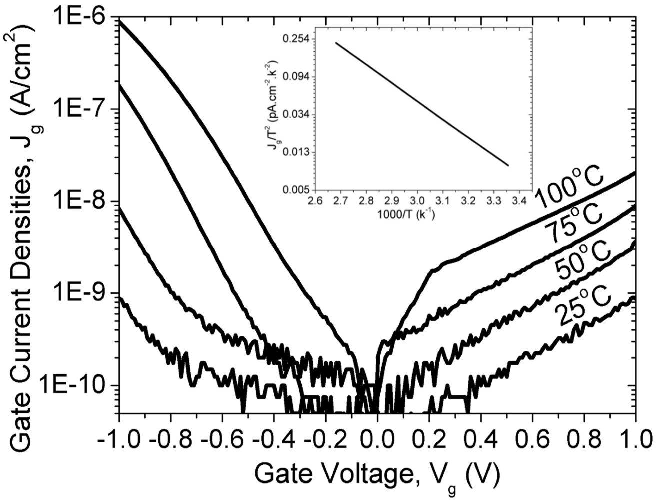


Figure 15: Gate leakage current (*J-V*) plots for 40,000 µm² area devices with an RTP of 400ºC. Inset: Schottky Emission's linear relationship of J/T^2 versus 10^3/T (V_g=1 V), with an activation energy of ~0.4 eV and a TiN/ZrO_2 barrier height of ~1.4 eV.

The structural and electrical properties of Er-doped HfO_2 films were assessed in planar capacitor DRAM test structures [26]. The major goal of this work was to determine the CET-leakage properties of atomic layer deposited $ErHfO_x$ films. The main results are as follows:

- Doping of HfO_2 with a few percent of Er stabilizes the high-*k* cubic/tetragonal phase in as-deposited $ErHfO_x$ films. This phase remains stable upon annealing up to 770°C (highest temperature used).
- *k*-values of ~37 are demonstrated for 500°C annealed $ErHfO_x$ films in the cubic/tetragonal phase containing approx. 5% of Er.
- MIM $ErHfO_x$ films annealed at 500°C with an Er concentration of approx. 5% show best CET values of ~0.85 nm at ~3×10^{-7} A/cm² leakage current density. These results do not meet the updated targets of a CET<0.7 nm and $J<1\times10^{-8}$ A/cm².

Further improvement of $ErHfO_x$ films can probably be achieved by additional optimization of deposition and anneal conditions, however, CET values at or below ~0.7 nm for HfO_2-based systems are not expected. Therefore, as current high-*k* dielectric development for DRAM capacitors needs to focus on materials with a target CET of ~0.5 nm and below, it seems unlikely that $ErHfO_x$ dielectrics will be used in future DRAM nodes.

3.8.4 Peer-reviewed papers published

Partner(s)	Title	Journal	
Tyndall, Qimonda, ASMM	*TiN/ZrO_2/Ti/Al Metal-Insulator-Metal Capacitors with sub-nm CET using ALD-deposited ZrO_2 for DRAM applications*	IEEE Electron Device Letters	[53]

3.9 NVM technology

In the frame of REALISE project, rare earths based oxides have been processed in the Numonyx pilot line in order to test their electrical properties as possible dielectrics in Non Volatile Memories (NVM). In particular, La_2O_3, $LaZrO_x$ and $ErHfO_x$ films have been integrated. These materials have been tested in capacitor structures obtained from the definition of an *ad hoc* short loop process (Figure 16).

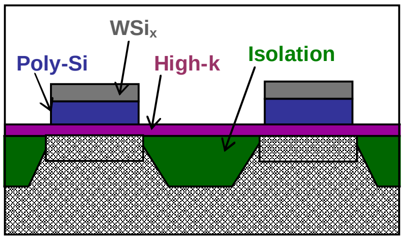


Figure 16: three mask capacitor cross section.

3.9.1 Activity

Task		Partners involved
Task 3.6	Patterning of Si test structure for NVM	Numonyx
Task 3.7	ALD of Ln_2O_3 onto test structure for NVM	ASMM, MDM
Task 3.8	Electrical testing of NVM test structure	Numonyx, MDM

3.9.2 Deliverables

Del. no.	Deliverable name	
D4	Assessment of electrical properties of La ternary in NVM test structure	[11]
D15	Assessment of electrical properties of ErHfOx in NVM test structures	[25]
EHSA	Environmental, Health and Safety Assessment	[19]

3.9.3 Description of result

In accordance with the project objective, rare earth based oxides have been integrated and subsequently electrically tested in capacitor structures designed *ad hoc* in order to screen the materials with respect of integrability (*i.e.* compatibility with thermal treatments and wet/dry chemistries, interaction with the adjacent materials) and electrical properties (leakage current at high/low field, *k* value, voltage breakdown). Further more, the material requirements are: EOT around 10-12 nm and a leakage current at 3-4 V lower than $J\sim10^{-15}$ A/cm^2.

All of the rare earth based materials have been deposited in MDM labs ([5], [20]) on Numonyx 200 mm wafers. In particular, integration of La_2O_3, $LaZrO_x$, $ErHfO_x$ has been tried. To be processed in the front end of line, all the wafers on which non conventional high-*k* materials are deposited must be metal free on the wafer backside and capped with a non-contaminant film on the wafer front side.

Alumina (the standard dielectric employed as blocking oxide in NVM R&D line) has been chosen as the capping layer.

First trials with La_2O_3 presented some marginalities from the integration point of view due to incompatibility of the stack composed by La_2O_3/Al_2O_3 with wet chemistries, furthermore the two layers undergo large intermixing, giving a sort of alloy.

Integration of $LaZrO_x$ films has been possible: this material is compatible with the wet chemistries, the thermal budget and the alumina cap layer in terms of intermixing [11]. The integrated films show electrical characteristics in terms of permittivity [11, 55] which are in good agreement with those measured for the film not inserted in the stack [52]. Actually, the only high-*k* material which is considered to be a feasible substitute of the Oxide-Nitride-Oxide employed as inter-poly dielectric in NVM is crystalline alumina [66]. Comparing the $LaZrO_x$ film with the standard alumina film in terms of leakage current and breakdown voltage, very interesting results emerge. This material presents a large breakdown *V* comparable to alumina ones. The leakage current must be considered at low voltages and at high voltages: at low *V* the alumina leakage current is lower than that measured for $LaZrO_x$ film, while at large *V* an inversion in the slope brings the $LaZrO_x$ leakage current to be lower than alumina leakage current. Looking at these results in terms of retention and program/erase of the cell, this means that alumina films behave better in retention while $LaZrO_x$ should increase the program/erase window [55].

Therefore, this $LaZrO_x$ material looks very interesting as a possible inter-poly dielectric in NVM, even if it does not fulfil completely the targets of leakage currents at low field. Further efforts should be invested in order to complete the integration of this material in a standard NVM (and not only in a capacitor structure) without any cap layer.

Finally, integration of $ErHfO_x$ has been performed [25]. The permittivity measurements have been carried out showing an unexpectedly low *k* value. This decrease in dielectric constant could be attributed to the mixing between $ErHfO_x$ and both the Si substrate and the Al_2O_3 cap.

3.9.4 Peer-reviewed papers published

Partner(s)	**Title**	**Journal**	
Numonyx & MDM	*Rare earth-based high-k materials for non-volatile memory applications*	Microelectr. Eng.	[55]

3.10 RF decoupling capacitor technology

The dielectric properties of rare earth oxides have successfully been evaluated for RF decoupling applications. The use of ALD for nanometre-controlled deposition of lanthanide-doped ZrO_2 and HfO_2 high-*k* films in high aspect-ratio trenches has been demonstrated and shows clear advantages from material properties and processing point of view.

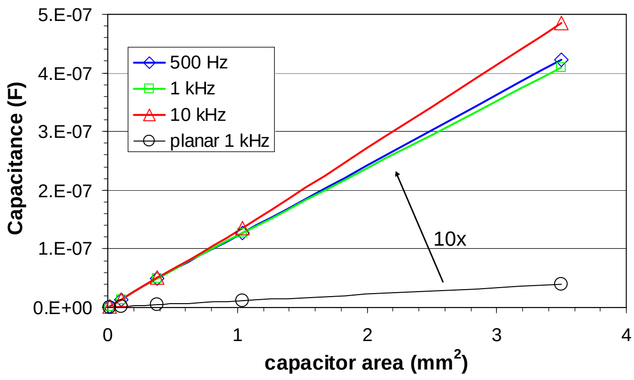


Figure 17: Capacitance as function of surface area of $LaZrO_x$ 3D MIM capacitor with La:Zr pulse ratio = 1:4 for various measurement frequencies. A capacitance density of 120 nF/mm^2 is achieved due to the 3D surface area enlargement.

3.10.1 Activity

Task		Partners involved
Task 4.4	Patterning of porous Si test structure for decoupling capacitor (150mm)	NXP
Task 4.5	ALD of La_2O_3 & Ln_2O_3 onto test structure for decoupling capacitor	ASMM
Task 4.6	Electrical testing of decoupling capacitor test structure	NXP

3.10.2 Deliverables

Del. no.	Deliverable name	
D7	Assessment of electrical properties of La ternary decoupling capacitor test structure	[14]
D17	Assessment of electrical properties of Ln-based decoupling capacitor test structure	[27]

3.10.3 Description of result

2D and 3D capacitor structures have been successfully manufactured by NXP and ASMM using MIS, MIM and MIMIS capacitor architectures and employing ALD $LaZrO_x$ and ALD $ErHfO_x$ as high-k dielectric and ALD TiN as metal electrodes. In the early stage of the REALISE project, planar and 3D MIS capacitors consisting of Si/$LaZrO_x$/metal (Al or TiN electrodes) were constructed with different La:Zr ratios. In the later phase, MIS and MIM $ErHfO_x$ capacitors were manufactured and compared against the $LaZrO_x$ based devices. A novel patterning scheme was developed using dry etching and wet cleaning techniques for MIS, MIM and MIMIS capacitors employing $LaZrO_x$ high-k films.

The ternary lanthanide compounds show clean C-V characteristics with consistently higher dielectric constants than the binary compounds. This has resulted in the fabrication of devices with capacitance densities of 120 nF/mm^2 and above. Leakage current and breakdown characteristics of the mixed oxide films also show improved performance compared to the binary compounds.

The successful deposition of high-k dielectric films and TiN metal electrodes in 3D pores has resulted in electrically measurable devices with state of the art dielectric properties. The relevant materials characteristics are summarised here:

- Doping of HfO_2 with a few percent of erbium stabilizes the high-*k* cubic phase in as-deposited $ErHfO_x$ films. The *k*-value improves significantly with increasing Hf or Zr concentration (Figure 18). An identical trend is observed for the MIS and MIM capacitors. The enhancement in dielectric constant is explained as a result of the formation of a cubic HfO_2 phase stabilized by the presence of erbium and the tetragonal ZrO_2 phase by the presence of lanthanum.

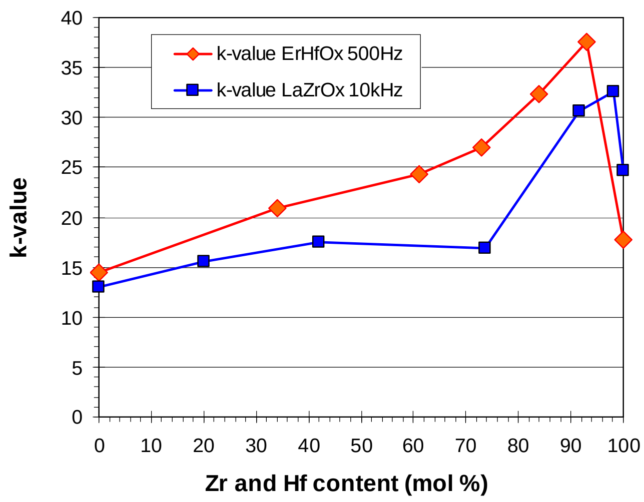


Figure 18: *k*-value comparison for $ErHfO_x$ and $LaZrO_x$ dielectrics in MIS capacitors in as-deposited films. The highest dielectric constant of *k*=38 is demonstrated for films deposited with an Er/Hf pulse ratio of 1:4 containing approximately 13 mol% of erbium. The $LaZrO_x$ film with a La:Zr pulse ratio of 1:9 has a *k*-value of 33.

- Films with high La or Er doping exhibit the highest breakdown fields (*i.e.* up 7-8 MV/cm). E_{BD} decreases with increasing Zr or Hf content, which is in line with the increase of the dielectric permittivity (Figure 19a). The figure of merit, *i.e.* a measure to derive the optimum between *k*-value and electrical breakdown field, shows that still an optimum in capacitance density can be obtained for the Zr and Hf-rich films with highest permittivity without sacrificing the electrical breakdown.

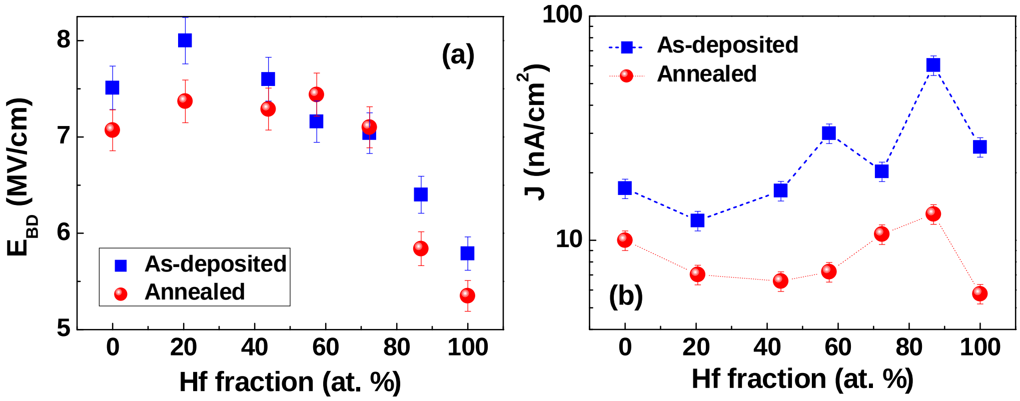
- Leakage current densities for the $ErHfO_x$ and $LaZrO_x$ films are below 1×10^{-7} A/cm² after FGA anneal at an electrical field of 1 MV/cm (Figure 19b).

- Step coverage of the ALD $ErHfO_x$ films is 75-80 % in 25 µm deep, 12:1 aspect ratio pores. These values are comparable to the ALD $LaZrO_x$ films and were obtained with standard processing conditions.

- The highest capacitance density of 120 nF/mm^2 was obtained in a 3D MIM decoupling test structure using a 30 nm thick $LaZrO_x$ high-k film with a dielectric constant of 36.

- For the MIS capacitors a much better dielectric constant, breakdown voltage, and leakage current could be obtained for the $ErHfO_x$ films due to the much better stability against Si diffusion.

- Upon comparing the $ErHfO_x$ and $LaZrO_x$ MIM capacitors with each other, no clear advantage could be found to favour one material over the other. For both films a maximum in dielectric permittivity could be achieved of approximately *k*~35-40.



(a) **(b)**

Figure 19: (a) Electric breakdown field of $ErHfO_x$ MIS capacitor as function of composition; (b) leakage current of $ErHfO_x$ MIS capacitor.

3.10.4 Peer-reviewed papers published

Partner(s)	**Title**	**Journal**	
NXP	*Remote plasma and thermal ALD of Al_2O_3 for trench capacitor applications*	Electrochem. Soc. Trans.	[41]
NXP	*ALD options for Si-integrated ultrahigh-density decoupling capacitors in pore and trench designs*	Electrochem. Soc. Trans.	[42]
NXP	*Growth Characteristics and Physical Properties of Remote Plasma and Thermal ALD of Al_2O_3 in a commercial 200mm ALD reactor*	J. Electrochem. Soc.	[43]
NXP & ASMM	*Spontaneous nanoclustering of ZrO_2 in atomic layer deposited $La_yZr_{1-y}O_x$ thin films*	Appl. Phys. Lett.	[49]
NXP & ASMM	*Enhanced electrical properties of atomic layer deposited La_2O_3 with embedded ZrO_2 nanoclusters*	Appl. Phys. Lett.	[50]
NXP & ASMM	*Silicon out-diffusion and aluminium in-diffusion in devices with atomic-layer deposited La_2O_3 thin films*	Appl. Phys. Lett.	[51]
NXP & ASMM	*Charge conduction mechanisms of atomic-layer-deposited Er_2O_3 thin films*	Appl. Phys. Lett.	[58]
NXP	*Maxwell-Wagner instability in bilayer dielectric stacks*	Appl. Phys. Lett.	[59]

3.10.5 Patents

In total 6 patents were filed by NXP.

Assignee	**Title**	**Inventors**	**Patent number**	**Date filed**
NXP	*Ultrahigh-density Capacitor*	L. Guiraud, F. Le Cornec, F. Roozeboom, J. Klootwijk, D. Chevrie	PH005852EP1	2 May 2006
NXP	*Miniaturized DC:DC converter*	D. Reefman, F. Roozeboom, J. Klootwijk	PH005924EP1	15 May 2006

NXP	*Ultrahigh-density Capacitors*	J. Klootwijk, F. Roozeboom, J. Ruigrok, D. Reefman	PH007319EP1	Apr 2007
NXP	*Ultrahigh density capacitors*	K. B. Jinesh, F. Roozeboom, W. Dekkers, J. Klootwijk	8157896.5	9 Jun 2008
NXP	*Integrated Ultrahigh-Density devices with functional layer stacks on robust high-aspect ratio topography*	F. Roozeboom, M. Goossens, W. Besling, N. Verhaegh	81355227EP01	30 Sep 2008
NXP	*nanocluster-embedded dielectrics*	K. B. Jinesh, W. F. A. Besling, R. Wolters, J. Klootwijk, F. Roozeboom	81355857EP01	28 Apr 2008

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16 REALISE Interim Activity Report IAR4, 29 Feb 2008, confidential internal document.

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