Thin films: processing & characterization
Application to functional complex oxides

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OUTLINE

• Introduction
  • Thin films
    • Why do we need to control the growth at nanometer scale?
• Thin films deposition methods
• Substrates: nature, preparation...
• Thin films characterizations
• Thin films of multiferroic compounds
Film (= layer)

Substrate

Thin films: \( t < 1 \mu m \)

For microelectronic applications: usually \( t < 100 \) nm

\( T \gg 1 \mu m \) : coating

Epitaxial film
La\(_x\)Sr\(_{1-x}\)MnO\(_3\) on SrTiO\(_3\) (001)

Amorphous
HfO\(_2\) on Si (001)

Polycrystalline film
SrTiO\(_3\) on Si (001)

The substrate can be non-planar (in such a case, conformal coverage is required)

Al\(_2\)O\(_3\) 300 nm on Si wafers with trench structures

TiN on patterned substrates

Application of films

- Protective coating (diffusion barrier, corrosion protection...)
  - Mechanical ...

Microelectronic applications

- Optics
  ...

Complex oxides (electron correlated systems):
  - High-T_c superconductors
  - Ferroelectrics
  - Magnetic, magnetoresistive
  - Multiferroics...

Integrated circuits: oxides with high permittivity

Complex oxides: large variety of physical properties

ABO_3

Dielectrics
  - LaAlO_3, SrTiO_3...

Ferroelectrics
  - BaTiO_3, PbTiO_3...

Pyroelectrics
  - LiNbO_3...

Ferromagnets
  - SrRuO_3, La_2/3Sr_1/3MnO_3...

Conductors
  - SrRuO_3, LaNiO_3...

Magnetoresistive
  - La_0.7Sr_0.3MnO_3...

Semiconductors
  - Nb-doped SrTiO_3...

Superconductors
  - YBa_2Cu_3O_7, (La,Sr)_2CuO_4...

Crystalline structures:
  - Perovskite or perovskite-related
  - Spinel
  - Pyrochlore
  - Rock salt
  - Fluorite
  - Layered structures e.g. Ruddlesen-Popper...

LaMnO_3 (AF/I)

La_0.7Sr_0.3MnO_3 (FW/M)
**Complex oxides: (strongly) correlated electron systems**

Coupling between spin, orbital, charge and lattice (static and dynamics effects)

\[ \text{\ldots} \rightarrow \text{Strong impact of an external excitation (H, E, \ldots) on these interactions} \]

Fundamental physics
- Understand coupling between order parameters
- Determine characteristic lengths of the system (including domains size)
- Understand size effects on the properties: when dimension(s) become(s) of the order of a characteristic length, physical properties change

Great potential for applications
- Memories (MRAM, Fe-RAM...)
- CMOS
- Sensors
- Actuators
- Catalysts

... 

**Thin films: properties engineering**

Thin films:
- Strain (lattice is strongly impacted by strain)
- Interface with substrate

Heterostructures: Multilayers, Nanostructured oxides
- Strain
- Interfaces between oxides
- Proximity effects

Materials (\ldots) engineering using the large number of possible spin, orbital, charge and lattice interactions (competing effects, cooperating effects...)

\[ \lambda \approx 10 \, \text{Å} \]

Need to control growth at unit-cell scale
Semiconductors:

Engineering of properties (charge carrier, band gap...) through doping, solid solution...

Oxides: Engineering of properties also possible!!


MOS field-effect transistor (MOS-FET):

\[ C_{\text{ox}} = \frac{\varepsilon_0}{t_{\text{ox}}} \]
SiO₂ ----> SiOₓNy -----> High K oxides (HfO₂, ...)

Equivalent Oxide Thickness (EOT)
EOT = 10 Å

Interfaces: Outmost importance
Need to control interfaces also!! Strong influence on overall properties of the stack
**Interfaces: Outmost importance**

*Equivalent Oxide Thickness (EOT)*

**EOT = 10 Å**

- **Gate**
  - HfO$_2$
  - 50 Å ($r = 20$)
  - Si

- **Gate**
  - HfO$_2$
  - 15 Å ($r = 20$)
  - SiO$_2$

**Lower interface:**

- **Chemical stability with Si**
- **Electrical compatibility**
  
  If HfO$_2$ directly on Si: severe degradation of mobility
  -> SiO$_2$ (~ 5 Å) necessary

  Interfacial defects have high impact on carrier mobility in channel

**High K oxide**

SiO$_2$ (Silicate ? Silicide ?)
High K oxide \[ \text{HfSiO}_y \text{ or HfO}_2 \]

Upper interface:
- Chemical stability with poly-Si or with metal?
  - \( \text{ZrO}_2 \) reacts with poly-Si
  - \( \text{HfO}_2 \) stable with poly-Si
- Electrical compatibility?
  - Poly-Si replaced by metal gate
  - Capping of metal in order to avoid oxygen diffusion
  - Tuning of metal work function with additives in high K or with additional layer on top of high K

Interfaces: Outmost importance

**Multilayers: succession of interfaces ---+ Properties may arise from the interfaces**

Herbert Kroemer, Nobel Price lecture 2000:

*About semiconductors heterostructures: "...the interface is the device"*
Oxides superlattices:

Field-effects


Substrate

Synthesis of thin films: main techniques

Physical Vapor Deposition (PVD): MBE, laser ablation, sputtering

Chemical Vapor Deposition (CVD), Atomic Layer Deposition (ALD)
Epitaxy: "Above" (epi) and "in an ordered manner" (taxis)

In solid-source MBE, ultra-pure elements (such as gallium and arsenic) are heated in separate quasi-
knudsen effusion cells until they begin to slowly evaporate. The evaporated elements then condense on
the wafer, where they may react with each other.
Example: Ga and As $\rightarrow$ gallium arsenide single-crystal

The term "beam" means that evaporated atoms do not interact with each other or any other vacuum
room gases until they reach the wafer, due to the long mean free paths of the beams.

Other variations include gas-source MBE, which resembles chemical vapor deposition.

MBE takes place in high vacuum or ultra high vacuum ($10^{-11}$ Torr) $\rightarrow$ slow deposition rate
$\rightarrow$ requires stringent control of impurities

Computer controlled shutters in front of each furnace allow a precise control of the thickness of each layer.

Intricate structures of layers of different materials may be fabricated this way. Such control has allowed
the development of structures where the electrons can be confined in space, giving quantum wells or even
quantum dots. Such layers are now a critical part of many modern semiconductor devices, including
semiconductor lasers and light-emitting diodes.
Molecular beam epitaxy: developed in the 1960's - need for making new crystalline materials for semi-conductors applications (concept of two layers with different semiconductors by H. Kroemer in the 50's).

Mostly at IBM (in Yorktown Heights, NY) and Bell Laboratories (in Murray Hill, NJ), 1968-1973

John R. Arthur Jr. and Alfred Y. Cho
A. Cho honoured with US National Medal of Technology (announced June 14th 2007 by Alcatel-Lucent)

Leo Esaki and Ray Tsu at IBM: concept known as superlattice ("a valuable area of investigation in the field of semiconductors")

"MBE deserves a place in the history books", by W. Patrick MCCRAY, Nature Nanotechnology May 2007, p.259

MBE played a central role in the growth and development of nanoscience and nanotechnology
RHEED monitoring during Molecular beam Epitaxy (MBE)

RHEED (Reflection High Energy Electron Diffraction) is often used for in situ monitoring the growth.

\[
\begin{align*}
\Theta &= 0 \\
\Theta &= 0.25 \\
\Theta &= 0.5 \\
\Theta &= 0.75 \\
\Theta &= 1 \\
\Theta &= 1.25 \\
\Theta &= 1.5 \\
\Theta &= 1.75 \\
\Theta &= 2
\end{align*}
\]
RHEED monitoring during Molecular beam Epitaxy (MBE)

Applications to oxides:

Need oxygen source for growing oxides: atomic oxygen usually used (differential pumping system)

Atomic sources (effusion cells) or ceramic which are evaporated using electron-beam guns

Quite widely used for high-K oxides research (G. Hollinger at INL-Lyon, J. Fompeyrine IBM Zürich, T. Schroeder IHP Germany, Osten Germany, G. Norga Italy, M. Fanciulli Italy, D. Schlom USA...)

Complex oxides films and heterostructures:

J.P. Locquet at IBM Zürich
D. Schlom USA
...

Molecular beam Epitaxy (MBE)
Pulsed laser deposition works by an ablation process (PVD technique). High power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired composition. Material is then vaporized from the target and deposited as a thin film on a substrate facing the target.

This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.
While the basic-setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex.

When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation... The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate.

A plume ejected from a SrRuO₃ target during pulsed laser deposition

1960: T.H. Maiman constructed the first optical maser using a rod of ruby as the lasing medium

1962: Breech and Cross used ruby laser to vaporize and excite atoms from a solid surface

1965: Smith and Turner used a ruby laser to deposit thin films
   → very beginning of PLD technique development

However, the deposited films were still inferior to those obtained by other techniques such as chemical vapor deposition and molecular beam epitaxy.

Early 1980’s: a few research groups (mainly in the former USSR) achieved remarkable results on manufacturing of thin film structures utilizing laser technology.

1987: Dijkkamp and Venkatesan prepared thin films of YBa₂Cu₃O₇ by PLD

In the 1990’s: development of new laser technology, such as lasers with high repetition rate and short pulse durations, made PLD a very competitive tool for the growth of thin films with complex stoichiometry.
Pulsed laser deposition

Applications to oxides:

Need oxygen source for growing oxides: not in ultrahigh vacuum
Ceramic target(s) needed - several targets can be used
Excimer laser ($\lambda = 248$ nm)
RHEED: need differential pumping system because of "elevated" background pressure due to oxygen

Widely used in laboratories (transfer of the target composition to the film composition, control of deposited thickness, more simple than MBE to set up)

Drawback: generate particles
Sputtering

PVD process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions.

Sputtered atoms ejected into the gas phase are not in their thermodynamic equilibrium state, and tend to deposit on all surfaces in the vacuum chamber.

A substrate (such as a wafer) placed in the chamber will be coated with a thin film.

Sputtering usually uses an argon plasma.
Standard physical sputtering is driven by momentum exchange between the ions and atoms in the material, due to collisions (Behrisch 1981, Sigmund 1987).

Analogy with atomic billiards: the ion (cue ball) strikes a large cluster of close-packed atoms (billiard balls).

Energy of impinging ions:
- $< 10$ eV: elastic backscattering of the ions
- $10 \text{ à } 1000$ eV: sputtering of the target
- $> 1000$ eV: ions implantation

The number of atoms ejected from the surface per incident particle is called the sputter yield and is an important measure of the efficiency of the sputtering process.

Sputter yield depends on:
- the energy of the incident ions ($>> 10$ eV), which depends on target gun's bias voltage
- Ar gas pressure
- the masses of the ions and of target atoms
- the binding energy of atoms in the solid

Various techniques are used to modify the plasma properties (especially its ion density) in order to optimize the sputtering conditions:

- Negative bias of the target
- RF sputtering: alternating current for biasing insulating target
- Magnetron: confinement of the plasma in the vicinity of the target

off-axis target: avoid sputtering of the film
Reactive sputtering: a reactive gas is added to the usual Ar sputtering plasma to shift compound-film stoichiometry in sputtering from a compound target or to deposit a compound from a metallic target.

1) Arise from a tendency for the electronegative elements to become depleted in compound sputtering. Although both elements must leave the surface at the target composition ratio in steady state, the sticking coefficient of the electronegative element at the substrate is likely to be lower resulting in a sub-stoichiometric deposit.

   --> addition of an appropriate amount of that element to the supply flow of sputtering gas

2) A small amount of oxygen or nitrogen is mixed with the plasma-forming gas. After the material is sputtered from the target, it reacts with this gas, so that the deposited film is a different material, i.e. an oxide or nitride of the target material.

   Ex: Ti target + nitrogen: TiN formation

Applications to oxides:

Ceramic target(s) or metallic target + oxygen - several targets can be used (shutters)

Widely used in laboratories (transfer of the target composition to the film composition however not systematic)
Chemical Vapor Deposition

Chemical routes: Classification

- **Solid precursor**
  - Evaporation: sublimators, bubblers, injection into an evaporator, aerosol in an evaporator
  - Adsorption: incorporation
  - Reaction in heterogeneous phase
  - Reaction in homogeneous phase
  - Substrate: ALD, CVD

- **Solid precursor in a solvent**
  - Liquid precursor: dip coating, spin coating, aerosol/spray
  - Liquid phase: MOD, Sol gel
  - Powder CVD (atm pressure)
  - Pyrosol (atm. pressure)

- **Substrate**
  - T < Tevap: Condensation of the precursor (liquid or solid)
  - T ≥ Tevap: Gas phase
Chemical vapor deposition (CVD)

Deposition of a solid film on a heated surface via chemical reaction(s)

\[ \text{Gas}_A \rightarrow \text{Solid}_B + \text{Gas}_C \]

Heterogeneous phase reaction(s) (gas/surface)

Source system
Generation of the gas phase

Transport of the gas and distribution

Reaction zone

exhaust

Different issues with CVD:

Type of source: how can I generate the gas phase? (it depends on the precursors)

How to promote the reactions:
- thermal (resistive, inductive, radiative (IR) heating)
- plasma (PE-CVD)
- UV
- laser

Working pressure: atmospheric pressure (APCVD) or low pressure (LPCVD)

Design of the reactor (vertical, horizontal, cold or hot walls, orientation of the substrate relatively to the gas flow, optical ports for in situ characterization...
Parameters of CVD

- flow of reactive species in the reactor
- type of precursors (and solvents)
- nature of gas and flow rates (carrier gas, e.g. Ar and reactive gas e.g. O₂)
- working pressure
- substrate temperature
- parameters related to other energy supply (plasma power, UV wavelength...)

Mechanisms involved in CVD

1) Transport of the reactive species towards the surface
2) Diffusion of the species through the boundary layer
3) Adsorption of the species at the surface
4) Chemical reaction(s) at the surface, diffusion on the surface, nucleation, growth
5) Desorption of the gaseous products
6) Diffusion of the gaseous products through the boundary layer
7) Evacuation of the gaseous products

The slowest step will be the limiting step for the growth rate
Mechanisms of the CVD process

Growth controlled by surface: the growth rate is limited by the kinetic of the chemical reactions, highly dependent on surface temperature.

Growth controlled by diffusion: the growth rate is limited by the income of the reactive species at the surface, not very dependent on surface temperature.

Chemical reactions used in CVD

Any chemical reaction which imply one or several gaseous reactive species and that can lead to the desired solid (with gaseous by-products)

**Thermal decomposition (pyrolysis):**

- \( \text{SiH}_4(g) \rightarrow \text{Si}(s) + 2 \text{H}_2(g) \)
- \( \text{Al}(	ext{OC}_3	ext{H}_7)_3 \rightarrow \text{Al}_2	ext{O}_3 + \text{C}_x\text{H}_y + \text{H}_2\text{O} \)
- \( \text{Al}(	ext{C}_4	ext{H}_9)_3 \rightarrow \text{Al} + 3 \text{C}_4\text{H}_8 + 3/2 \text{H}_2 \)

**Reduction:**

- \( 2 \text{AX}(g) + \text{H}_2(g) \rightarrow 2\text{A}(s) + 2 \text{HX}(g) \)
- \( \text{WF}_6(g) + 2 \text{H}_2(g) \rightarrow \text{W}(s) + 6 \text{H}_2\text{F}(g) \)
- \( 3 \text{NbCl}_6(g) + 6\text{C}_2\text{H}_4(g) + 19/2 \text{H}_2(g) \rightarrow \text{Nb}_3\text{Ge}(s) + 19 \text{HCl}(g) \)

**Oxidation:**

- \( 2 \text{AX}(g) + \text{O}_2(g) \rightarrow 2\text{AO}(s) + \text{X}_2(g) \)
- \( \text{SiH}_4(g) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2 \text{H}_2\text{O}(g) \)
- \( \text{SiH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2 \text{H}_2\text{O}(g) \)
- \( \text{Zn}(	ext{C}_2\text{H}_5)_2 + 7 \text{O}_2(g) \rightarrow \text{ZnO}(s) + 4 \text{CO}_2 + 5\text{H}_2\text{O}(g) \)

**Polymerisation:**

- \( n \text{AB} \rightarrow (\text{AB})^n \)
- \( \text{Si}_2\text{C}(\text{CH}_3)_6\text{O} \rightarrow _{(\text{Si}(\text{CH}_3)_2)}\text{O}_n \)
Hydrolysis: \[ AX(g) + H_2O(g) \rightarrow AO(s) + HX(g) \]

\[ SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4 HCl(g) \]

Nitridation: \[ AX(g) + NH_3(g) \rightarrow AN(s) + HX(g) \]

\[ 3 SiCl_4(g) + 4 NH_3(g) \rightarrow Si_3N_4(s) + 12 HCl(g) \]

\[ GaCl + NH_3(g) \rightarrow GaN + H_2(g) + HCl(g) \]

Carburation: \[ AX_4(g) + CH_4(g) \rightarrow AC(s) + 4 HX(g) \]

\[ SiCl_4(g) + CCl_4(g) + 4H_2(g) \rightarrow SiC(s) + 8HCl(g) \]

Reactions of synthesis between two (or more) volatile compounds

- Hydride + Halide, OM + hydride, OM + OM...
- Ga(CH_3)_3(g) + AsH_3 \rightarrow GaAs(s) + 3 CH_4(g)
- Cd(CH_3)_2 + H_2Se(g) \rightarrow CdSe(s) + 2 CH_4(g)

Combined reactions ...

Gas phase generation

Crucial point for the CVD process

Precursors:

- **Gas**: ex: \[ SiH_4(g) \rightarrow Si(s) + 2 H_2(g) \]
- **Liquid**: need to be evaporated
- **Solid**: need to be evaporated

How to perform the evaporation??

Objective: stable gas phase
Gas phase generation: classical ways

Solid precursor

The gas phase is controlled by:
- source temperature
- pressure
- carrier gas flow rate
- amount of precursor (surface)

Evaporation rate vs $T^\circ$ for $Y$(tmhd)$_3$, $Ba$(tmhd)$_2$ and $Cu$(tmhd)$_2$

The evaporation rate depends strongly on the evaporation temperature.

Liquid precursor: Bubblers

The gas phase is controlled by:
- bubbler temperature
- bubbler pressure
- carrier gas flow rate
- amount of liquid
Precursors requirements

- Volatility as high as possible (minimizing of evaporation temperature) with high vapor pressure (for reasonable growth rate)

- Adequate temperature window between evaporation and decomposition (thus $T_{\text{vap}} < 300^\circ\text{C}$)

- Thermal stability (no decomposition during heating)

- By-products of the reactions must be gaseous

- Toxicity, environmental and safety issues, handling, storage (shelf life), price...

With classical sources, it is difficult to:
- control the vapor flow at low pressure
- obtain a high vapor pressure
- use thermally unstable precursors

Example: superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$ (first results with CVD in 1988)

Precursor for Y, Ba, Cu?

Halides: evaporation temperature too high (> 800°C)

Organometallic molecules: lower evaporation temperature (< 250°C)

β-diketonates

$M(2,2,6,6\text{ tetramethyl 3,5 heptane dionate})_{x} = M(\text{tmhd})_{x}$

tmhd ligand
\( \text{Y(tmhd)}_3 \)

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{(H}_3\text{C)}_2\text{C} & \quad \text{O} \\
\text{O} & \quad \text{Y} \\
\text{O} & \quad \text{O} \\
\text{C(CH}_3)_3 & \quad \text{Y} \\
\text{C(CH}_3)_3 & \quad \text{C} \\
\text{C} & \quad \text{C(CH}_3)_3 \\
\text{CH} & \quad \text{C(CH}_3)_3 \\
\text{(CH}_3)_3 & \quad \text{H}
\end{align*}
\]

Innovative sources for the generation of the gas phase

Some precursors (especially for Ba, Sr, Ca and Rare-earth) exhibit:

- Bad thermal stability
- Sensitivity to humidity
- Evaporation temperature close to the decomposition temperature

Drift of the vapor pressure during deposition !!!

QUESTION

How to generate a stable gas phase from unstable precursors ?

- Maintain precursors at room temperature
- Evaporate micro-quantities of precursors in a “flash” manner
Innovative sources

“flash” evaporation of the precursors

Solid sources (solid precursor):
- solid stick introduced in a sharp thermal gradient

drawback: mixing of powders difficult to control

Liquid sources (liquid precursor or solid precursor dissolved in a solvent):
- delivery of the liquid in an evaporator via:
  - a micro-pump
  - a syringe
  - a liquid mass flow
  - an injector
  - an aerosol

Alternative source: injection source (LMGP-CNRS)

Pressurisation under Ar

Micro-valve

Glass container

Injection of micro-quantities of liquid in an evaporator (T ~ 250°C)
- “flash” evaporation
- liquid precursor maintained at room temperature

CNRS (LMGP) 1993 - 1994 patents - licenced by CNRS to AIXTRON (France, Europe, USA)
Alternative source: injection source (LMGP-CNRS)

Injection: pulsed regime (pressure oscillations)

Control of the gas phase in injection-CVD

Reactives species flow rate in gas phase controlled by:
- injection frequency (~ 0.1 to few Hz)
- opening time (~ 1 ms / 10 ms)
- dilution of precursors solution
- solvent (viscosity)
- differential pressure between liquid contained and evaporator

Remember: for classical source this control is performed through:
- evaporation temperature
- pressure
- carrier gas flow
Advantages of this injection delivery scheme

- Thermally unstable precursors can be used
  (precursors maintained at room T° under an inert gas / flash volatilisation)

- Deposition of complex oxides : unique liquid solution can be used
  (mixture in a single cocktail of several precursors)
  stability of the gas phase composition

- Large growth rate range possible

- No dead volume : growth stops as injection is stopped

- Sequential use of several injectors
  growth of heterostructures, multilayers

TriJet™

The Liquid Precursor Delivery and Evaporation System

- Long term stability
- High growth rates
- High precursor efficiency
- Precise flow control
- High purity and high deposition rates
- Simplified gas supply system
- High purity oxide thin films
- Area coverage
- High deposition rates
- Broad spectrum of precursors
- Easy to operate
- Easy to maintain
- Easy to clean
- Easy to use

AIXTRON
Alternative source: injection source - other examples

Liquid injection system based on mass-flow controllers

Bronkhorst system

Liquid flow valve

Liquid flow meter

MFC

Gas

Gas/liquid mix

Evaporator

Continuous injection of liquid into the evaporator

Modelling of CVD

Need to simultaneously model both the complex chemistry and the complex fluid flow

Chemistry:
Need to know the reactions pathways and the kinetic constant of the different reactions
--- difficult to identify all the reactions (for a simple case of Si, the number of simultaneous homogenous and heterogeneous reactions is of a few tens)

Unimolecular reaction (dissociation, isomerisation)

Bi-molecular reaction

CH₄ + .H ↔ .CH₃ + H₂

.H + CH₃C₂H₅ ↔ C₂H₆ + .CH₃

.H + C₂H₆ ↔ .C₂H₅

kinetic of the reactions:
for homogenous reaction: Arrhenius-type law
for heterogeneous reaction: more difficult to determine and model

See papers from M. Pons, M. Allendorf, and also Sandia laboratory
**Horizontal reactors**: Planetary reactors for mass production

(Planetary concept developed by Philips and under exclusive license to AIXTRON)

- Quartz tube
- Stainless steel chamber

Horizontal laminar flow
Design of the reactors

Vertical reactors

A showerhead is used for the precursor gas distribution

200-300 mm MOCVD equipment for oxide deposition

ST / LETI-CEA

http://www.thomasswan.co.uk/
Example: Deposition of high-K HfO₂ oxide by CVD

**Which precursor?**

- **Hf(Cl)₄**
- **[Hf(OR)₄]**
- **Hf(OEt)₄**
- **Hf(OC(CH₃)₂)₄ = Hf(O’Bu)₄**
- **Hf(acac)₄**
- **Hf(tmhd)₄**

**Halides**
- Low volatility solids
  - Et = C₂H₅

**Alkoxides**
- Tendency to oligomerise
- Highly air and moisture sensitive

**β-diketonates**
- High evaporation temperature

\[ \text{tBu} = \text{C} \quad \begin{array}{c} \text{CH₃} \\ \text{CH₃} \\ \text{CH₃} \end{array} \]

Examples of compounds deposited by injection MOCVD

**HfO₂ deposition: influence of the precursor**

**Hf(OtBu)₄ in hexane**

The amorphous films are porous!!

Tert-butoxide ligand undergoes a catalytic hydrolytic decomposition reaction in the presence of trace water

C. Dubourdieu, LMGP
TEM : M. Audier, LMGP
Example: Deposition of high-\( K \) \( \text{HfO}_2 \) oxide by CVD

Which precursor?

- \( \text{Hf(NMe}_2)_4 \) : high sensitivity to moisture, \( \text{M}_p \approx 75 \, \degree \text{C} \)

- \( \text{Hf(NEt}_2)_4 \) : high sensitivity to moisture, \( \text{M}_p \approx 42 \, \degree \text{C} \)

- \( \text{Hf(OtBu}_2\text{(dmae)}_2 \) : low sensitivity to moisture, \( \text{M}_p \approx 75 \, \degree \text{C} \)

- \( \text{Hf(OtBu}_2\text{(mmp)}_2 \) : low sensitivity to moisture, \( \text{M}_p \approx 75 \, \degree \text{C} \)

---

Example: Deposition of \( \text{HfO}_2 \) by CVD

Precursor: \( \text{Hf(OtBu}_2\text{(mmp)}_2 \)

Solvent: Octane

Temperature: 350°C

Total pressure: 0.13 kPa

\( \text{Ar + O}_2 \) (\( \text{P}_{\text{O}_2} = 0.09 \, \text{kPa} \))

Control of the thickness via the injected volume of precursor

C. Dubourdieu, LMGP

TEM: G. Van Tendeloo, EMAT, Anvers
Deposition of HfO₂: effect of the reactive species flow rate

Decrease of the reactive species flow impinging on the substrate

Decrease of the interfacial layer thickness

Example: Deposition of HfO₂ by CVD

Epitaxial films of complex oxides

La₀.₇Sr₀.₃MnO₃ on SrTiO₃ (001)

β-diketonates

Evaporation Temp. 250°C

Ts = 700°C

P = 5 Torr (Ar + O₂)

P₂O₂ = 1/3 Pₜot

Example: Deposition of CMR manganites
Multilayers deposition by CVD

Oxide superlattices (epitaxial multilayers)

$C_{RaNMO_3} \approx 11.4 \text{ Å}$

Peroxite structure

$C_{perov} \approx 3.9 \text{ Å}$

B u.c.

S u.c.

β-diketonates precursors

$P = 5 \text{ Torr}$

Ts: 700 - 900°C

Example: Deposition of Ta$_2$O$_5$ by UV-assisted CVD

Which precursor?

- Ta $(OEt)_4 (O \ CH2 CH2 N Me2)$

Deposition of Ta$_2$O$_5$ as low as 350°C!!

UV helps to decompose the precursor

Si

SiO$_2$

Ta$_2$O$_5$

Deposition of Ta$_2$O$_5$ as low as 350°C!!

UV helps to decompose the precursor
Example: Deposition of $Y_2O_3$ by plasma-assisted CVD

PhD thesis C. Durand (UJF, 2004)

Atomic Layer Epitaxy (ALE)
Atomic Layer Deposition (ALD)
Atomic Layer Deposition (ALD) or Atomic Layer Epitaxy (ALE)

Sequential exposure of the substrate surface to different precursors

In-between pulses of precursors: purge of the reactor with an inert gas

Cycle de croissance:
- pulse of precursor A
- purge
- pulse of precursor B
- purge

Ideally, growth is self-limited by saturation of the surface (self-limited by adsorption à la surface)

the thickness of the film is directly proportional to the number of cycles

Advantages:
- Simple and precise control (in principle) of the thickness of the films
- Uniformity over large surfaces
- Conformal coverage over very large aspect ratio (1:50)
- Low temperature deposition
- Nanolaminates (multilayers) deposition

Limitations (or particularities):
- Low growth rates (100-300 nm/h)

BUT: high productivity since simultaneous deposition on a large number of wafers is possible (of large area)
- ex: 82 glass substrates of 155x265 mm² simultaneously covered in an ALD reactor at Planar International for electroluminescent displays

Main applications:
- Electroluminescent displays
- Solar cells
- Microelectronics: synthesis of high K dielectrics, diffusion barriers and electrodes

commercially used in the fabrication of magnetic read-heads (for insulating layers, mainly Al₂O₃) as well as for flat panels
Compounds synthesized by ALD


Oxides

Dielectrics:
- TiO₂, Ta₂O₅, ZrO₂, HFO₂, Al₂O₃, Nb₂O₅, SrTiO₃, BaTiO₃, Y₂O₃, MgO, CeO₂
  ex: Ta₂O₅/HFO₂

Transparent conducting / Semiconductors:
- In₂O₃, In₂O₃:Sn (ETO), In₂O₃:F, In₂O₃:Zr, SnO₂, SnO₂:Sb, ZnO, ZnO:Al, GeO₂

Superconductors:
- YBa₂Cu₃O₇

Fluorides:
- CaF₂, SrF₂, ZnF₂

Nitrides:
- NbN, TiN, TaN, MoN, AlN, GaN, InN, SiNx

III-V compounds:
- GaAs, AlAs, InP, GaP, InAs, Al₆Ga₄As₆, Ga₆In₄As₄, Ga₆In₄P₄

II-VI compounds:
- ZnS, ZnSe, ZnTe, ZnS₁₋ₓSex, CaS, SrS, BaS, CdS, CdTe, MnTe, HgTe, Hg₃Cd₂Te₄, Zn₃Te₅
- ZnS:M (M = Mn, Tb, Tb), CaS:M (M = Eu, Ce, Tb, Pb), SrS:M (M = Ce, Pb, Tb)

Elements:
- Si, Ge, Cu

Others:
- La₂S₃, PbS, In₂S₃, CuGaS₂, SiC

From Infineon (web source)
Atomic Layer Deposition (ALD): examples of realisation nanolaminates + conformal coverage

From Infineon (web source)

Example: growth of Ta$_2$O$_5$ by ALD

**Cycle:**
- Pulse of Ta(OC$_2$H$_5$)$_5$ - carrier gas N$_2$
- Purge N$_2$
- Pulse of H$_2$O
- Purge N$_2$

**Effect of the substrate temperature on the growth rate**

**Effect of the pulse time of H$_2$O on the growth rate**

**Thickness / number of cycles**

Al₂O₃ and HfO₂ grown by ALD

Pulse of metallic precursor

Purge of the metallic precursor

Pulse of the reactant

Purge of the reactant

D. Blin (ASM)
Al₂O₃ and HfO₂ grown by ALD

Importance of the starting surface (needs OH bonds at the surface)

D. Blin (ASM)

Importance of the starting surface in ALD growth


H₂O / HfCl₄

Test different surfaces:

HF-last: HF acid removes native oxide

Chemical oxide: DI/O₃: HF last + deionized H₂O rinse (with 5ppm O₂)

RTO SiO₂: HF-last + RTO in O₂

RTO SiO₂: HF-last + RTO in 60% O₂/40% NO
Importance of the starting surface in ALD growth


HfO₂ growth on different starting surfaces: HF-last, chemical SiO₂ oxide, RTOSiO₂, RTNO Si-O-N...

Slope of linear regression fit to the chemical oxide data:
1.26 ±0.01 x 10¹⁴ Hf/cm²/cycle

Maximum HfO₂ coverage per ALD cycle: 9.15x10¹⁴ HfO₂/cm²

Only 14% coverage is achieved per cycle

Steric hindrance or lack of reactive sites result in only partial monolayer growth per cycle
Coating of carbon nanotubes

Substrate:
Nature, orientation, preparation, surface
**Substrate: choice, preparation**

Which substrate?

Depends on targeted film: Epitaxial, polycrystalline, amorphous films

Depends on application:
- need for electrode (SrRuO$_3$, RuO$_2$, Pt, …)?
- need for integration on semiconductors (Si, III/V…)

--- lattice parameters, surface orientation, surface preparation (cleaning, surface reconstruction, vicinal surfaces)...

Can be used not only to change growth orientation but also domains orientations, anisotropy...

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**Growth mechanisms**

Layer-by-layer growth (Frank van der Merwe): 2D

Step flow growth: 2D

Island growth (Volmer-Weber): 3D

Mixed growth (Stranski-Krastanov)
Films growth

Growth of crystalline surfaces at atomic scale:

TLK (ou TSK) model: Terrace-Ledge-Kink (or Terrace-Step-Kink)

Terrasse - Lisière (marche) - Cran

Epitaxy: Growth of a single crystal (A) on a single crystalline substrate (B)

A=B homoeptaxy

A>B heteroepitaxy

- Choose substrate of same crystalline structure (e.g. perovskite) and with small lattice mismatch \((a_A-a_B)/a_B\)

- If mismatch too large: use sacrificial buffer layer where relaxation will takes place with dislocations formation

- Case of epitaxial phase stabilization

Both film and substrate are strained
Epitaxial phase stabilisation

RMnO₃ : "perovskite structure" (Pnma)  
RMnO₃ : hexagonal structure

Ce  Pr  Nd  Pm  Sm  Eu  Gd  Tb  Dy  Ho  Er  Tm  Yb  Lu  La  Y

As bulk: stabilization of hexagonal DyMnO₃ (synthesis at 1600°C and quenching)  
No other case reported to our knowledge

As thin films: find appropriate substrate  
<--- epitaxial stabilization

\[ \frac{1}{2}R_{2}O_{3} + \frac{1}{2}Mn_{2}O_{3} \rightleftharpoons RMnO₃ \]

\[ \Delta H (RMnO₃), kJ/mol \]


Epitaxial phase stabilisation for cubic YMnO₃

YMnO₃ : "perovskite structure" (Pnma)  
YMnO₃ : hexagonal structure

Ce  Pr  Nd  Pm  Sm  Eu  Gd  Tb  Dy  Ho  Er  Tm  Yb  Lu  La  Y

Choice of substrate of high importance  
<--- epitaxial stabilisation

Epitaxial stabilisation

YMnO₃ hexagonal

YMnO₃ perovskite

Substrate of perovskite structure  
(SrTiO₃, LaAlO₃)

YSZ (111)  
Pt (111)  
Si (111)
Epitaxial phase stabilisation for hexagonal DyMnO$_3$

Choice of substrate of high importance

R MnO$_3$: “perovskite structure” (Pnma)
R MnO$_3$: hexagonal structure

Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
La

DyMnO$_3$ perovskite
Substrate of perovskite structure
(SrTiO$_3$, LaAlO$_3$)

DyMnO$_3$ perovskite

Epitaxial
stabilisation

DyMnO$_3$ hexagonal

(111) YSZ, (111) MgO
(111) Pt, (111) Si

Critical thickness of order of 25 nm
(for $t > t_c$, the perovskite phase grows)

Hexagonal structure over the entire film’s thickness

TEM: H.W. Zandbergen, Delft university
Collaboration with the group of A. Kaul, Moscow

DyMnO$_3$

EuMnO$_3$

I.E. Graboy et al., Chemistry of Materials 15, 2632 (2003)
In situ study of iron oxide growth: epitaxial stabilisation of $\gamma$-$\text{Fe}_2\text{O}_3$

STO substrate 5 inj. 15 inj. 50 inj. $T_S = 500^\circ\text{C}$ $\gamma$-$\text{Fe}_2\text{O}_3$

STO substrate 5 inj. 10 inj. 50 inj. $T_S = 550^\circ\text{C}$

STO substrate 5 inj. 10 inj. 50 inj. $T_S = 600^\circ\text{C}$ $\gamma$-$\text{Fe}_2\text{O}_3$ + $\alpha$-$\text{Fe}_2\text{O}_3$

Substrate preparation - substrate surface: SrTiO$_3$

* SrTiO$_3$: TiO$_2$- or SrO-terminated surface


HF-buffered solutions (etching) + annealing

--> termination may have a strong impact on growth of oxide
Morphological phase diagram for SrRuO$_3$/SrTiO$_3$ (001)

- Terrace width and flux are important

Hong et al. PRL 95, 095501 (2005).

**In situ study by AFM of iron oxide growth by MOCVD:**

*Effect of injection frequency (reactive species flow rate)*

- **f = 0.1 Hz**
  - STO substrate
  - 10 inj.
  - 50 inj.
  - 100 inj.

- **f = 1 Hz**
  - STO substrate
  - 15 inj.
  - 50 inj.
  - 90 inj.

- **f = 5 Hz**
  - 5 inj.
  - 10 inj.
  - 50 inj.
  - 100 inj.

Substrate surface: vicinal surfaces

C. Dubourdieu, T. Baron, Grenoble
By varying the vicinal angle of the substrate, we can induce drastic changes to the ferroelectric domain structure.

We can effectively engineer BFO(001) to have any type of domain structure we want.

Drawback → Surface morphology is rougher.

Controlling Domains – Vicinal Substrates

Substrate surface: vicinal surfaces

Substrate surface orientation

* (001) SrTiO$_3$: non polar BiFeO$_3$ on SrTiO$_3$ (001): what's happen at the interface??

(BiO)+ / (FeO$_2$)- on (SrO) / (TiO$_2$) planes

* (001) LaAlO$_3$: (LaO)+ / (AlO$_2$)- polar planes: when stacking SrTiO$_3$ with LaAlO$_3$: how do charges distribute at interfaces?? (H. Hwang et al.)

(110) LaAlO$_3$: non polar surface

* Different surface orientation can be used to modify magnetic anisotropy for example (J. Fontcuberta)
**SrTiO₃: surface reconstruction**

2x2 surface reconstruction observed on bare (100) SrTiO₃ after annealing at 700°C under oxygen (surface diffraction at ESRF, ID32, collaboration J. Zegenhagen, C. Dubourdieu)

→ impact on growth of ultrathin films (2x2 unit cell for ultrathin SrTiO₃ films grown on SrTiO₃ (100)

→→ impact on physical properties?

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**The clean Si (111) - 7x7 reconstructed surface**

Atomic surface structure
Si(111)-1x1

Diffraction pattern of atomically clean Si(111)
LEED: Low energy electron diffraction

STM: Scanning tunneling microscope

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L. Libralesso, PhD Grenoble, UJF (2006) -
STM study with increasing Pr$_2$O$_3$ film coverage

- Undisturbed Si(111) - 7×7 around the islands
- Pr$_2$O$_3$ : 2D triangular islands
  - Homogenous island size : ≈ 150-200 Å
  - Balance step flow + layer by layer growth

2D smooth layers

L. Libralesso, PhD Grenoble, UJF (2006)

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The clean Si (001) - 2×1 reconstructed surface

- LEED
  - LEED pattern (53eV) of Si(001) after e-beam heating @ 1250°C

- STM
  - Si (001): 2×1 reconstructed surface

Growth of Pr$_2$O$_3$ on Si (001)

Bare substrate

90° domains

90° domains

L. Libralesso, PhD Grenoble, UJF (2006)
ALD of ZrO$_2$ on HF-last Si: islands growth

Dependence of growth on surface preparation

Growth of HfO$_2$ on Ge substrate

Dependence of growth on deposition technique and/or surface preparation

Courtesy T. Conard, IMEC
Characterizations of thin films
Physico-chemical & micro(nano) structural characterization of thin films

- Thickness
- Composition (cations and oxygen content) - elemental profiles
- Domains structure
- Crystalline structure (average, distortions) - amorphous
- Cations valence - Nature of bondings
- Defects (vacancies, dislocations, twinnings...)

Interfaces !!

Nature of the interfaces
(composition, thickness....)

mesoscopic, micrometric, nanometric

Thickness determination

Thickness measurement: not trivial!

- Mask part of the film: measure step height
- X-ray reflectometry (XRR)
- X-ray diffraction: fringes
- Ellipsometry (spectroscopic): need optical properties of the materials
- Transmission electron microscopy (destructive!)
- XPS
- ...

Thickness measurement: not trivial!
Composition determination

Composition measurement: not trivial

Energy Dispersive X-ray spectrometry (EDX), Wavelength Dispersive X-ray spectroscopy (WDS): requires etalons

X-ray Fluorescence

X-ray photoelectron spectroscopy (XPS) or ESCA (Electron spectroscopy for composition analysis): Surface analysis
Composition determination requires precise calibration from known composition sample analysis

Secondary Ions Mass Spectrometry (SIMS)

Rutherford Backscattering Spectrometry (RBS): no etalon

Oxygen stoichiometry: cannot be precisely determined in thin films

However, oxygen stoichiometry drives/influences oxides properties!!!

(SrTiO$_3$: becomes semiconducting if oxygen deficient...)

Crystalline structure determination

X-ray diffraction (reciprocal space mapping, various scans configurations...)

For surfaces (interfaces): surface diffraction (need for synchrotron source)

Infra-red and Raman spectroscopies: very powerful to discriminate between different crystalline structure and/or to evidence small lattice distortions that can sometimes not be detected by X-ray diffraction
X-ray diffraction (ESRF) n/2θ scans

d-spacings (out of plane)
roughness at interfaces
Interdiffusion

Crystalline structure?

Raman spectroscopy:
e_{LSMO} ~ 30/40 Å : orthorhombic
e_{LSMO} ~ 100 Å : rhombohedral
(bulk structure)

XPS analysis: determination of bonds and atoms environment - chemical selectivity

Y-O-Si / SiO_2/Si stack

Growth of SiO_2 and silicate favored
for low species flow rate
Defects identification
(dislocations, twins, GB, oxygen or cation vacancies, impurities...)

Optical microscopy
Transmission electron microscopy (local probe)
X-ray topography
EPR

...
Antiphase boundaries can be generated by substrate steps and they can be also annihilated on stacking faults.

Blocks can be usually considered as obtained by the rotation by π/3 and shift by ~c/6 (or only shift by ~c/3).

Need to combine several characterization techniques

Different interactions (electrons/matter, ions/matter, photons/matter...)
Different probing lengths
Average information / local information
Many groups - see presentation of R. Ramesh (Monday) for an overview of state of the art research on BiFeO₃.

Group of R. Ramesh, Berkeley, US

J. Wang et al., Science 307, 1203b (2005)
and many others!!! (lecture on Monday)

Group of A. Barthélémy & A. Fert, UMR CNRS-Thalès, Palaiseau, France


All PLD

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BiFeO₃ thin films


MOCVD:

C. Dubourdieu, LGMP - Grenoble
J. Théry, et al., Chemical Vapor Deposition 13, 232 (2007)
BiFeO$_3$ by MOCVD: difficult control of stoichiometry

Bi precursor highly sensitive to air ---> difficult control of stoichiometry

Bi-rich film

![Image](image1.png)

\[ \frac{R_f}{R_s} = 0.78 \]

\[ \frac{R_f}{R_s} = 0.43 \]

\[ \text{Magnetization (emu/cm}^3\text{)} \]

\[ \text{Magnetic field (Oe)} \]

XPS:

- Fe$^{2+}$ present
- Fe$^{3+}$ has multiple binding environment
- Under-oxidised γ-Fe$_2$O$_3$?

J. Théry et al., Chemical Vapor Deposition 13, 232 (2007)

J. Dho, M.G. Blamire, Cambridge

J. Fontcuberta, Barcelona

K. Dörr, Halle

T. Noh, Seoul, Korea

N. Fujimura, Japan

C. Dubourdieu, France

Still many open questions for ReMnO$_3$ thin films

- Phase transitions in thin films?
- Ordering temperatures?
- Domains size...
- Magnetoelectric effect? (first order ME effect not possible in bulk)
- Dependence of polarization on film thickness? (possible enhancement of polarization through strain?)
- What governs leakage currents?

YMnO$_3$, ReMnO$_3$ thin films

Exchange bias experiments (first papers in 2005)
**Bi$_2$FeCrO$_6$:**

Ab initio calculation indicate multiferroism:


Predicted to be multiferroic (P ~ 80 $\mu$C/cm$^2$) -> attempts to prepare this compound as thin films

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Group of A. Pignolet, INRS, Montreal, Canada


A. Pignolet et al., "Epitaxial thin films of multiferroic with B-site cationic order", Archiv - Cond. Matter

PLD films (Ts = 680°C, 9 mTorr O$_2$) - post deposition anneal at 400°C

Fe$^{3+}$/Cr$^{3+}$ cation ordering necessary!!

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Sr$_2$FeMoO$_6$: half metallic (fully spin-polarized), with Tc (ferromagnetic/paramagnetic) larger than room temperature
Bi$_2$NiMnO$_6$:


PLD films (Ts = 630°C, 0.4 Torr) - post deposition anneal at 450°C

Ferromagnetic behavior with Tc ~ 100 K and ferroelectric behavior with P ~ 5 μC/cm$^2$

Conclusions and perspectives:

Tremendous progress in deposition techniques: sub-nanometer control of the growth of thin films

Crucial role of interfaces in the final properties: need to be precisely controlled

Physico-chemical characterization requires the combination of different techniques probing the sample at different scales and using different interaction types

(high-K oxides research field has triggered the development of suited metrologies)

Possibility to develop oxide heterostructures for new properties that will arise from interfaces effects and from tailoring of charges, orbitals and spins couplings

Just the beginning as compared to the semiconductor heterostructures field!!

New phenomena will certainly come up in the future for oxides heterostructures

Combining oxides and semiconductors: take advantage of both --→ new heterostructures