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Advanced Atomic Layer Deposition and Epitaxy Processes

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Single-crystal oxide insulators grown epitaxially on GaAs, Ge and GaN by ALE

Outline

Atomic Layer Epitaxy (ALE)

ALE of single-crystal La_2O_3 on GaAs(111)

CMOS circuits with La_2O_3 on GaAs(111)

ALE of single-crystal La_2O_3 on Ge(111)

ALE of single-crystal (Mg,Ca)O on GaN(0001)

ITRS roadmap

GaAs has Many Traps at Oxide Interfaces

=> very large frequency dispersion

=> very low drive currents

$\sim 10^{13} \text{ cm}^{-2}$ traps at GaAs interface with oxides

$< 10^{11} \text{ cm}^{-2}$ traps at Si/SiO₂ interface

=> GaAs MOS transistors are much poorer than Si

Solution: epitaxial single-crystal La₂O₃ on GaAs

=> $\sim 10^{11} \text{ cm}^{-2}$ traps at GaAs/La₂O₃ interface

=> **First CMOS transistors ever made on GaAs**

Atomic Layer Epitaxy (ALE)

Sequential, self-limiting surface reactions make alternating layers:

Benefits of ALE:

- High-quality epitaxial interfaces with few traps
- Atomic level of control over film composition
⇒ nanolaminates and multi-component materials
- Uniform thickness over large areas and inside narrow holes
- Smooth surfaces
- High density and few defects or pinholes
- Low deposition temperatures (for very reactive precursors)
- Pure films (for suitably reactive precursors)
- Full-wafer semiconductor-grade production equipment available

Amidinate Precursors for Trivalent Metals

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy,
Ho, Er, Tm, Yb, Lu, **Y**, Sc, In, Ru, Ti

R = H (formamidinate, fmd)

R = CH₃ (acetamidinate, amd)

Now produced commercially by the Dow Chemical Company

Vaporization of Lanthanum Amidinate Precursor

tris(N,N'-diisopropyl-formamidinato)lanthanum

$\text{La}((^i\text{Pr}_2\text{N})_2\text{CH})_3$

abbreviated $\text{La}(\text{fmd})_3$

Most volatile lanthanum compound known

Complete evaporation without decomposition or residue

ALE of Lanthanum Oxide, La_2O_3

Precursors: H_2O and $\text{La}(\text{fmd})_3$

$\text{La}(\text{fmd})_3$ at 120 °C, substrate at 300 °C

slope => 0.16 nm per cycle

line starts at origin
=> no delay in nucleation

ALE La_2O_3 is Epitaxial on GaAs(111)A

TEM

Lattice Constant Matching:
 $a(\text{La}_2\text{O}_3) = 2.0008 \times a(\text{GaAs})$
or 0.04% mismatch

High Resolution XRD

Atomic layer epitaxy of GaAs(111)/La₂O₃

Side view of
GaAs(111)/La₂O₃

top view

CV characteristics of GaAs(111)/ $\text{La}_{2-x}\text{Y}_x\text{O}_3$

Closer Lattice Match to GaAs => less dispersion

Mismatch =>

-3.32 %

-0.64 %

+0.04 %

Interface Trap Densities

Closer Lattice Match to GaAs => Fewer Traps

Summary of GaAs CMOS

GaAs nMOSFET with La_2O_3 epitaxial dielectrics

- High drain current of 376 mA/mm is obtained from GaAs nMOSFET with $1\mu\text{m}$ gate length
- Current $I_{on}/I_{off} \sim 10^7$, subthreshold slope as low as 74 mV/dec
- A mean D_{it} of $1.7 \times 10^{12} \text{ cm}^{-2} \cdot \text{eV}^{-1}$, using $SS = 60(1 + qD_{it}/C_{ox})$

GaAs nMOSFET with La_2O_3 epitaxial dielectric

□ Peak transconductance $G_m \sim \underline{190 \text{ mS/mm}}$

□ Peak electron effective mobility $\sim \underline{1150 \text{ cm}^2/\text{Vs}}$

GaAs pMOSFET with La_2O_3 epitaxial dielectric

- Maximum drain current of 30 mA/mm is obtained from GaAs pMOSFET with $1\mu\text{m}$ gate length
- $I_{\text{on}}/I_{\text{off}} \sim 10^4$ and $\sim 10^3$ for the pMOSFETs with $1\mu\text{m}$ gate length annealed at 780°C and 800°C , respectively

GaAs pMOSFET with La_2O_3 epitaxial dielectric

- A transconductance of 12 mS/mm is obtained from GaAs pMOSFET with $L_g = 1\mu\text{m}$
- The peak effective hole mobility is around 180 cm^2/Vs .

CMOS GaAs inverters

□ Peak gain of 12 is obtained with $V_{DD} = 3\text{V}$

CMOS GaAs NAND logic gate

NAND logic	Inputs	$V_{in,a}$	1	0	1	0
		$V_{in,b}$	1	1	0	0
	Output	V_{out}	0	1	1	1

CMOS GaAs NOR logic gate

NOR logic	Inputs	$V_{in,a}$	1	0	1	0
		$V_{in,b}$	1	1	0	0
	Output	V_{out}	0	0	0	1

CMOS GaAs 5-stage ring oscillator

*5 inverters connected
in series mode*

CMOS GaAs 5-stage ring oscillator

- ❑ At $V_{DD} = 2V$, the fundamental oscillation frequency is at 2.2 MHz
- ❑ The fundamental resonance frequency increases from 0.35 MHz at $V_{DD} = 1V$ to 3.87 MHz at $V_{DD} = 2.75V$.

How to Translate these Results to GaAs(100)

ALE La_2O_3 and LaLuO_3 are polycrystalline, not epitaxial, on GaAs(100)

Electrical measurements of capacitors show many traps at interface

Wet Etching GaAs(100) Exposes (111) Surface

=> epitaxial La_2O_3 on GaAs(111) facets

Orientation to Form GaAs(111) Facets

WaveFET Structure on GaAs(100)

- Ti/Au Gate
- 10nm Al_2O_3
- 5nm La_2O_3
- GaAs(100) substrate

WaveFET GaAs Transistor Performance

Epitaxy of $\text{La}_{1.7}\text{Y}_{0.3}\text{O}_3$ on Ge(111)

Capacitors with $(\text{La,Y})_2\text{O}_3$ on Ge(111)

High-performance pMOS transistors are expected using this epitaxial interface

Possible Epitaxial Oxides for GaN

Phase Diagram of (Ca,Mg)O

Miscibility gap for most compositions

Metastable compositions decompose at about 600 °C

=> Need to deposit (Ca,Mg)O at $T < 600\text{ °C}$ to avoid decomposition

Phase equilibrium diagram for the system CaO-MgO. Solid

J. Am. Ceram. Soc. **46**, 314 (1963)

2 Precursors for ALE of Magnesium Oxide, MgO

bis(*N,N'*-di-*sec*-butylacetamidinato)

magnesium

Liquid

bis(*N,N'*-di-*tert*-butylacetamidinato)

magnesium

Solid

ALD bubbler temperatures 90 – 110 °C

Residue < 1% (clean evaporation)

Chose the liquid on left because of its ready purification by distillation and easier handling

ALD of MgO at 300 °C, low enough to avoid thermal decomposition of (Ca,Mg)O

3 Precursors for ALE of Calcium Oxide

**bis(*N,N'*-di-*tert*-butyl-
acetamidinato)
calcium**

Sublimes at 185-190°C

Low volatility
Reactive to H₂O

**bis(*N,N'*-diisopropyl-
acetamidinato)
calcium**

Sublimes at 135-140°C

Higher volatility
Reactive to H₂O

**bis(*N,N'*-diisopropyl-
formamidinato)
calcium**

Sublimes at 95-100°C

**Superior precursor:
Highest volatility
Reactive to H₂O
Scaled up production**

ALD of CaO at 300 °C, low enough to avoid decomposition of (Ca,Mg)O

Electron Diffraction from Epitaxial (Ca,Mg)O on GaN(0001)

Epitaxial orientation :
(Ca,Mg)O(111) // GaN (0001)

Beam Direction [11-20]

Composition of (Ca,Mg)O by RBS on Carbon Substrates

Aluminum in capping layer of ALD Al_2O_3

Lattice Constant Mismatch

Dosing ratio Mg:Ca=1:3; RBS: Mg:Ca=1:3

2theta=71.09 d=1.325nm mismatch = 2.2%
(Vegard's law prediction: mismatch = 3.7%)

FWHM=0.23deg

(Ca,Mg)O is a good insulator on GaN or InAlN

Large band offsets for both conduction and valence bands of MgO

Materials **2012**, 5, 1297-1335

Capacitor with (Mg,Ca)O on InAlN => Very Few Traps

Almost no frequency dispersion
=> few states at the interface.

AC conductance extracts very low D_{it}
in the bandgap, around 10^{11} cm^{-2}

Drain Current vs. Gate Voltage for InAlN Transistors

The (Mg,Ca)O gate insulator reduced the gate leakage by four orders of magnitude, from 10^{-8} to 10^{-12} A/mm.

The subthreshold slope is nearly ideal at 64 mV/dec.

Summary

Atomic Layer Epitaxy (ALE) forms high-quality epitaxial interfaces

ALE $\text{La}_2\text{O}_3/\text{GaAs}(111)$ => both p- and n- type capacitors with low dispersion

=> the first CMOS circuits with both channels in GaAs

ALE $\text{La}_2\text{O}_3/\text{Ge}(111)$ => epitaxial structures

ALE $(\text{Mg,Ca})\text{O}/\text{GaN}$ or InAlN => capacitors with low dispersion

ALE $(\text{Mg,Ca})\text{O}/\text{InAlN}$ => transistors with low gate leakage

ALE is a scalable process for making high-performance devices

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