

ALD Reactor Architectures ESH Implications

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Outline

ALD Introduction

>ALD Reactors

Process Control

> A Possible ESH Application for ALD

≻A Footnote: ISO14000 Certification





Atomic Layer Deposition M. Ritala and M. Leskela 2002

- Uses sequential <u>chemisorbed</u> self-limiting and selfpassivating "monolayer" reactions on a heated surface
- Reactive Precursors are alternately pulsed onto the surface, separated by an inert purge gas
- Each half-reaction (e.g. for Metal and non-metal) follows exponential or Langmuir kinetics
- \geq Initiation is key to a continuous startup of process
 - e.g surface preparation to achieve: Si-OH





Generic ALD Process Flow

Time







Varieties of ALD

➤ Thermal

- $-ZnCl_2 + H_2S -->ZnS + 2HCl$ (Suntola, 1989)
- $-WF6 + Si_2H_6 -> W + 2SiHF_3 + 2H_2$ (Klaus, 2000)

≻Plasma

 $-SiH_2Cl_2 + *H -->Si + HCl$ (Imai, 1994)





Recent Popular ALD Films After S. George, 1994

- > Al₂O₃ (TMA)
 - $\text{Al-OH} + \text{Al}(\text{CH}_3)_3 \rightarrow \text{Al-O-Al}(\text{CH}_3)_2 + \text{CH}_4$
 - $\text{Al-O-Al}(\text{CH}_3) + \text{HOH} \rightarrow \text{Al-O-Al-OH} + \text{CH}_4$
- ≻HfO₂ (Hafnium Chloride)
 - Hf-OH + HfCl₄ \rightarrow Hf-O-HfCl₃ + HCl
 - Hf-Cl +HOH \rightarrow Hf-OH + HCl



Al₂O₃ in Bottle Shaped Trench (Courtesy of Infineon, Gutsche, et.al. 2001)





GENUS

Materials Engineering - Alloys <u>and Stacks</u> "StrataGem Vision"

(HR TEM is lower right corner of trenches, Sneh,et.al., 2001)





Genus StrataGem²⁰⁰ Production System









ALD Reactors

All commercial reactors are now flow type with viscous or transition to molecular flow

Single Wafer, Multiwafer

- Horizontal Flow
- Vertical Flow
- ➢ Batch, Minibatch
 - Horizontal Flow





Reactor Guidelines Conventional Wisdom (e.g. Ritala, Sneh...)

- Self-limiting growth ensures precursor fluxes do not need to be uniform over the substrate
- > Still, need rapid switching, exposure and purge
- Small Reactor volume and heated walls recommended
- Growth rate (Å/cycle) and ~few seconds/cycle ok for 50Å films (15wph)





Single Wafer Horizontal Flow Suntola US #4,389,973 ('83), Seminal Disclosure







Precursor Diffusion Broadening Suntola US #4,389,973('83), Seminal Disclosure







Important Points

Diffusion Broadening is a Fundamental Limitation Controlling Pulse Separation

Classical diffusion model

- $P(x,t) = P_0 \operatorname{erfc} (x/2^*(Dt)^{1/2})$
- >Purge Gas Velocity sets macro flow
 - -v = S/A, (S: pumping speed, A: reactor area)





Batch Horizontal Flow Suntola, US #5,711,811 ('98)







Batch Horizontal Flow with Loading Mechanism Gadgil, US #5,879,459 ('99)







Batch Horizontal Flow Hyun, US#6,042,652 (2000)





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Multi Wafer Vertical Flow Yoder US# 5,281,274 ('93); Tischler & Bedair Localized Steady Flow, Rotating Wafers









Single Wafer Vertical Flow

Hyun (2000) Shows as Prior Art







Manifold and Single Wafer Vertical Flow Sneh, US #6,503,330 (2003)







ALD Reactors

- System Approaches
 - Drop ALD into a core CVD 200mm, 300mm system
 - Use an ALD heritage system and add handling
- >ALD Processes Scaling for wafer size
 - With the right hardware and operational methods, scaling can be demonstrated quickly





Handler and Chamber Views

> Simplified design with access and ease of maintenance





Single Wafer

- SW Process Control
 - Insitu Processes (plasma)
- > Std. Vac. Wafer Handling
 - Cluster Tool Flexibility
- > Many Film Metrics Estab.
- In Ltd. Production (TFH)
 In Pilot Production (SC)
- TP/Cost ok (ultra thin films)
- Cost > Thermal Furnaces
- So far, use limited to ultra thin films

Batch

- Higher Throughput
- Lower Cost
- Potential for Thick Films
- In Ltd. Production (FPED) Under Evaluation (SC)
- Backside deposition
- ≻ Horizontal flow \rightarrow 2 r
- ? Process Control



ALD Process Control A Study of the Variance in Growth Rate with Temperature, Pressure, Pulse, and Purge Times,

Ref. Londergan, et.al. ECS 2002





ALD Process Window

Temperature: hydroxyl coverage

Pressure: residence time



Al₂O₃:
$$\Delta$$
Gr.Rt./ Δ T ~ -1x10⁻³ Å/cycle °C
HfO₂: Δ Gr.Rt./ Δ T ~ -2x10⁻³ Å/cycle °C

 Δ Gr.Rt./ Δ P ~ 2x10⁻⁴ Å/cycle mTorr Δ Gr.Rt./ Δ P ~ 4x10⁻⁴ Å/cycle mTorr





Saturation Characteristics of Al₂O₃

TMA: "Classic" ALD Behavior
 H₂O: Approaches Saturation







Water Purge Characteristics: Al₂O₃

Can operate at low purge times

if parasitic CVD added to ALD meet requirements







HfO.

ALD Process Window

| | $A1_2O_3$ | \mathbf{mo}_2 |
|--|------------------------|------------------------|
| Δ Gr.Rt. / Δ Deposition Temperature [Å/cycle °C] | - 1 x 10 ⁻³ | - 2 x 10 ⁻³ |
| Δ Gr.Rt. / Δ Process Pressure [Å / cycle mTorr] | 2 x 10 ⁻⁴ | 4 x 10 ⁻⁴ |
| Δ Gr.Rt. / Δ Metal Precursor Pulse Time [Å/cycle ms] | < 10 ⁻⁶ | $< 3 \times 10^{-5}$ |
| Δ Gr.Rt. / Δ Metal Precursor Purge Time [Å/cycle ms] | - 5 x 10 ⁻⁶ | - 1 x 10 ⁻⁵ |
| Δ Gr.Rt. / Δ Water Pulse Time [Å / cycle ms] | 2 x 10 ⁻⁴ | 4 x 10 ⁻⁴ |
| Δ Gr.Rt. / Δ Water Purge Time [Å / cycle ms] | - 1 x 10 ⁻⁵ | - 1 x 10 ⁻⁵ |

Excellent control of Al₂O₃ and HfO₂





ESH Implications

- ≻Waste management
 - Consider the separation and entrapment of precursors and by-products in the exhaust zone
 - Opportunity to reclaim of precious elements
- Reactor design with reclaim functionality
 - For minimal precursor use
 - To limit downstream precursor mixing





Schema of Down-stream Precursor Entrapment Process



Schematic of the Down-stream Precursor Separation Process. A, B : Reactive Precursors, P : Purge, A : Precursor for Separation & Recycling.





Generic Example Approach

- Closed-loop arrangement with fast gas switching valves in inlet manifold and a fast switching valve with a predetermined delay down stream
- > Unused precursor may be collected in a trap
 - Coolant or adsorption (passive mode)
 - Heterogeneous reaction, e.g reactively plate out material (active mode)





Concluding Remarks

Many reactor varieties exist

 Pros and cons under evaluation

 Process control excellent and demonstrated
 Scaling ALD from 200 to 300mm demonstrated
 Improved ALD reactor design is possible
 Precursor recovery a potential opportunity





ISO 14001 Environmental Management System The Benefits

- > Environmental Objectives part of Formal Management Reviews.
- Increased Employee Awareness about the Impact they have on the Environment at Work and at Home.
- > Normalized Objectives for Reduction, Recycling, Reuse and Substitutions
- > Compliance with Local, State and Government Laws and Regulations
- Distinguishes Companies who are Concerned about the Environment Worldwide
 - Genus: An ISO 14,000 Certified Company





ISO 14001 Environmental Management System Accomplishments at Genus

- The Product Development Process Incorporates Environmental Awareness. Product Substitutions, Reuse and Recycling are Evaluations and design Criteria.
- ➢ Reduced Non-Hazardous Waste Disposal by 25%.
- ➢ Reduced Electricity Use by 25%.
- Completed a Less Toxic Chemical Substitution without Process Degradation.







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