ALD Nucleation and Area-Selective Deposition

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Outline

1. Nucleation during ALD
   • Inhibited, Island Growth

2. New model for Island Growth
   • Use Growth Rate, Fit to starting defect density
   • Definition of Selectivity
   • Approach for Selective Deposition Comparison

3. Area-Selective Deposition
   • Motivation
   • Methods to achieve selectivity
   • Examples comparing selectivity data

4. Atomic Layer Etching
Shapes of Thin Film Nuclei

Three surface tensions: \( \gamma_{v1}, \gamma_{v2}, \gamma_{12} \)

Force Balance Equation:
\[
\gamma_{v1} = \gamma_{12} + \gamma_{v2} \cos \theta
\]
equilibrium contact angle

Wetting condition:
\[
\gamma_{v1} = \gamma_{12} + \gamma_{v2}
\]
Common Growth Modes

Weber-Volmer (WV)

Frank-Van der Merwe (FM)

Stranski-Krastanov (SK)

(balance of forces; 1\textsuperscript{st} layer wets surface, subsequent layers do not)

\[ \gamma_{v1} < \gamma_{12} + \gamma_{v2} \]

\[ \gamma_{v1} > \gamma_{12} + \gamma_{v2} \]
2D vs 3D Nucleation

**2D:** ALD TiO$_2$ on ITO

W Song et al. JACS (2014)

**3D:** ALD Pt on TiO$_2$


2D – small nuclei coalesce  
3D – larger nuclei coalesce
ALD Thermochemistry

OH + Al(CH₃)₃ → O-Al(CH₃)₂ + CH₄

First Half-Reaction

C. Musgrave
What do we see experimentally?

TiCl$_4$/H$_2$O

Selective Deposition

Direct growth

Si-OH

Si-H

Inhibited Growth

Thickness (Å)

Cycle

0 50 100 150 200 250 300
Inhibited Growth

- Nuclei form via deposition on...
  - Defects present on starting surface?
  - Defects generated during deposition?
  - Both?
  - What are the defects?
Controlling Nucleation

ALD Island Growth Models
- 2003 Alum & Green
- 2004 Puurunen & Vandervorst
- 2007 O. Nilsen et al.

ALD Blocking Layers
- ZnO: Yan, Marks, Chang et al. 2001

CVD Selectivity
- W, Si: Many authors
- Co: Yang et al. 2013

Improve Understanding of Nucleation and Selectivity

Metals → Metals
Dielectrics ↔ Dielectrics
Island Growth Expected from Chemistry

- **Steady-State ALD**: Brønsted–Lowry acid/base reaction
  - OH (acid) $\rightarrow$ H$^+$ + CH$_3$ ligand (base).
  - O$^-$: conjugate base; CH$_4$ is conjugate acid
  - **Surface maintains oxidation state**
    A: Si-OH + Al(CH$_3$)$_3$ $\rightarrow$ Si-O-Al(CH$_3$)$_2$ + CH$_4$
    B: Si-O-Al(CH$_3$)$_2$ + H$_2$O $\rightarrow$ Si-O-Al(OH)$_2$ + 2 CH$_4$

- **ALD Nucleation**: on metal (Si)
  - **Surface changes oxidation state**
    Si-H + H$_2$O $\rightarrow$ Si-OH (Si$^0$ $\rightarrow$ Si$^{+1}$)
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We can Fit Curve Using Island Growth Model

Geometric Island Distribution:

Multi-regional equation for surface coverage:

\[ S_{isl}^{(I)} = \pi \left( \frac{r}{b} \right)^2, \]

\[ S_{isl}^{(II)} = \left( \frac{r}{b} \right)^2 \left\{ \pi - 4 \left[ \arccos \left( \frac{b}{2r} \right) - \frac{b}{2r} \sin \left( \arccos \left( \frac{b}{2r} \right) \right) \right] \right\}, \]

\[ S_{isl}^{(III)} = 1. \]
We can Fit Curve Using Island Growth Model

Geometric Island Distribution:
O. Nilsen et al. JAP (2007)

Multi-regional equation for thickness:

\[
\mu = \begin{cases} 
(2/3)N_d \pi r^3, & r \leq R_{cov} \\
N_d \left\{ \pi R_{cov}^2 \sqrt{r^2 - R_{cov}^2} + \left(\frac{\pi}{6}\right)[3R_{cov}^2 + (r - \sqrt{r^2 - R_{cov}^2})^2][r - \sqrt{r^2 - R_{cov}^2}] \right\}, & r > R_{cov},
\end{cases}
\]
Random Model More Realistic than Geometric

Geometric Distribution:

Random Distribution:
Growth “Defect” Sites: Present and Created

On starting surface or passivation layer

Created during ALD

Defects on starting surface:
\( \dot{N} > 0.0 \text{ nm}^{-2} \)

Generated during ALD:
\( \dot{N} > 0 \text{ nm}^{-2} \text{s}^{-1} \)
Shape of Curve Determined by Defect Density

Fewer “Defect” Nucleation Sites (present or created)
Avrami Equation: Surface coverage vs time

\[ A_{\text{extended}} = \text{same size, no overlap} \]
\[ > A_{\text{film}} \]
\[ > A_0 \text{ (large t)} \]
easy to find vs t

Growth Rate: \( \dot{G} \); and Starting Nuclei Density: \( \hat{N} \)

During \( t = 0 \) to \( \tau \): \( A_{\text{ext}} = \pi A_0 \dot{G} \hat{N} \tau^2 \)

Avrami Equation:

\[ \frac{dA_{\text{film}}}{dA_{\text{ext}}} = 1 - \frac{A_{\text{film}}}{A_0} \]
Avrami Equation: Thickness vs time

- Surface Coverage
  
  \[ \frac{A_{film}}{A_0} = 1 - \exp\left( -\pi \dot{G} \hat{N} \tau^2 \right) \]

- Film thickness vs time – *one equation*

  \[ T_{film}(t) = \int_0^t A_{film} \dot{G} \, d\tau \]

- Need only: \( \dot{G} \) and \( \hat{N} \) to find \( T_{film}(t) \)

- Measure \( \dot{G} \), fit \( \hat{N} \)
Measure $\dot{G}$, fit $\hat{N}$

**Data:** HfO$_2$ ALD on SiO$_2$ and a-C:H

Stevens et al. Chem Mat (2018)
Avrami Model Fits Most Data Sets

Green et al. JAP 2002
HfO₂ ALD:
HfCl₄/H₂O on SiO₂ and Si-H

\[ \dot{G} = 0.052 \text{ nm/cycle} \]
\[ \dot{N} = 0.07 \text{ nm}^{-2} \]

R. Puurunen JAP 2004
HfO₂ ALD:
HfCl₄/H₂O on SiO₂ and Si-H

\[ \dot{G} = 0.047 \text{ nm/cycle} \]
\[ \dot{N} = 0.020 \text{ nm}^{-2} \]
Exception: Dynamic Coalescence

Observed for Pt ALD

Grillo et al. Chem Mat (2017)
Selectivity in Chemical Reactions

- A Chemical Reaction:
  \[ R_1 + R_2 \rightarrow D \quad \text{Desired} \]
  \[ R_1 + R_2 \rightarrow U \quad \text{Undesired} \]

- Definitions of Chemical Selectivity:

\[
D_{SU} = \frac{\text{Moles of } D \text{ produced}}{\text{Moles of } U \text{ produced}}
\]

\[
D_{SU} = \frac{\text{Rate of } D \text{ production}}{\text{Rate of } U \text{ production}}
\]

- \[ S_2 \]

\[
S_2 = \frac{\text{thickness on } S_1}{\text{thickness on } S_2}
\]

\[
S_2 = \frac{\theta_{S_1} - \theta_{S_2}}{\theta_{S_1} + \theta_{S_2}}
\]

\[ \theta = \text{Surface coverage} \]

Gladfelter, ChemMat (1993)

\[ S_2 \text{ changes with thickness} \]
Definitions of “Selectivity” in Deposition

1. Thermodynamics:
   “Selectivity, $R_{\Delta G}$ = ratio of driving force of the reaction on the desired surface to that on the undesired surface”
   **What is reaction with defects?**
2. Elemental Counts:
   “From the ratio of elemental counts, selectivity is 2000 to 1”:
   **Depends on thickness**
3. Film Thickness:
   “Selectivity is $\sim 6$ nm before substantial nucleation on non-growth surface”:
   **“Substantial” ?**
   “Selectivity is the amount of film we can grow in the desired region before nucleation in the non-growth region sets on.”
   **Depends on measurement method**
4. Film Growth Rate:
   “These deposition rates indicate a selectivity of $>185$”:
   **Depends on thickness**

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Singh et al. Chem Mat (2018)
Kalanyan et al. Chem Mat (2016)
Reinke et al. ACS AMI (2015)
McDonnell et al. JPCC (2013)
Carlsson & Boman JVSTA (1985)
Empirical Definition of Selectivity

• Gladfelter, Chem. Mat. 1993:
  Selectivity:
  \[ S_2 = \frac{\theta_{S1} - \theta_{S2}}{\theta_{S1} + \theta_{S2}} \]
  \( S \) ranges from 0 to 1

• \( \theta_{S1}, \theta_{S2} \): Coverage on “growth” and “non-growth” surfaces
  – \( \theta_s \) from SEM, TEM, AFM, STM, etc.
  – Atomic %: from XPS, AES, RBS, etc.

• Problem: Selectivity value changes with thickness, growth time
Nucleation Model and Definition of Selectivity

Fewer nucleation sites

Improved Selectivity

\[ S_2 = \frac{\theta_{S1} - \theta_{S2}}{\theta_{S1} + \theta_{S2}} \]

\[ S_2 = 0.9; \quad \frac{\theta_{S2}}{\theta_{S1}} \approx 0.052 \]

\[ t_s = 0.9 = 5.1 \text{ nm} \]
Example: $S = 0.9; t_{S=0.9} = 1.3 \text{ nm}$

\[
1S_2 = \frac{\theta_{S1} - \theta_{S2}}{\theta_{S1} + \theta_{S2}}
\]

Data from: Stevens et al. Chem Mat (2018)
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FIN-FET Transistor

Source: Samsung Exynos, 14nm FinFET, TECHINSIGHTS, 2015
“Self-Aligned Via” – Used Now
“Fully-Aligned Via” Needs Area-Selective Deposition
Approaches to Area-Selective Deposition

Inherent

Activated

Passivated
1. Pattern Si/SiO$_2$
2. ALD W: $\text{WF}_6 + \text{Si}_{(s)} \rightarrow \text{W} + \text{SiF}_4$: $\Delta G << 0$
   $\text{WF}_6 + \text{SiO}_2 \rightarrow$: $\Delta G >> 0$

Kalanyan et al. Chem Mat (2016)
Activated

1. Electron/ion beam + MeCpPtMe₃
2. ALD Pt: MeCpPtMe₃/O₂ at 300°C

\[ \dot{G} = 0.04 \text{ nm/cycle} \]
\[ \hat{N} = 0.05 \text{ nm}^{-2} \]
\[ t_{s=0.9} = 0.6 \text{ nm} \]

\[ \dot{G} = 0.04 \text{ nm/cycle} \]
\[ \hat{N} = 0.0005 \text{ nm}^{-2} \]
\[ t_{s=0.9} = 7.0 \text{ nm} \]

Mackus et al. JPPC (2013)

PO₂ = 2 mTorr

PO₂ = 800 mTorr
Activated

1. Pattern Pt
2. ALD Fe₂O₃: O₂ / t-butyl ferrocene at 250°C

Singh et al. Chem Mat (2018)
Passivated

Hydrophobic

Precursor Pulse

No adsorption on SAM

Reactant Pulse

Argon Purge

Hydrophilic

Argon Purge

KJ Park et al. APL (2005)
1. Solution coating of octadecyl-trichlorosilane (ODTS) monolayer on patterned SiO₂
2. HfO₂ ALD: Tetrakis(dimethyl-amido)hafnium Hf(N(CH₃)₂)₄ + H₂O

Deposition only on Si-H regions
Auger – No growth on oxide/ODTS regions

R.Chenet et al. APL (2005)
Renew surface and extend selectivity

Etching, Removal, Cleaning
...add third step.

Deposition: Etch/Renew:

Multiple steps...

Thickness

Number of ALD Cycles

Repeat
1. Solution deposit octadecylphosphonic acid (ODPA) SAM on Copper
2. Al₂O₃ ALD: TMA/H₂O at 150C
3. Acetic acid wet-etch removes SAM and nuclei

After wet etch:

\[
\hat{N} = 5 \times 10^{-5} \text{ nm}^{-2} \quad t_{S=0.9} = 20 \text{ nm} \\
\hat{N} = 2 \times 10^{-6} \text{ nm}^{-2} \quad t_{S=0.9} > 100 \text{ nm}
\]
1. Vapor deposit dodecanethiol (DDT) SAM on Copper
2. ZnO ALD: DEZ/H₂O at 150°C
3. Repeat

\[ \dot{G} = 0.18 \text{ nm/cycle} \]

\[ \hat{N} = 5 \times 10^{-7} \text{ nm}^{-2} \]

\[ t_s = 0.9 > 200 \text{ nm} \]

Fit Quality?

Hashemi et al. ACS AMI (2016)
In-situ Cleaning

1. Pattern Cu/SiO₂
2. ZrO₂ ALD: ZyALD/Ethanol at 200°C
3. Ethanol reduces CuO, inhibits ALD

Selvaraj et al. JVST (2014)
1. Expose Hacac (vapor inhibitor) to patterned SiO$_2$/Al$_2$O$_3$, adsorbs on SiO$_2$
2. One cycle of SiO$_2$ Plasma ALD: BDEAS (H$_2$Si[N(C$_2$H$_5$)$_2$]) & O$_2$ plasma
3. Repeat

\[ \dot{G} = 0.09 \text{ nm/cycle} \]

\[ \dot{N} = 0.032 \text{ nm}^{-2} \]

\[ t_s = 0.9 = 0.8 \text{ nm} \]

\[ \dot{N} = 0.020 \text{ nm}^{-2} \]

\[ t_s = 0.9 = 1.1 \text{ nm} \]

\[ \dot{N} = 0.007 \text{ nm}^{-2} \]

\[ t_s = 0.9 = 1.8 \text{ nm} \]

Mameli et al. ACS Nano (2017)
ALD + Etching

1. ~4 cycles Ta₂O₅ Plasma ALD: TBTDET & O₂ on pattern TiN/SiO₂ surface
2. NF₃ plasma etch
3. Repeat

Deposition
\[ \dot{G} = 0.10 \text{ nm/cycle} \]
\[ \hat{\eta} = 0.05 \text{ nm}^{-2} \]
\[ t_{s=0.9} = 1.0 \text{ nm} \]

Deposition + Etch
\[ \dot{G} = 0.04 \text{ nm/cycle} \]
\[ \hat{\eta} = 0.0002 \text{ nm}^{-2} \]
\[ t_{s=0.9} = 11.0 \text{ nm} \]

Vallat et al. JVSTA (2017)
WF₆ etches TiO₂ but not Al₂O₃ – Not Self-limiting

Ti + W + O + F …at Equilibrium:

< 100°C: WO₃(s) + TiF₄(s)
≥ 220°C: WO₂F₂(g) + TiF₄(g)

Al + W + O + F …at Equilibrium:

< 100°C: WO₃(s) + AlF₃(s)
≥ 220°C: WO₂F₂(g) + AlF₃(s) Solid
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Self-Limiting Plasma/Ion Atomic Layer Etching

Self-Limiting Thermal Atomic Layer Etching

Self-Limiting Thermal Atomic Layer Etching

Fluorination

Ligand-Exchange

HF → H₂O

Al₂O₃ → AlF₃ → AlF(CH₃)₂

Etched Layer Thickness

Younghee Lee, C. Huffman, S.M. George, Chem Mat (2016)
Self-Limiting Thermal Atomic Layer Etching

Younghhee Lee, C. Huffman, S.M. George, Chem Mat (2016)
Self-Limiting ALE: TiO$_2$ + WF$_6$/BCl$_3$

\[ \text{WF}_6 + \text{TiO}_2 \rightarrow \text{WO}_3(s) + \text{TiF}_4(s) \]

\[ \text{BCl}_3 + \text{WO}_3(s) + \text{TiF}_4(s) \rightarrow \text{BF}_3(g) + \text{WOCl}_4(g) + \text{TiCl}_4(g) + \text{B}_2\text{O}_3(s) \]

\[ \lesssim 190\text{C:} \]

Quartz Crystal Microbalance

Lemaire & Parsons, Chem Mat (2017)
Selective Area CVD of Cobalt

- CVD chemistry currently ahead of ALD for selective deposition

Selective Co CVD
Up to 9 nm

C.-C. Yang et al. Microelectronic Engineering (2013)
Summary

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