

Chemical Vapor Deposition and Atomic Layer Deposition

Anil Kottantharayil
Department of EE, IIT Bombay

1

Outline

- Introduction
- Physical Vapor Deposition (PVD)
 - Conceptual system
 - Evaporation
 - Film growth processes
 - Sputter deposition
 - Pulsed laser deposition
- Chemical Vapor Deposition (CVD)
 - Thermal CVD
 - CVD kinetics
 - Plasma enhanced CVD (PECVD)
- Atomic Layer Deposition (ALD)

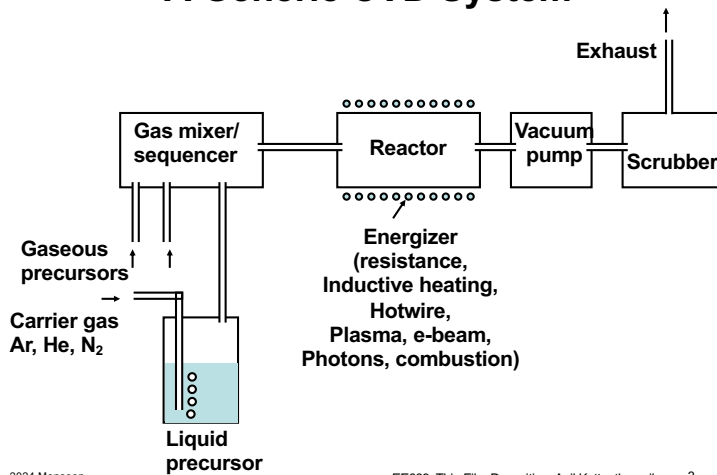
2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil

2

2

A Generic CVD System



2024 Monsoon

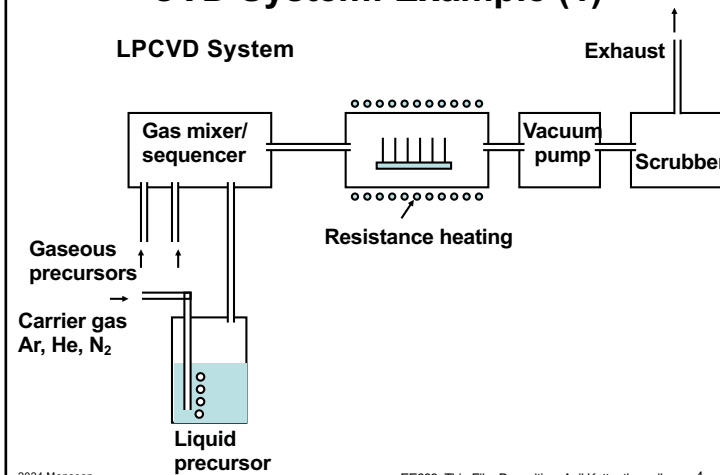
EE669: Thin Film Deposition: Anil Kottantharayil

3

3

CVD System: Example (1)

LPCVD System

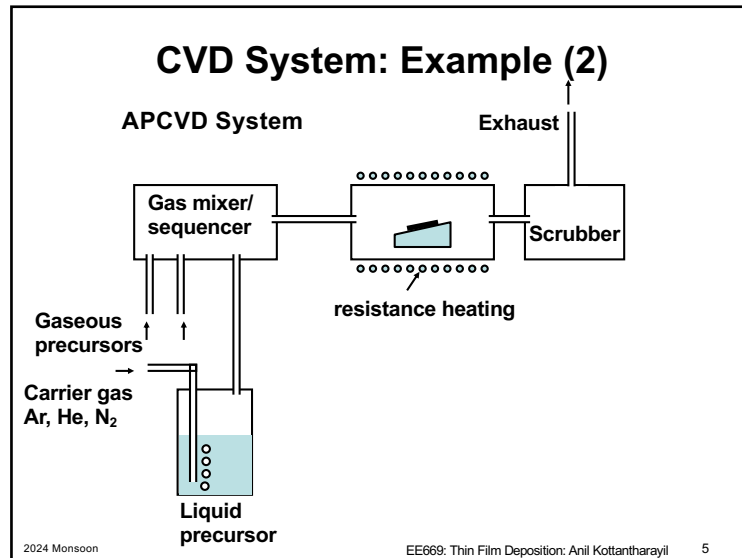


2024 Monsoon

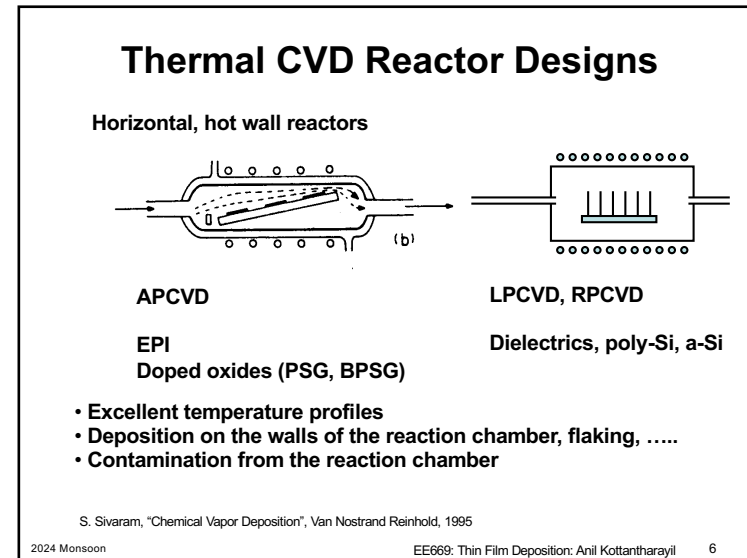
EE669: Thin Film Deposition: Anil Kottantharayil

4

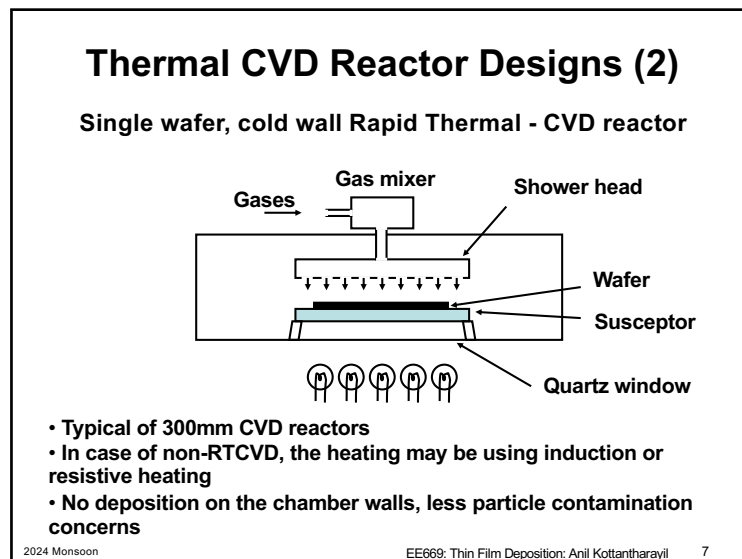
4



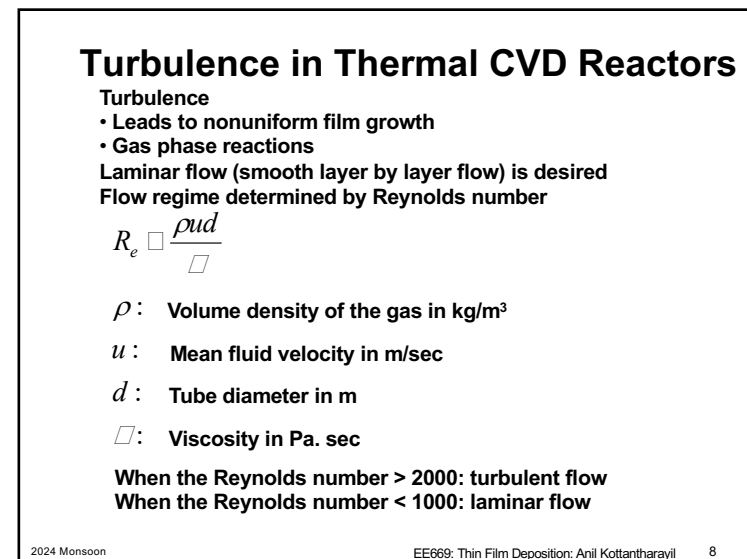
5



6

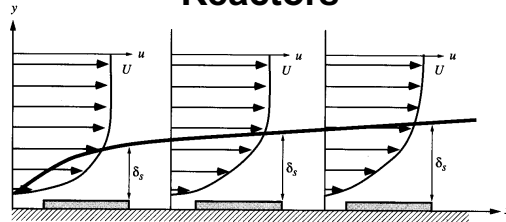


7



8

Boundary Layer in Thermal CVD Reactors



$$\delta_s(x) \propto \left(\frac{\Delta x}{\rho U} \right)^{1/2}$$

Where all the parameters are as defined on slide 8. U is the velocity of the gas in the main flow above the boundary layer.

Plummer et al., "Silicon VLSI Technology", Prentice Hall, 2000

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 9

9

Boundary Layer in Thermal CVD Reactors (2)

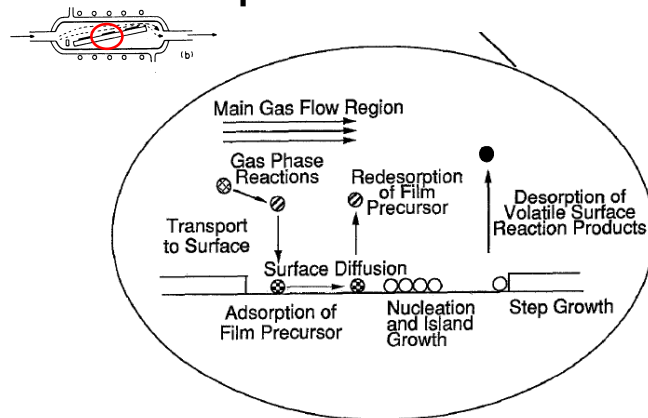
- The boundary layer plays an important role in determining the layer growth kinetics
- In laminar flow regime, the reactants are transported from the main flow by diffusion to the wafer surface through the boundary layer
- Reaction byproducts are transported from the wafer surface to the flow through the boundary layer
- Thicker the boundary layer, longer it takes for the reactants to diffuse to the wafer surface \rightarrow lower reactant flux arriving on the wafer surface \rightarrow slower film growth rate if the growth is limited by availability of reactants

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 10

10

Deposition Process



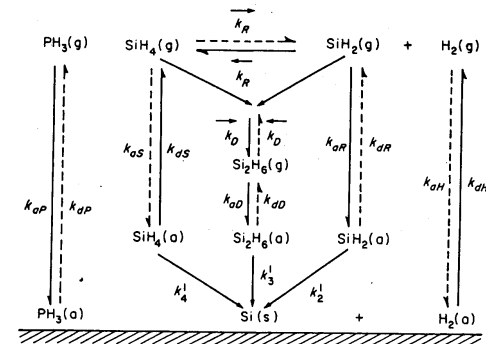
D. G. Coronell and K. F. Jensen, J. Computer-Aided Materials Design, 1993, pp. 3-26

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 11

11

Deposition Process: Reaction pathways



Si deposition by thermal decomposition (pyrolysis) of SiH_4

Hitchman and Jensen, Chapter 1 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 12

12

Deposition Process: Reaction pathways (2)

Pyrolysis of SiH_4 is one of the best understood CVD process: 27 contributing reactions out of the 120 possible elementary reactions

→ Complex to analyze

- Gas phase chemical reactions
- Adsorption rates
- Surface reactions
- Desorption rates

An easier approach for the study of deposition rates is to consider the overall reaction as one of the rate limiting steps.

Such an analysis has its limitations.

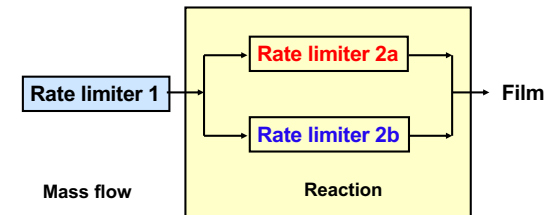
Hitchman and Jensen, Chapter 1 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 13

13

CVD kinetics



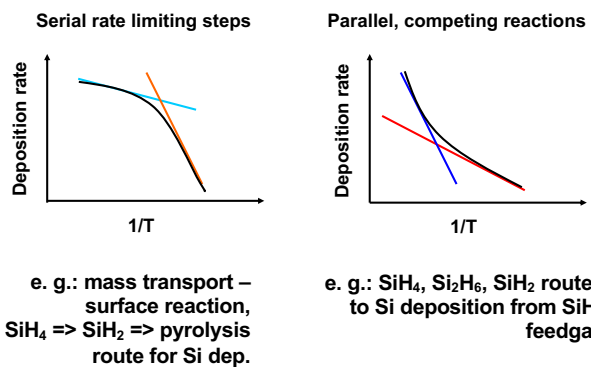
Hitchman and Jensen, Chapter 1 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 14

14

CVD kinetics (2)



2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 15

15

CVD kinetics (4)

The deposition process consist of the following:

1. Transport of the reactants through the boundary layer to the wafer surface
2. Adsorption of the reactants on the wafer surface. Re-emission of the adsorbed species back into the boundary layer.
3. Surface processes, including decomposition, reaction, surface migration and nucleation
4. Desorption of by-products from the surface to the boundary layer
5. Transport of the by-products across the boundary layer into the main flow

Mass transport

Surface reactions

Not rate limiting

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 16

16

CVD Kinetics (5)

- The rate of deposition in cm/sec can be obtained as

$$t'_{film} = \frac{1}{\frac{1}{k_s} + \frac{1}{h_G}} \frac{C_G}{N}$$

- Where,
 - k_s is the surface reaction rate in cm/sec
 - h_G is the mass transfer coefficient in cm/sec, $= D/\delta_s$
 - C_G is the concentration of the precursor in the main flow, in molecules per cm^3
 - N is the number density of the product atoms in the growing film. Example: $N = 5 \times 10^{22}$ atoms per cm^3 for Silicon

For derivation, see the Plummer 2023

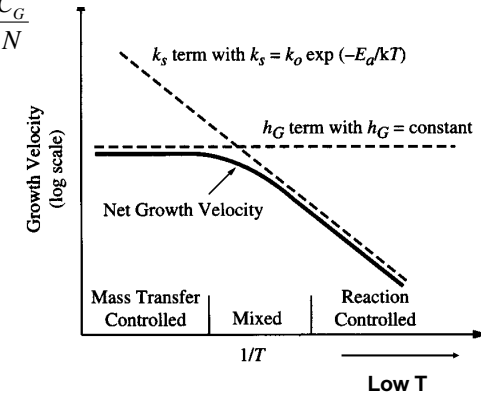
2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 17

17

CVD Kinetics (6)

$$t'_{film} = \frac{1}{\frac{1}{k_s} + \frac{1}{h_G}} \frac{C_G}{N}$$



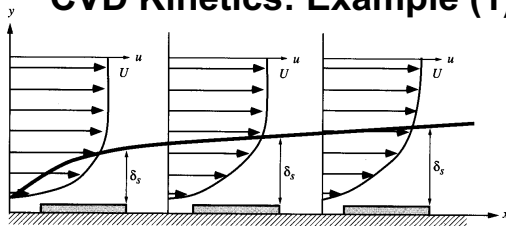
Silicon VLSI Technology, J. D. Plummer, M. D. Deal, P. B. Griffin

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 18

18

CVD Kinetics: Example (1)



- In mass transport limited regime, growth rate decreases with x
- It takes more time for reactants to diffuse through the thicker boundary layer

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 19

19

CVD Kinetics: Example (2)

$$t' \propto \frac{1}{\frac{1}{k_s} + \frac{1}{h_G}} \frac{C_G}{N} \propto \frac{1}{\frac{1}{k_s} + \frac{1}{\frac{D}{\delta_s}}} \frac{C_G}{N}$$

- In a gas, diffusivity is inversely proportional to pressure
- As pressure is reduced $\Rightarrow D$ increases $\Rightarrow h_G$ increases
- Even though the boundary layer thickness also increases, the increase is significantly less than the increase in D

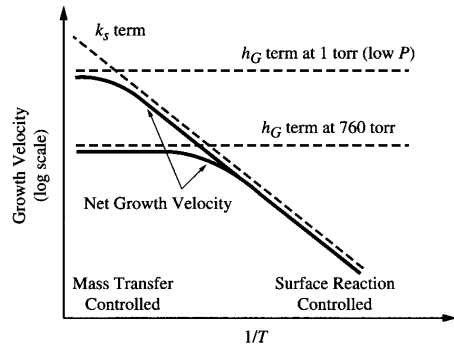
2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 20

20

CVD Kinetics: Example (2a)

Low Pressure Chemical vapor deposition (LPCVD)



Higher temperature deposition in reaction controlled regime.

Silicon VLSI Technology, J. D. Plummer, M. D. Deal, P. B. Griffin

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 21

21

References

CVD:

- Hugh O. Pierson, Handbook of chemical vapor deposition (CVD) : principles, technology and applications, Noyes Pub., 1992.
- Langmuir, "The vapor pressure of metallic Tungsten", Physical Review, November 1913.
- S. Sivaram, "Chemical Vapor Deposition: thermal and plasma deposition of electronic materials", Van Nostrand Reinhold, 1995.
- Ohshita et al., Thin Solid Films, 1 March 2002, pp. 215.
- Sears and Salinger, "Thermodynamics, Kinetic Theory and Statistical Thermodynamics", Third Ed. Narosa Pub. House, : 1975.
- <http://encyclopedia.airliquide.com>
- J. D. Plummer, M. D. Deal, and P. B. Griffin, "Silicon VLSI technology : fundamentals, practice and modeling", Prentice-Hall, 2000.

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 22

22

References

CVD:

- D. G. Coronell and K. F. Jensen, J. Computer-Aided Materials Design, 1993, pp. 3-26.
- Hitchman and Jensen (ed.), "Chemical Vapor Deposition Principles and Applications", Academic Press, 1993.
- Koenig and Maissel, IBM J. R & D, 1970.
- Angus Rockett, "Material Science of Semiconductors", Springer Verlag, 2008

ALD:

- Collection of Ph. D. thesis on ALD available at <http://www.cambridgenanotech.com/klc/theses.php>
- Jill Becker, Ph. D. thesis, MIT, 2002.
- R. L. Puurunen, Journal of Applied Physics 2005.
- R. L. Puurunen, Journal of Applied Physics 2004.
- R. L. Puurunen, Ph. D. thesis, University of Helsinki, available at <http://lib.tkk.fi/Diss/2002/isbn9512261421/isbn9512261421.pdf>

2024 Monsoon

EE669: Thin Film Deposition: Anil Kottantharayil 23

23