Lecture-10

Atomic Layer Deposition

Two-Dimensional Nanostructures Cont…

(Ref: Guozhong Cao;
Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

Atomic Layer Deposition (ALD)

- ALD is a unique thin film growth method
- It differs from other thin film deposition methods
- Most distinctive feature of ALD has

  - Self-limiting growth nature

  - Each time only one atomic/molecular layer grow

  - Best possibility to control film thickness (~ nm range)

- Ritala & Leskela published excellent reviews on ALD

- In literature, ALD is also called as:

    - Atomic Layer Epitaxy (ALE)

    - Atomic Layer Growth (ALG)

    - Atomic Layer CVD (ALCVD), and

    - Molecular Layer Epitaxy (MLE)

- ALD can be considered as special modification of
  - Chemical Vapor Deposition, or
  - Combination of
    - (i) Vapor-Phase Self-Assembly, and
    - (ii) Surface Reaction
- In a typical ALD process,
  - Surface is activated by chemical reaction

- Introduction of precursor molecules in chamber

  - They reacts with active surface species

  - Form chemical bonds with substrate

- Precursor molecules do not react with each other

At this stage:

- No more than one molecular layer will be deposited

- In the next stage, monolayer is activated again

  - Through chemical reaction

  (Monolayer of precursor molecules that are chemically bonded to the substrate)

- Either the same or different precursor molecules

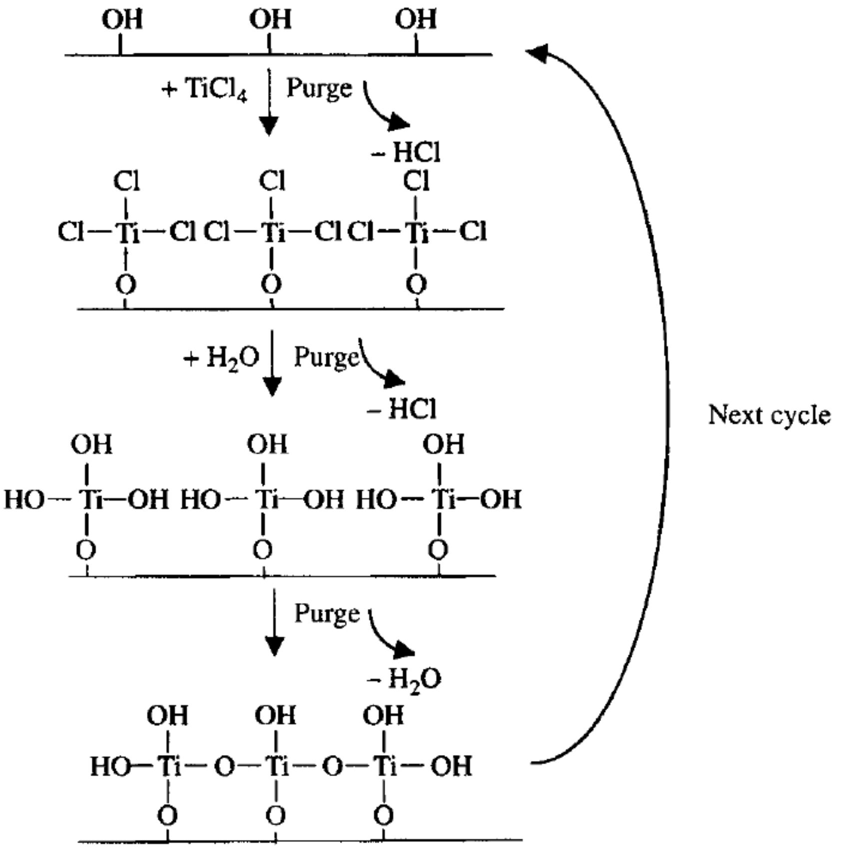
  - Subsequently introduced to deposition chamber

  - React with activated monolayer (previously deposited)

- As the steps repeat, more molecular or atomic layers

  - Deposited one layer at a time

- The process of titania film growth by ALD.
- Initially, the substrate is hydroxylated
- Precursor, titanium tetra-chloride is introduced



Schematic illustrating the principal reactions and processing steps for the formation of titania film by ALD

- Titanium tetrachloride will react with

  - Surface hydroxyl groups

  - Through surface condensation reaction

  $TiCl_4$ + (HO)Me → Cl_3Ti-O-Me + HCl

  where, Me: Metal or Metal Oxide Substrates

- Reaction will stop when all surface hydroxyl groups

  - Reacted with titanium tetrachloride

- Thereafter, purging process of following take place

  - Gaseous by-product, HCl, and

  - Excess precursor molecules

- Water vapor is subsequently added to the system

- Titanium trichloride undergo hydrolysis reaction:

(chemically bonded onto the substrate surface)

$$Cl_3Ti\text{-}O\text{-}Me + H_2O \rightarrow (HO)_3Ti\text{-}O\text{-}Me + HCl$$

- Neighboring hydrolyzed Ti precursors subsequently condensate to form Ti-O-Ti linkage:

$$(HO)_3Ti\text{-}O\text{-}Me + (HO)_3Ti\text{-}O\text{-}Me$$

$$\rightarrow Me\text{-}O\text{-}Ti(OH)_2\text{-}O\text{-}Ti(HO)_2\text{-}O\text{-}Me + H_2O$$

- By-product HCl and excess H_2O will be removed from the reaction chamber.

- One layer of TiO_2 is grown by

  - Completion of 1-cycle of chemical reactions

- Surface hydroxyl groups are ready to react with

  - Titanium precursor again in next cycle

- By repeating the above steps, second & many more

  - TiO_2 layers can be deposited in controlled way

- Growth of ZnS film by ALD process
- Precursors for synthesis: $ZnCl_2$ and H_2S
- In the process of synthesis:
  - $ZnCl_2$ is chemisorbed on the substrate
  - Then H_2S is introduced to react with $ZnCl_2$
  - ZnS monolayer is deposited on substrate
  - HCl is released as a by-product

Requirements for ALD precursors

Requirement	*Comments*
Volatility	For efficient transportation, a rough limit of 0.1 torr at the applicable maximum source temperature Preferably liquids or gases
No self-decomposition	Would destroy the self-limiting film growth mechanism
Aggressive and complete reactions	Ensure fast completion of the surface reactions and thereby short cycle times Lead to high film purity No problems of gas phase reactions
No etching of the film or substrate material	No competing reaction pathways Would prevent the film growth
No dissolution to the film	Would destroy the self-limiting film growth mechanism
Un-reactive byproduct	To avoid corrosion Byproduct re-adsorption may decrease the growth rate
Sufficient purity	To meet the requirements specific to each process
Inexpensive	
Easy to synthesize & handle	
Nontoxic and environmentally friendly	

- Compared to other vapor phase deposition methods

  - ALD offer advantages in following aspects:

  (i) Precise control of film thickness, and

  (ii) Conformal coverage

- Precise control of film thickness is due to

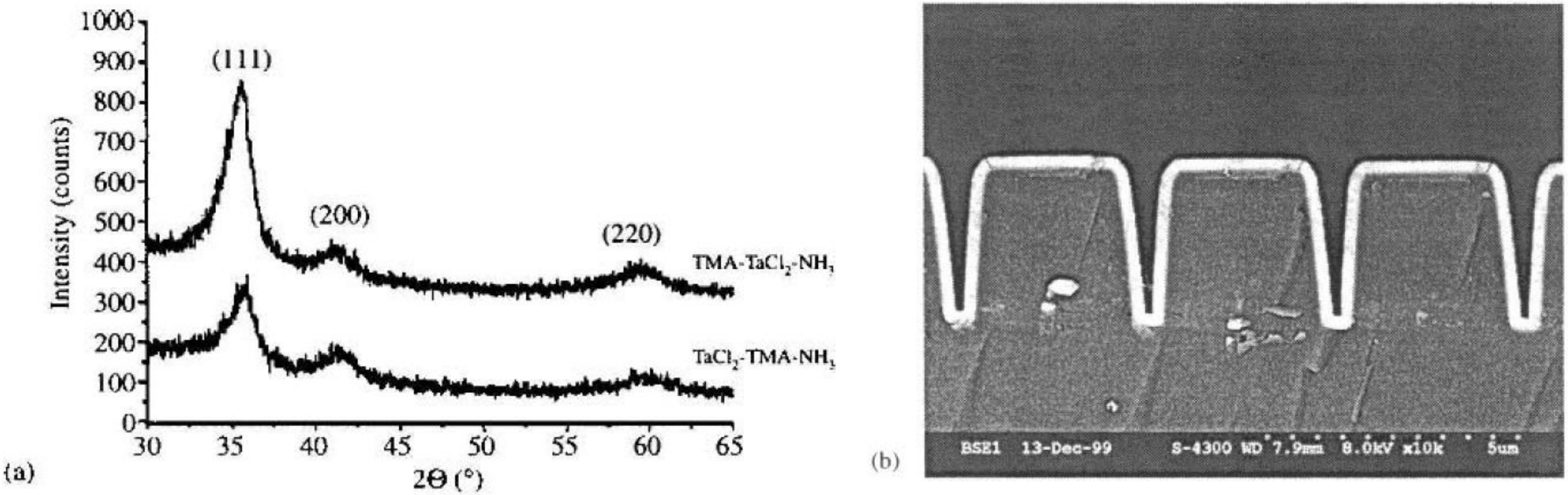
  - Nature of self-limiting process, and

  - Thickness of a film can be set digitally

(By counting number of reaction cycles)

- Film deposition is immune to variations caused by
  - Nonuniform distribution of Vapor, or
  - Temperature in the reaction zone
- It leads to the conformal coverage during synthesis process
- Excellent conformal coverage can be achieved when
  - At all surfaces, sufficient precursor doses &
  - pulse time reaches saturated state at each step
  - no extensive precursor decomposition takes place

- Polycrystalline film shows perfect conformality
- Deposition Temperature: 350°C
- Precursors: $TaCl_5$, NH_3 & Trimethylaluminum (TMA)



(a) X-ray diffraction Spectra, (b) Cross-sectional SEM image of 160 nm Ta(Al)N(C) film on patterned silicon wafer

Ref.: P.Allen, M.Juppo, M.Ritala, T.Sajavaara, J.Keinonen, and M.Leskela, J. Electrochem. Soc., 148(2001)G566.

- ALD is an established technique for production of

    - large area electroluminescent displays, and

    - likely future method for the production of

        # Thin films needed in micro-electronics

- Many potential applications of ALD are discouraged

    - Due to its low deposition rate, typically < 0.2 nm

        (less than half a monolayer per cycle)

- For silica deposition, to complete a cycle of reactions

  - typically requires more than 1 min

- Some recent efforts have been directed towards

  - development of rapid ALD deposition method

- For example, highly conformal layers are deposited

    - amorphous silicon dioxide, and

    - aluminum oxide nano-laminates

    - @ rate of 12 nm or < 32 monolayers per cycle

- Method is referred as “alternating layer deposition”

- Exact deposition mechanism in each cycle is unknown
- Precursor employed in experiment,
    - tris(tert-butoxy)silanol, can react with each other
    - thus the growth is not self-limiting

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