Al$_2$O$_3$, Its Different Molecular Structures, Atomic Layer Deposition, and Dielectrics

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Project Proposal

- Tunneling versus crystalline structure.
  - Al₂O₃: Evaluate the structures of aluminum oxide on “as-deposited” Antenna-Coupled Metal-Oxide-Metal Diodes (ACMOMD) with aluminum oxide after annealing at 1100°C (e.g., 2hrs), using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Electron Energy Loss Spectroscopy (EELS).
  - Measurement: curvature coefficient for Metal-Oxide-Metal diodes (MOMs) with oxides of different crystal structures.
  - HfO₂: For further study, incorporate hafnium oxide with aluminum oxide in forming thin layers using ALD and assess structure/function relationship.

- Currently, we are at the point of analyzing surface of the MOM diodes and analyzing crystalline structures.
Aluminum oxide has several crystalline structures; all form as a result of annealing to specific temperatures. Alpha alumina (α- Al₂O₃) is the most stable and is created when the aluminum oxide is annealed to at least 1100°C.

This crystalline structure can be used as a dielectric device due to the structure of its molecules. This allows electron tunneling to be limited when the device is turned off but allows tunneling when an electric current is running through the device.

Al₂O₃ is a good choice for being a dielectric for several reasons:
- It has band gap of ~9eV; this is 2.8eV greater than that of SiO₂.
- It has a dielectric constant of ~9. This is more than twice the dielectric constant of SiO₂ (another compound used for dielectrics).
- Al₂O₃ has several different molecular structures, each occurring from annealing to different temperatures.
- Aluminum oxide is relatively stable at high temperatures, making it more versatile than other dielectric compounds.
- Each distinct type of aluminum oxide has its own distinct properties. For example, when tested with Fourier Transform Infrared (FTIR) and Ultra-Violet (UV) radiation, transmittance for different types of Al₂O₃ varied. (see charts on next two slides)
Fig. 1. FTIR spectra of prepared aluminum oxide films on Si substrates: (a) recorded from as-deposited films by ECR-PLD from a metallic Al target with oxygen plasma assistance, (b) recorded from films annealed at 1000 °C in air and (c) recorded from films annealed at 1100 °C in air.
Fig. 4. UV and IR optical transmission spectra of (a) as-deposited aluminum oxide films on sapphire substrates and (b) $\alpha$-Al$_2$O$_3$ films on sapphire substrates prepared by ECR-PLD and followed by heat annealing at 1100 °C in air. (c) For comparison, a transmission spectrum of a bare sapphire substrate is also displayed.
Properties of Al₂O₃

- Aluminum oxide can possess several different structures. As the compound is annealed for longer periods of time and at higher temperatures, it changes structure, which ultimately influences the properties of the compound.
  - The transition of Al₂O₃ with heat:
    - Gibbsite → Boehmite (γ-AlOOH) → γ-Alumina (γ-Al₂O₃) → δ-Alumina (δ-Al₂O₃) → θ-Alumina (θ-Al₂O₃) → α-Alumina (α-Al₂O₃)
    - The end of this anneal process will yield the most thermodynamically stable of all the forms: α-Alumina (α-Al₂O₃).

- Several other transition aluminas have been identified such as η, κ, χ, and β aluminas.
- As a result of α-alumina’s molecular structure, it is thought to be a good dielectric.
- It also has thermodynamic stability when used with Si.
- The figures on the following slides show some of the different structures of Al₂O₃. Notice how much the structure changes from Gibbsite to α-Alumina.
Models of $\text{Al}_2\text{O}_3$ Crystalline Structure

Unit Cell of $\text{Al}_2\text{O}_3$

Closest Packing Model (Oxygen)

Tetrahedral “Holes” in Closest Packing Array

Octahedral “Holes” in Closest Packing Array

http://www.chem.lsu.edu/htdocs/people/sfwatkins/ch4570/lattices/lattice.html
Structure of Gibbsite

Structure of γ-Alumina (γ- Al₂O₃)

Fig. 1 Model for the spinel structure of γ-Al₂O₃ with all the tetrahedral and octahedral cationic sites filled by Al atoms for clarity.

Structure of $\alpha$- $\text{Al}_2\text{O}_3$
Spectroscopic Characteristics of $\text{Al}_2\text{O}_3$

- Each structure of $\text{Al}_2\text{O}_3$ has its own distinct spectroscopic results.
- As crystalline structure begins to form, FTIR can identify different atomic bonds by different wavenumbers.
- The spectra of $\alpha$-$\text{Al}_2\text{O}_3$ can be identified by distinct peaks at 440, 567 and 650 cm$^{-1}$.
- Amorphous (not annealed) $\text{Al}_2\text{O}_3$ has a broad band of absorbance from 500-900 cm$^{-1}$. This illustrates the vacancies and lack of consistency in the bond length of Al and O.
- X-ray Diffraction is another technique used in this study, where an X-ray is shot at the sample and analyzed by how the X-rays diffract off of the sample. From that, the results can be used to identify the structure of the sample.
Atomic Layer Deposition (ALD)

- Introduced in 1974 by Dr. Tuomo Suntola in Finland, ALD is used to deposit very thin layers of material onto substrate. These layers are about the thickness of one atom.
- ALD is one of the most accurate processes commonly used for depositing thin layers onto substrate.
- More recently, ALD has been used in the production of dielectrics.
- ALD process:
  1. Releases precursor gas pulses for deposition one layer at a time.
  2. Introduces a second gas to react with the first, making a monolayer of film on the surface of the wafer.
  3. Since each pair of gas cycles is one layer, the process can be controlled precisely by the number of depositions. Steps one and two are repeated as necessary.
Atomic Layer Deposition (ALD)

Advantages and disadvantages of ALD

Advantages:
- The process uses stoichiometric films with a large area.
- It is more precise than similar techniques.
- There is no heating needed for deposition.
- ALD has a gentle deposition process, allowing for a much larger range of wafer composition.

Disadvantages:
- The ALD process is much slower than chemical vapor deposition (CVD).
- The type and variety of materials deposited is fair compared to other processes.
References

- Myo Min Thein, Atomic Layer Deposition (ALD), http://courses.ee.psu.edu/ruzyllo/ee518/Atomic%20Layer%20Deposition.ppt#256,1,AtomicLayerDeposition(ALD).
Thank You!!

- We would like to thank the University of Notre Dame for making RET available on their campus for us.

- Also, I would like to give many thanks to:
  - Douglas Sisk, Ph.D., My mentor for this project
  - Badri Tiwari, Graduate student working with us on this project
  - Wolfgang Parod Ph.D., Our mentor from the University of Notre Dame