Al_2O_3, Its Different Molecular Structures, Atomic Layer Deposition, and Dielectrics

Mark Imus

Douglas Sisk, Ph.D., Mentor

Marian High School

RET Program

University of Notre Dame

Project Proposal

- Tunneling versus crystalline structure.
  - Al_2O_3: 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.
  - HfO_2 : 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.

Background Information

- Aluminum oxide has several crystalline structures; all form as a result of annealing to specific temperatures. Alpha alumina (α- Al_2O_3) 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.
- Al_2O_3 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 $SiO_{2.}$
  - It has a dielectric constant of ~9. This is more than twice the dielectric constant of SiO_2 (another compound used for dielectrics).
  - Al_2O_3 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 Al_2O_3 varied. (see charts on next two slides)

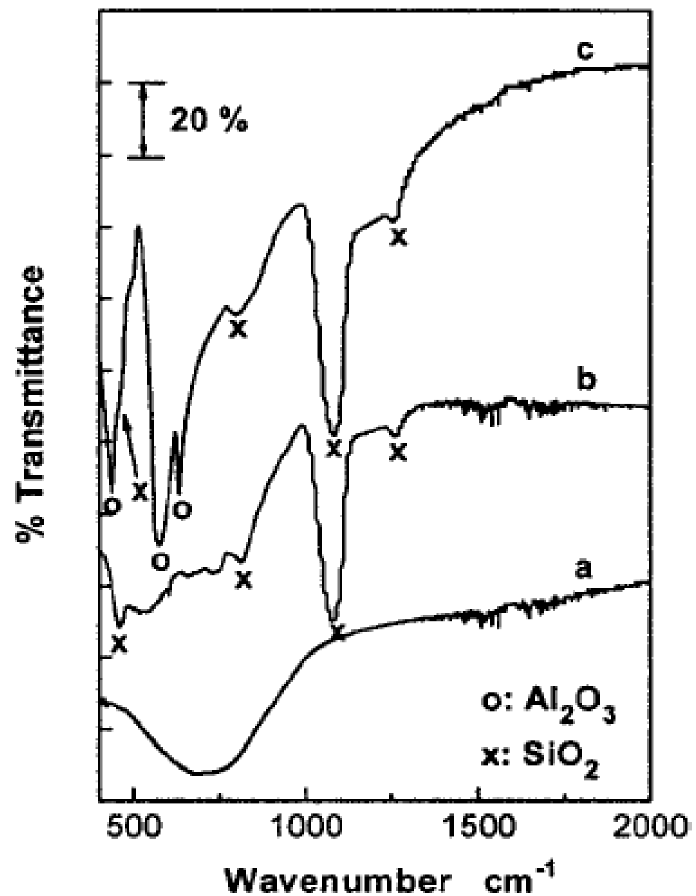


FIG. 1. FTIR spectra of prepared aluminum oxide films on Si substrates: (a) recorded from as-deposited films by ECR-PLD from a metallic Al target with oxygen plasma assistance, (b) recorded from films annealed at 1000 °C in air and (c) recorded from films annealed at 1100 °C in air.

- D. Yu, et al., J. *Vac. Sci Technol.* A, **26**, 380, (2008).

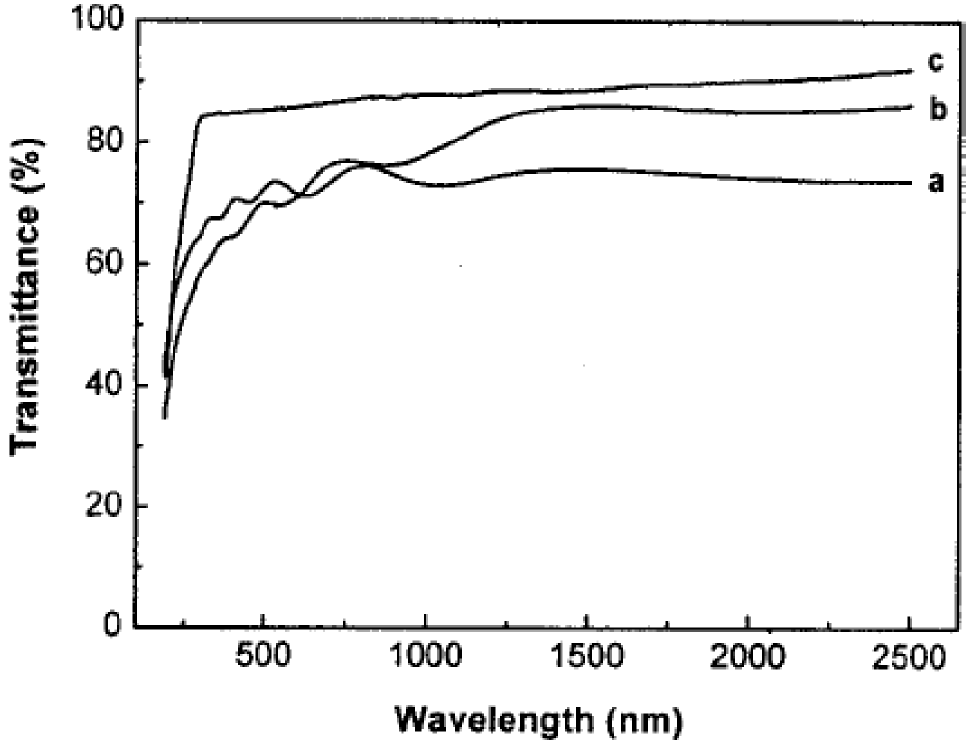


FIG. 4. UV and IR optical transmission spectra of (a) as-deposited aluminum oxide films on sapphire substrates and (b) α-Al_2O_3 films on sapphire substrates prepared by ECR-PLD and followed by heat annealing at 1100 °C in air. (c) For comparison, a transmission spectrum of a bare sapphire substrate is also displayed.

D. Yu, et al., J. *Vac. Sci Technol*. A, **26**, 380, (2008).

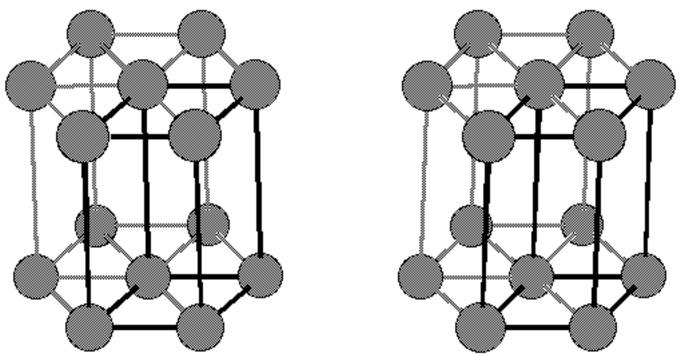
Properties of Al_2O_3

- 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 Al_2O_3 with heat:
    - Gibbsite→Boehmite (γ-AlOOH)→γ-Alumina (γ- Al_2O_3)→δ-Alumina (δ- Al_2O_3)→θ-Alumina (θ -Al_2O_3)→α-Alumina (α- Al_2O_3)
    - The end of this anneal process will yield the most thermodynamically stable of all the forms: α-Alumina (α- Al_2O_3).

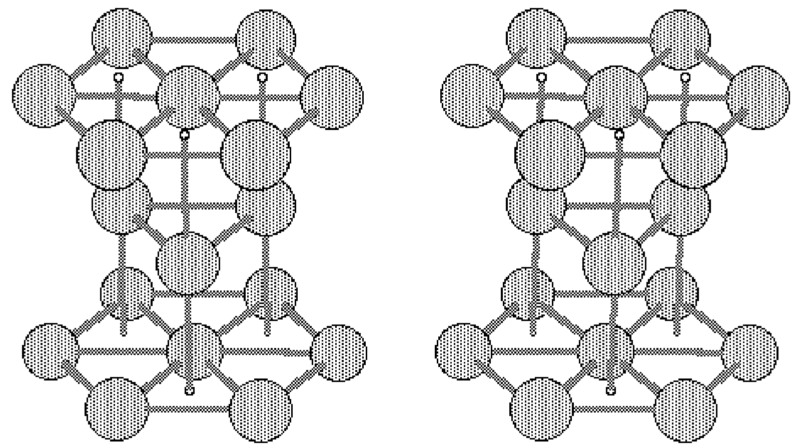
- Several other transition aluminas have been identified such as η, κ, χ, and β aluminas.
- As a result of α-alumina's molecular structure, it is thought to be a good dielectric.
- It also has thermodynamic stability when used with Si.
- The figures on the following slides show some of the different structures of Al_2O_3. Notice how much the structure changes from Gibbsite to α-Alumina.

Models of Al_2O_3 Crystalline Structure

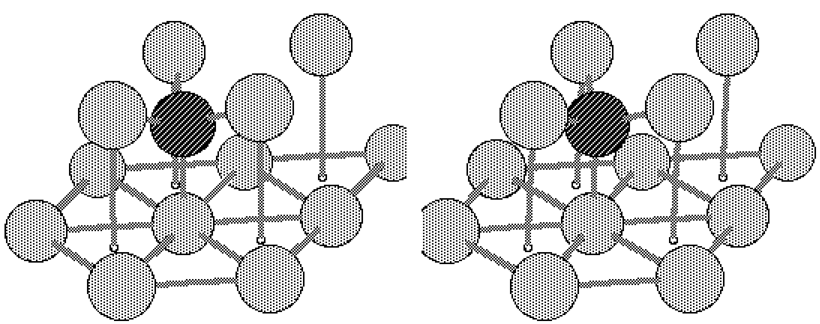
Unit Cell of Al_2O_3



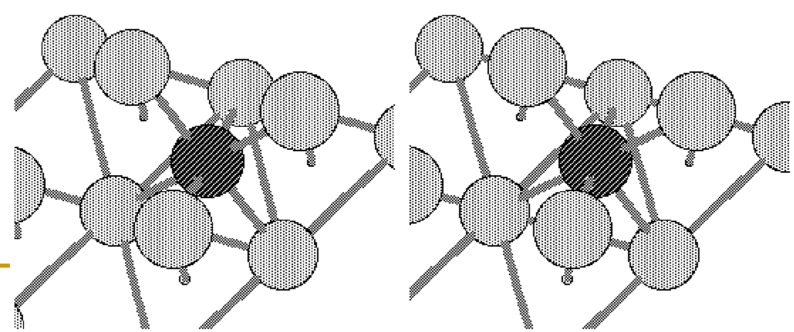
Closest Packing Model (Oxygen)



Tetrahedral “Holes” in
Closest Packing Array

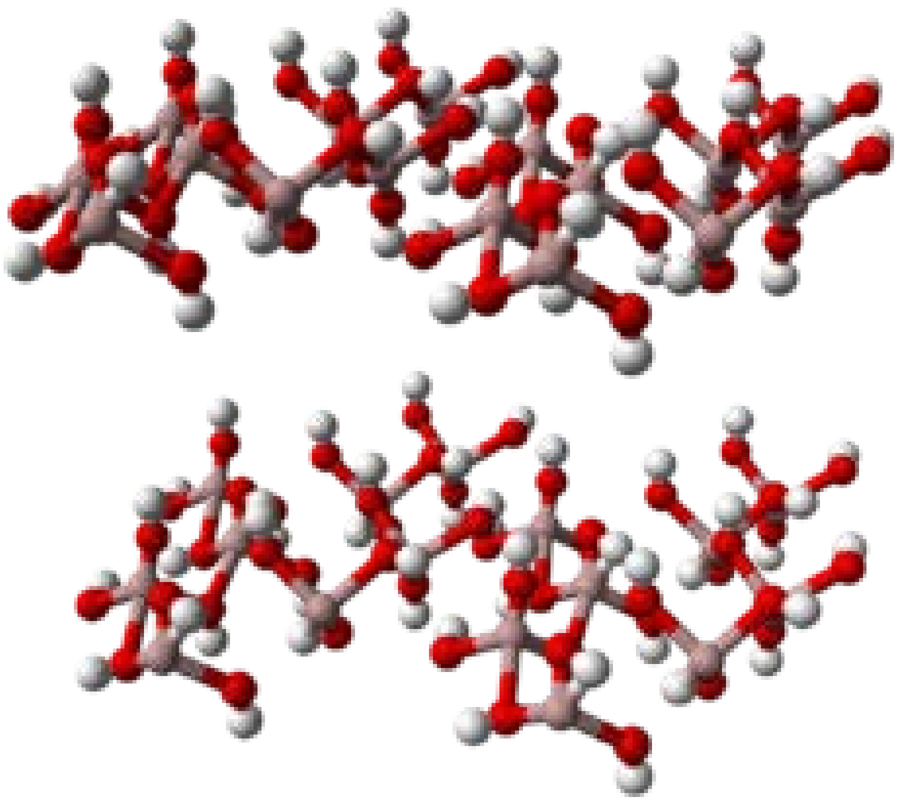


Octahedral “Holes” in
Closest Packing Array



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

Structure of Gibbsite



http://wpcontent.answers.com/wikipedia/commons/thumb/f/f6/Gibbsite-crystal-3D-balls.png/250px-Gibbsite-crystal-3D-balls.png

Structure of γ-Alumina (γ- Al_2O_3)

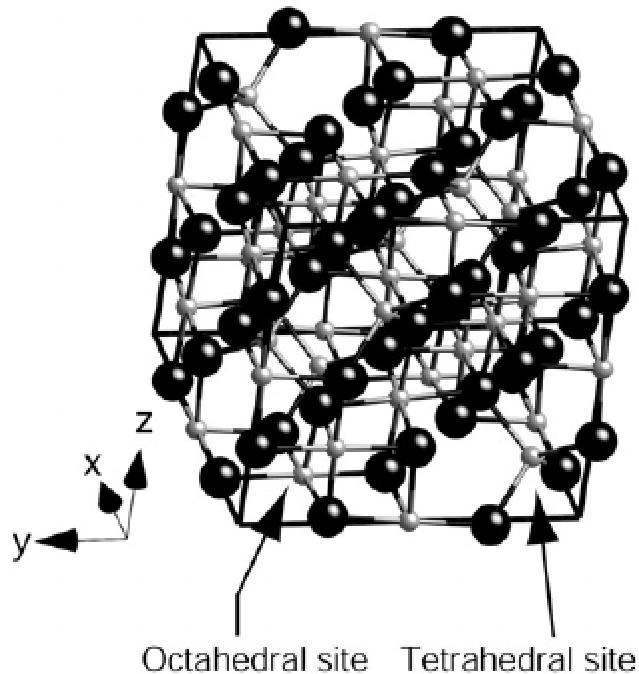
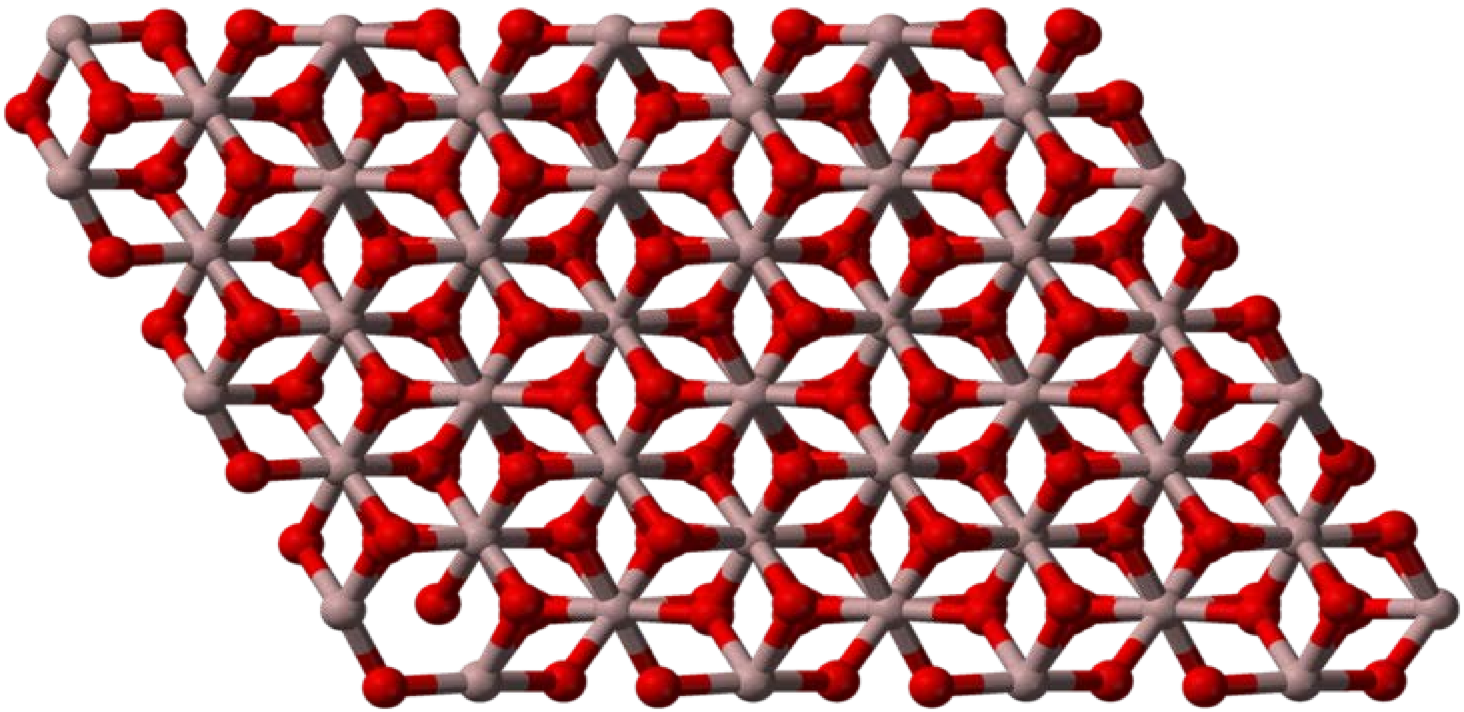


Fig. 1 Model for the spinel structure of γ-Al_2O_3 with all the tetrahedral and octahedral cationic sites filled by Al atoms for clarity.

Taken from Heijnsbergen et al.,Phy. Chem. Chem. Phys., 5, 2515 (2003).

Structure of α- Al_2O_3

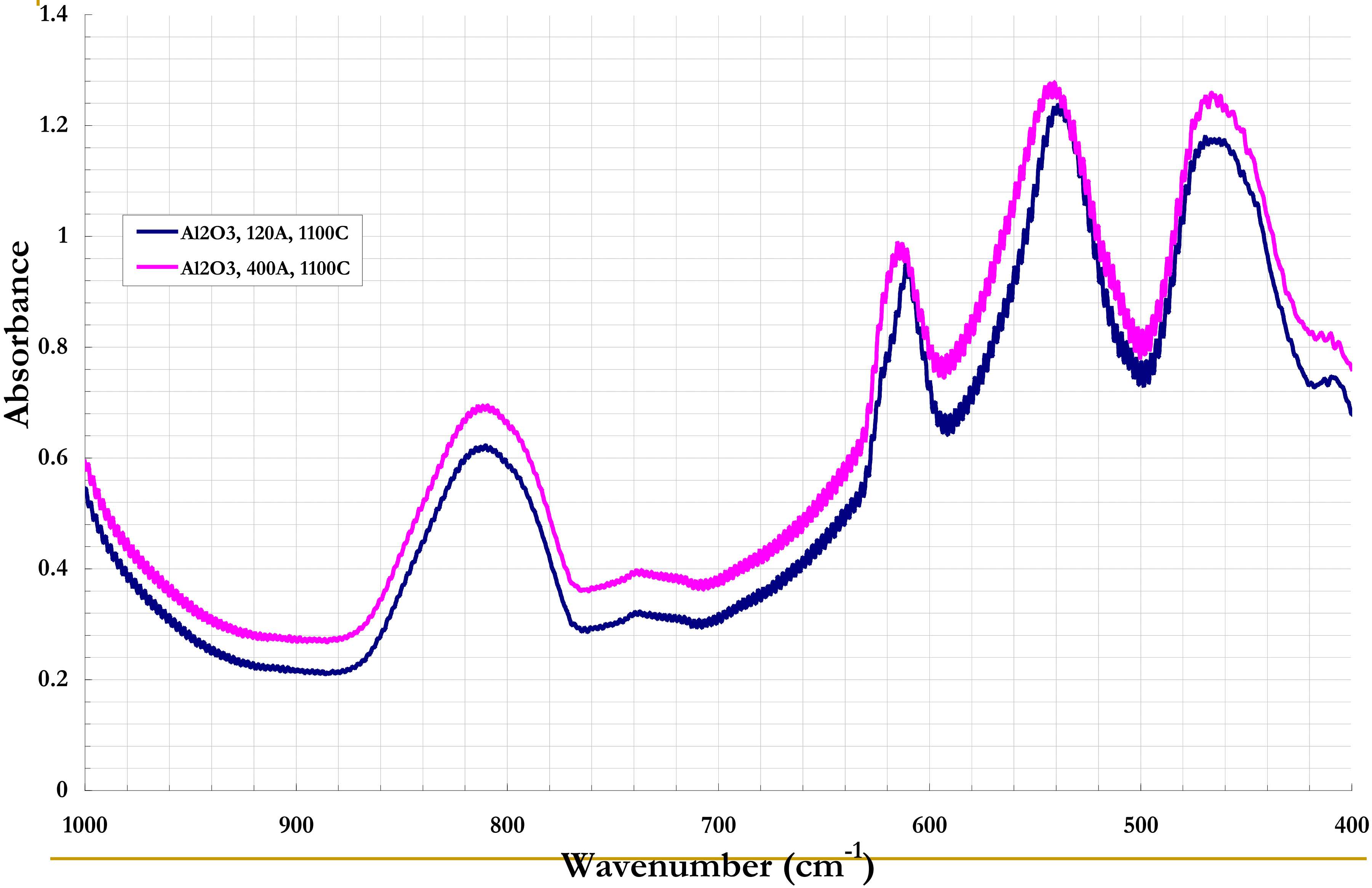


http://upload.wikimedia.org/wikipedia/commons/thumb/c/cc/Corundum-3D-balls.png/800px-Corundum-3D-balls.png

Spectroscopic Characteristics of Al_2O_3

- Each structure of Al_2O_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 α- Al_2O_3 can be identified by distinct peaks at 440, 567 and 650 cm^{-1}.
- Amorphous (not annealed) Al_2O_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.

FTIR Spectra Al_2O_3



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

- D. Yu, F. Lu, N. Xu, J. Sun, Z.F. Ying, and J. D. Wu, J. *Vac. Sci Technol*. A, **26**, 380, (2008).
- Y. Chang, F Ducroquet, L.G. Gosset, A. Sibai, V. Dashtizadeh, J.F. Damelcourt, G. Rolland and F. Martin, *J. Phys. IV France,* **11,** 139 (2001).
- G. Paglia, Doctoral Dissertation, (2004).
- Myo Min Thein, Atomic Layer Deposition (ALD), http://courses.ee.psu.edu/ruzyllo/ee518/Atomic%20Layer%20Deposition.ppt#256,1,AtomicLayerDeposition(ALD).
- Arradiance Unveils GEM-D2 Atomic Layer Deposition System, http://www.azonano.com/news.asp?newsID=12634

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