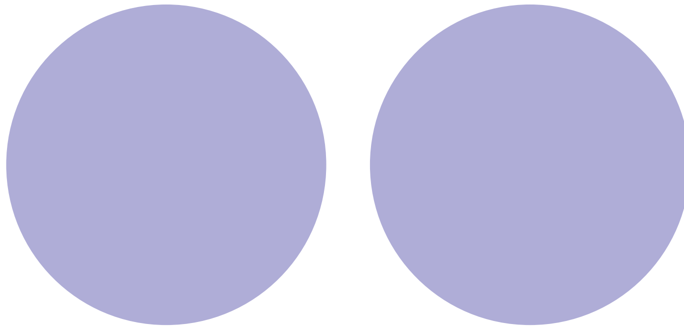
Effects of NH_3 as a Catalyst on the Metalorganic Chemical Vapor Deposition of Al_2O_3



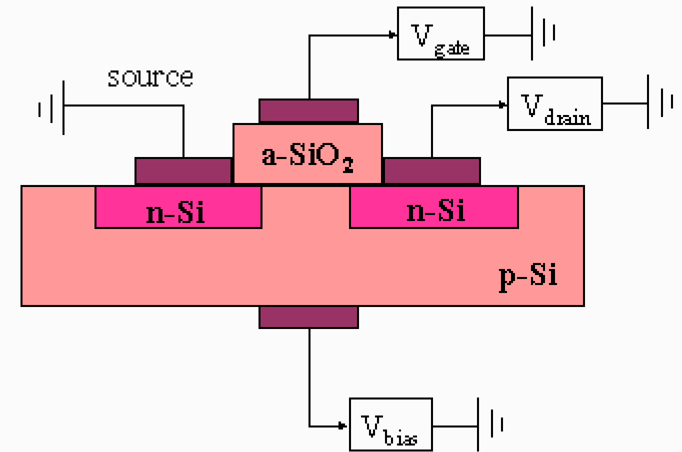
Final Presentation for REU program
August 3rd, 2006

Ashlynne Rhoderick
University of South Carolina
Department of Chemical Engineering

Advisor: Dr. Christos Takoudis
University Of Illinois-Chicago
Department of Chemical Engineering

Motivation for Research

- Need for increased circuit density
  - Fitting more transistors on each wafer
- Physical limit of SiO_2
  - High leakage current
  - Reliability
  - Boron penetration
- Finding a new dielectric
  - SiO_2 $\kappa = 3.9$
  - Need a higher κ dielectric



- $C = \kappa \varepsilon_0 A/t$
  - C- capacitance
  - κ- dielectric coefficient (or relative permittivity)
  - ε_0- permittivity of free space (8.85×10^{-3} fF/μm)
  - A- area of capacitor
  - t- thickness of the dielectric

http://www.hpc.unm.edu/~acpineda/research/movies/movies.html

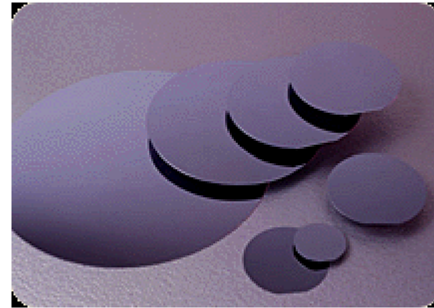
Why Al_2O_3 as a possible dielectric?

- Positive characteristics
  - κ=9
  - Thermodynamically stable in contact with Si
  - Very stable, robust
  - High band gap (9 eV)
  - It can combined with other high k dielectric material

- Experiment with NH_3
  - Hope that it will
    - Increase the deposition rate of Al_2O_3
    - Decrease deposition temperature
    - Decrease amount of impurities in film

Set Up of Experiment

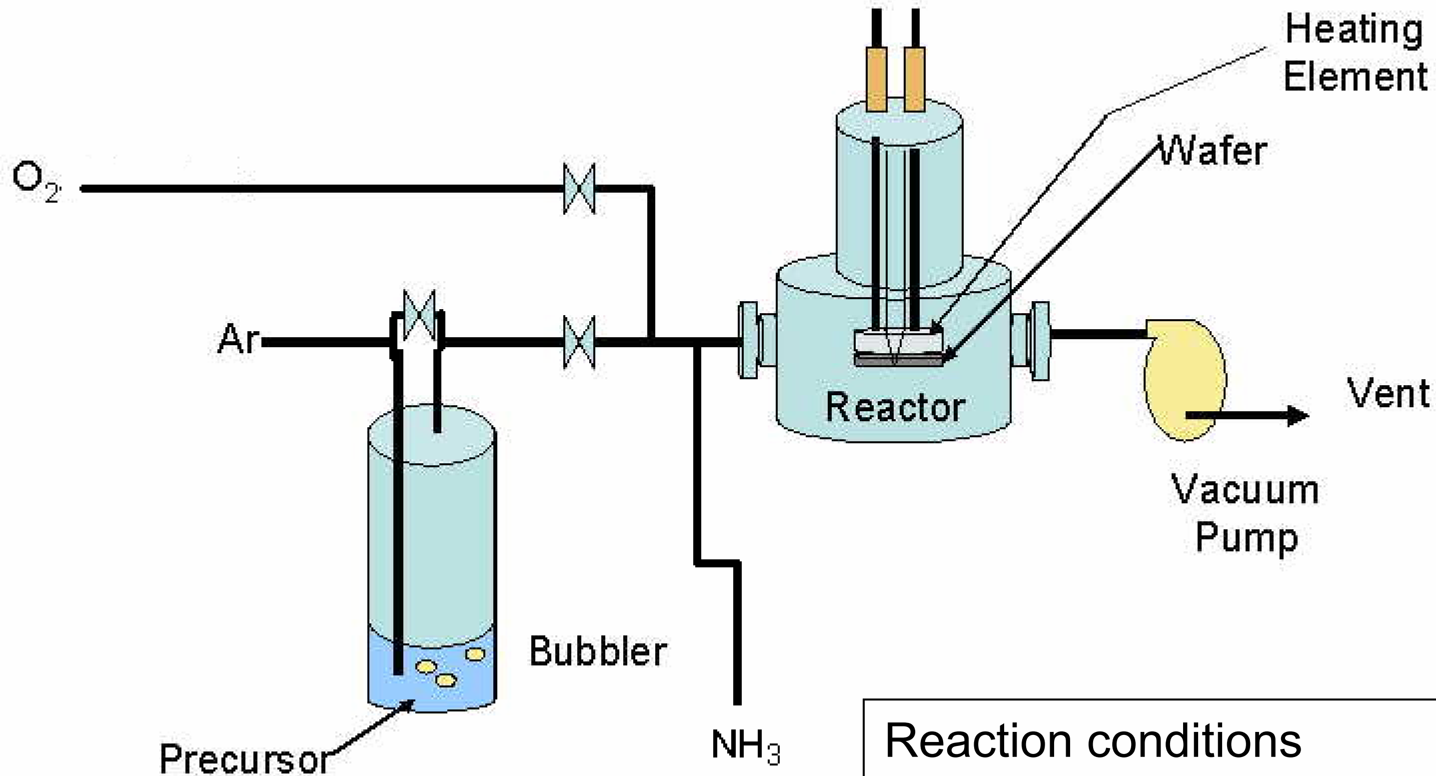
- Cut 2 cm x 2 cm silicon wafers



http://www.imps.co.uk/imps%2013-11-03/index_act.htm

- Cleaning procedure
  - Ultrasonic cleaning-loosens particles (1 min)
  - Distilled water- removes particles (3 min)
  - 4:1 H_2SO_4/H_2O_2- remove organic material (15 min)
  - Distilled water (3 min)
  - 49% HF- remove native silicon oxide (15 sec)
  - Distilled water (3 min)
  - Dry with nitrogen

Metal Organic Chemical Vapor Deposition



Reaction conditions

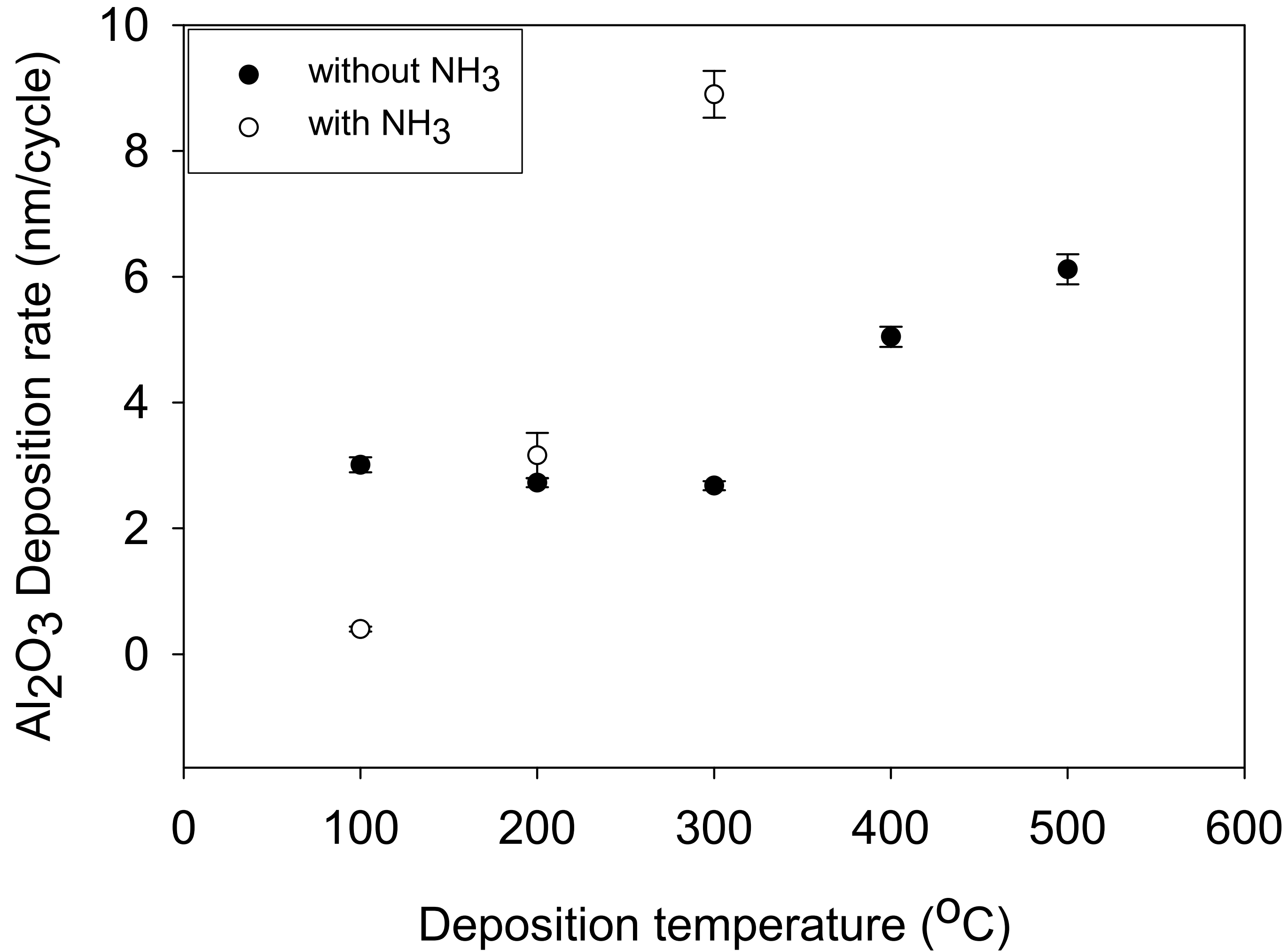
- Deposition temperature: 100, 200, 300, 400, and 500°C
- Deposition pressure: 0.7-0.8 torr

Anand Deshpande Ph.D. Thesis, UIC (2005)

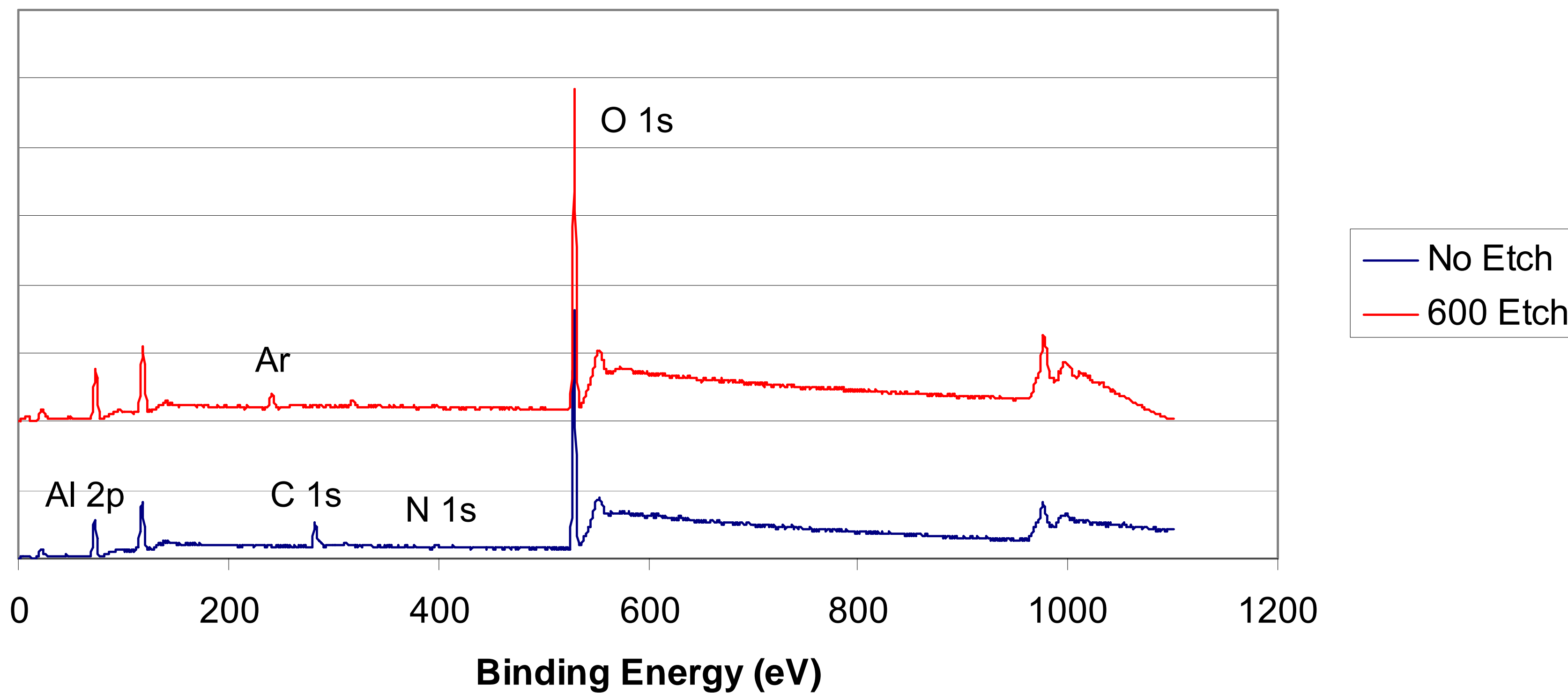
Analysis Techniques

- Ellipsometric Spectroscopy
  - Thickness
- X-Ray Photoelectron Spectroscopy (XPS)
  - Stoichiometry, Composition
- Fourier Transform Infrared Spectroscopy (FTIR)
  - Composition

Comparing the Results



XPS Analysis



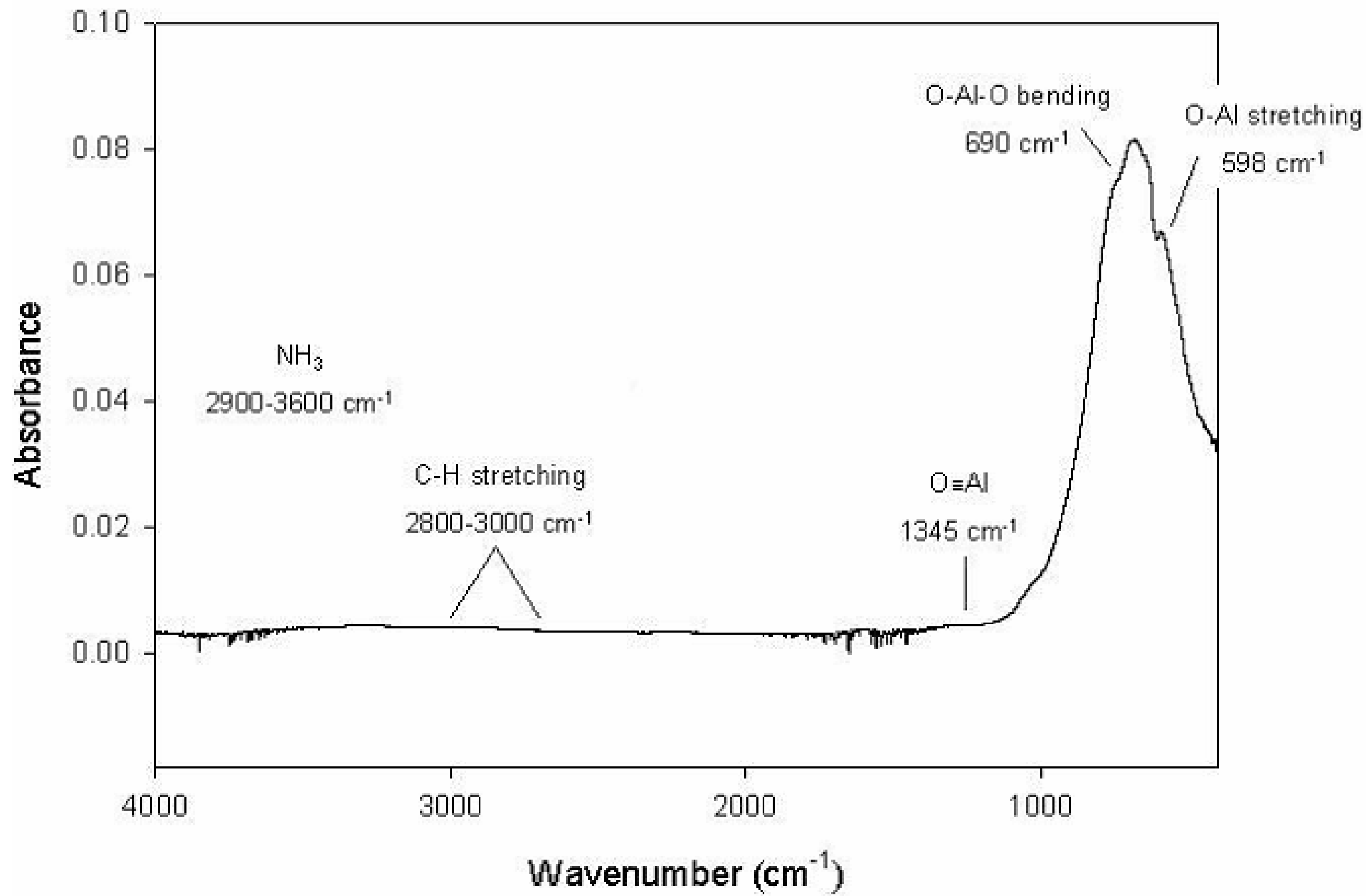
XPS Analysis: Stoichiometric

O/Al ratio	Sample1	Sample3	Sample2	Sample4
	No NH_3		NH_3	
Temperature (C)	300	200	300	200
No Etch	1.596	1.619	1.671	1.638
300 sec Etch	1.490	1.493	1.608	1.540
600 sec Etch	1.472	1.479	1.560	1.534

From 2006 experiments

- 2004 experiments by A. Roy Chowdhuri and C.G. Takoudis
  - Stoichiometric ratio of O/Al was 2.0 ± 0.1

FTIR Analysis



Conclusions and Future Work

- NH_3 raised the deposition rate in the temperature range of 200-300°C
- Without Ammonia
  - Absorption controlled until 300°C
  - Reaction controlled after 300°C
- With Ammonia
  - Reaction controlled from 100-300°C
  - At 100°C ammonia gets absorbed therefore less TMA is absorbed results in lower Al_2O_3 deposition rate
- Purity of the film was not compromised
- Continue to perfect use of NH_3 in the deposition of Al_2O_3

References

- Brewer, R.T. et al. (2004) Ammonia pretreatment for high-k dielectric growth on silicon. Applied Physics Letters. 85, 3830-3832.
- Chowdhuri, A. Roy and Takoudis, C.G. (2004) Investigation of the aluminum oxide/ Si (1 0 0) interface formed by chemical vapor deposition. Thin Solid Films. 446, 155-159.
- Hiremane, Radhakrishna. (2005) From Moore's Law to Intel Innovation—Prediction to Reality. Technology @ Intel Magazine. 1-9.
- Jung, Sung-Hoon and Kang, Sang-Won (2001) Formation pf TiO_2 Thin Films using NH_3 as Catalyst by Metalorganic Chemical Vapor Deposition. Japan Society of Applied Physics 40, 3147-3152.
- Klaus, J.W. and George, S.M. (2000) Atomic layer deposition of SiO_2 at room temperature using NH_3-catalyzed sequential surface reactions. Surface Science. 447, 81-90.
- Klein, T.M. et al. (1999) Evidence of aluminum silicate formation during chemical vapor deposition of amorphous Al_2O_3 thin films on Si(100). Applied Physics Letters. 75, 4001-4003.
- Krug, C. et al. (2000) Atomic Transport and Chemical Stability during Annealing of Ultrathin Al_2O_3 Films on Si. 85, 4120-4123.
- Ong, C.W. et al. (1997) Structural Studies of reactive Pulsed Laser-Deposited CN_x Films by X-ray Photoelectron Spectroscopy and Infrared Absorption. Journal of The Electrochemical Society. 32, 2347-2352.
- Ogita, Y. et al. (2003) Al_2O_3 formation on Si by catalytic chemical vapor deposition. Thin Solid Films. 430, 161-164.
- Pradhan, Siddhartha K. et al (2003). Growth of TiO2 nanorods by metalorganic chemical vapor deposition. Journal of Crystal Growth. 256, 83-88.
- Takahashi, Hisao et al. (1991). Alterations in Hepatic Lipids and Proteins by Chronic Ethanol Intake: A High-Pressure Fourier Transform Infrared Spectroscopic Study on Alcoholic Liver Disease in the Rat. Alcoholism: Clinical and Experimental Research. 15, 219.
- Wilk G.D. and Wallace, R.M. (2001) Exploring the Limits of Gate Dielectric Scaling. Semiconductor International. 153-158.
- Wilk, G.D. et al. (2001) High-k gate dielectrics: Current status and materials properties considerations. Applied Physics Review 89, 5243-5275.
- Wilk G.D. and Wallace, R.M. (2002) High K Gate Dielectric Materials. MRS Bulletin. 192-197.

Acknowledgements

- NSF EEC-0453432 Grant, Novel Materials and Processing in Chemical and Biomedical Engineering (Director C.G. Takoudis), funded by the DoD-ASSURE
  and NSF-REU Programs
- NSF CTS-0630470 & 0434201 GOALI: Atomic-scale Investigation of High Dielectric Constant Thin Films Using In Situ and Other Techniques, (Director C.G. Takoudis)
- REU program at the University of Illinois-Chicago
- NSF and DoD
- Peggy Song
- Dr. Christos Takoudis