High Rate Growth of SiO_2 by Thermal ALD Using Tris(dimethylamino)silane and Ozone

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Simply ALD

Introduction: Thermal ALD of SiO_2

Many Existing SiO_2 ALD Processes are Unsatisfactory

A few examples

(1) TEOS Process, tetraethoxysilane, $Si(OCH_2CH_3)_4$

- Reacts with H_2O when catalyzed by NH_3 or amines, even at room temperature
- 0.07-0.08 nm/cycle at 300 K

J. D. Ferguson,a E. R. Smith,a A. W. Weimer,b and S. M. George, *J. Electrochem. S.*, **151** (8), G528-G535 (2004)

- Too slow, required large exposures ($\sim 10^{10}$ L) for surface reactions to reach completion (1 L $= 10^{-6}$ Torr-s)

Introduction: Thermal ALD of SiO_2

(2) 3-aminopropyltriethoxysilane process, O_3 and H_2O:

$H_2N(CH_2)_3Si(OCH_2CH_3)_3$

- Self-catalyzed hydrolysis due to existence of amino group

- 120-250°C, GPC=0.05~0.06nm/cycle

J. Bachmann, R. Zierold, Y. T. Chong, R. Hauert, C. Sturm, R. Schmidt-Grund, B. Rheinlnder, M. Grundmann, U. Gosele, and K. Nielsch, *Angew. Chem. Int. Ed.* **47**, 6177-6179 (2008).

- High quality SiO_2
- Slow process (requires two oxidants H_2O and O_3)
- Unreacted precursor caused frequent damages to vacuum pumps

Introduction: Thermal ALD of SiO_2

(3) TDMAS (or 3DMAS)-H_2O_2 Process:

tris(dimethylamino)silane, $[(CH_3)_2N]_3SiH$

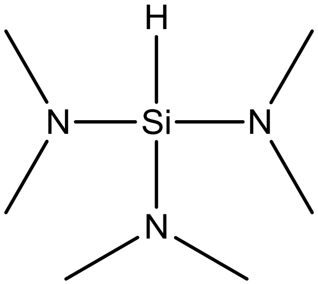
- First reported to be a reactive precursor with H_2O_2 oxidant

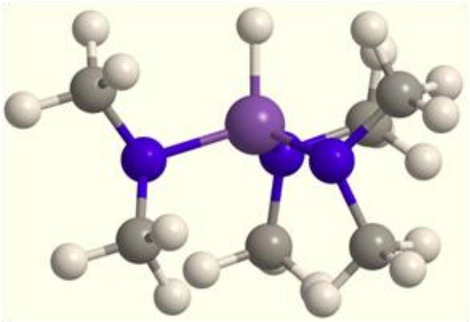
B. B. Burton, S. W. Kang, S. W. Rhee, and S. M. George, *J. Phys. Chem. C* **113**, 8249–8257 (2009)

- Precursor can be used in a wide temperature range: 150-550°C
- Inability of H_2O_2 to remove all Si-H bonds at lower temperatures usable temperature $\geq$ 450°C
- Low thermal stability of H_2O_2

The TDMAS – O_3 Process

TDMAS, $[(CH_3)_2N]_3SiH$



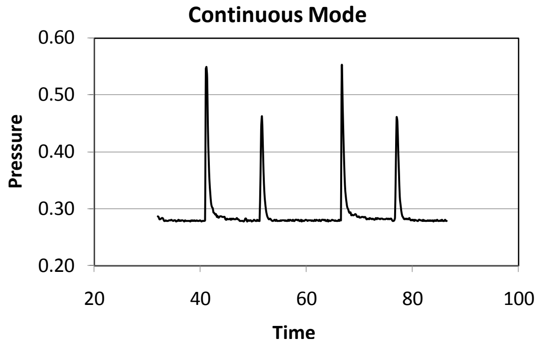


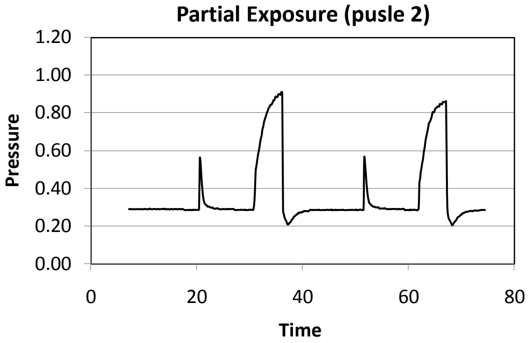
- High vapor pressure at ambient temperature

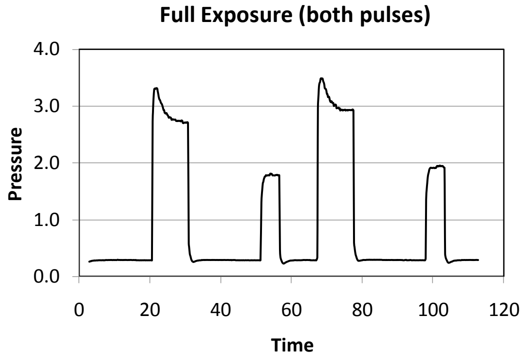
  BP=145-148°C, 16mmHg at 4°C

  no heating needed
- Insoluble in H_2O
- No reaction with H_2O or O_2 up to 350°C

Three Different Reaction Modes







Cambridge NanoTech's ALD Reactors

(1) Continuous Mode

- Normal pulse/purge steps for all precursors

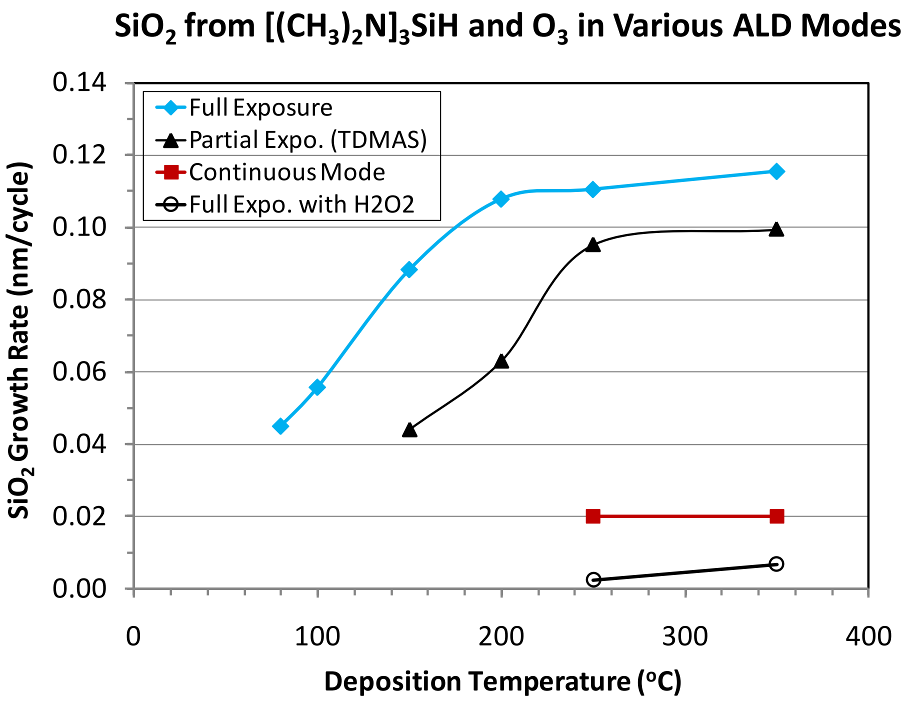
(2) Partial Exposure Mode

- One precursor with an extra hold step (pulse/hold/purge), staying in reactor longer to increase residence time
- Different from an extended pulse time

(3) Full Exposure Mode

- All precursors with pulse/hold/purge steps

The TDMAS – O_3 Process



Continuous:

very low growth rate
~ 0.02 nm/cycle

Partial Expo:

TDMAS exposure (28 sec.) key to high growth rate

Full Expo:

O_3 exposure (7 sec.) further increased growth rate

Growth rate much lower with H_2O_2

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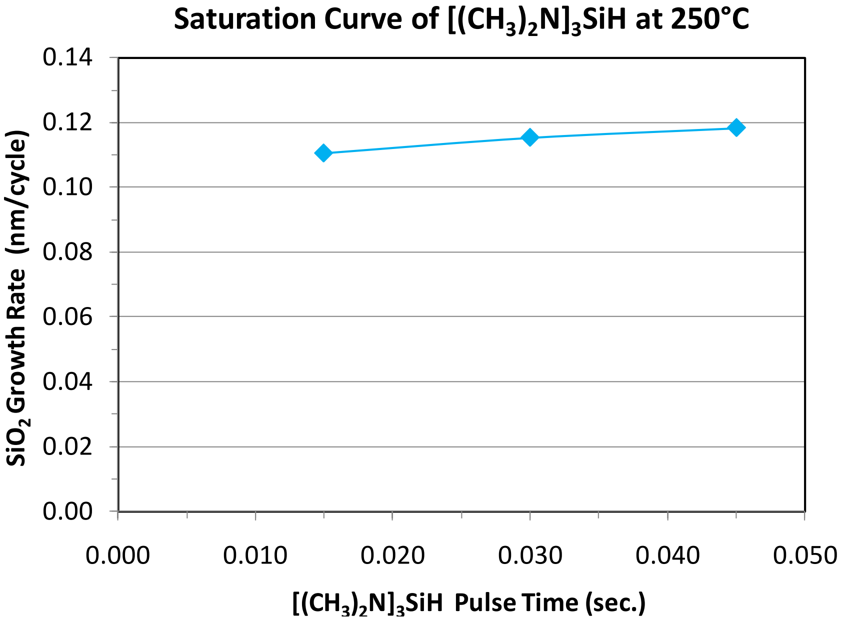
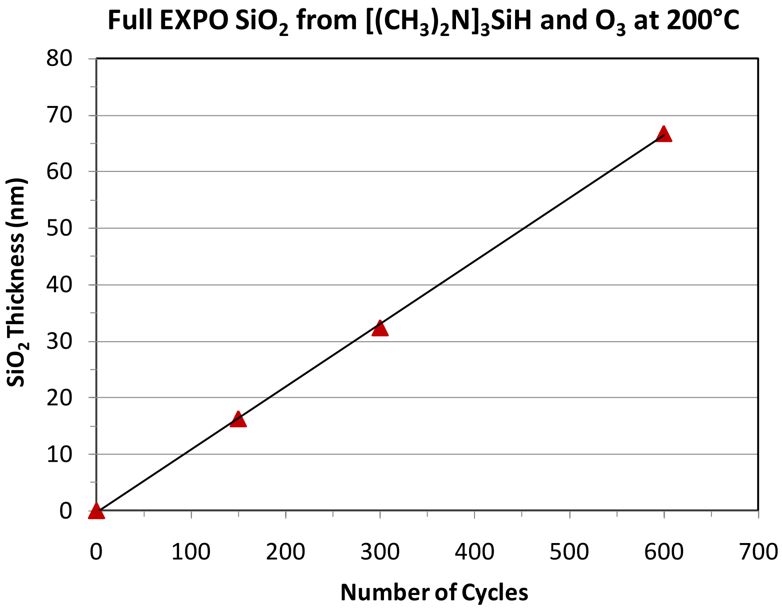
TDMAS Saturation and Linear Growth

- Deviation from a flat saturation curve with TDMAS dose could be due to less than full saturation from limited exposure time
- Growth is linear without nucleation delay
- Process completely repeatable

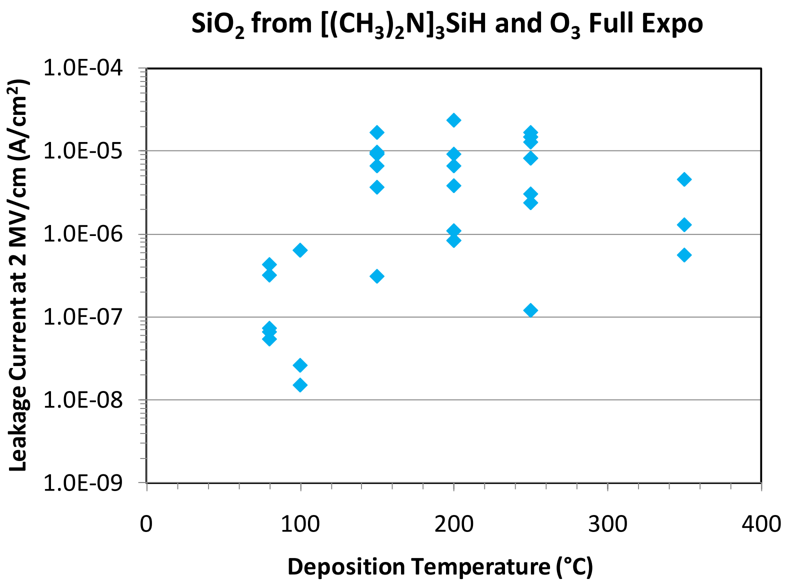

Saturation Curve of $[(CH_3)_2N]_3SiH$ at 250°C

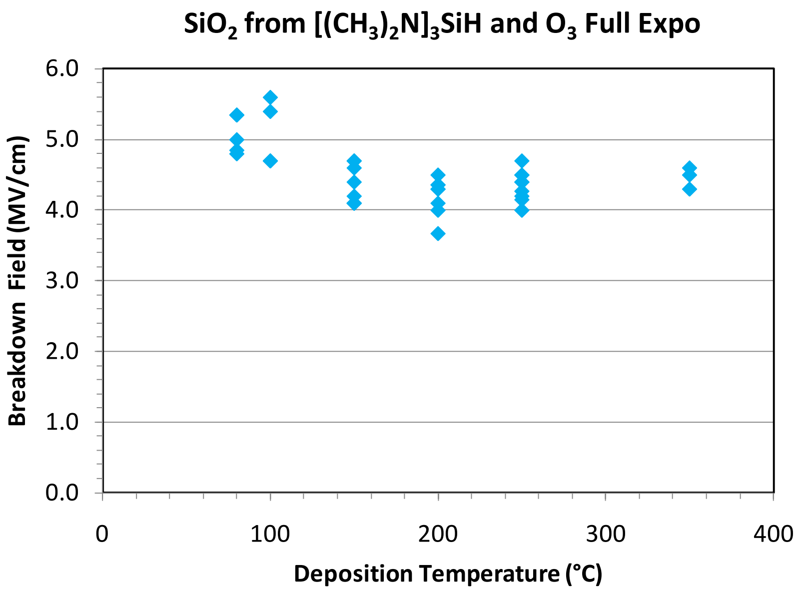

Full EXPO SiO_2 from $[(CH_3)_2N]_3SiH$ and O_3 at 200°C

Electrical Properties by mercury probe

Leakage Current and Breakdown Strength

- Data scattered due to changing properties with time
- 80-120°C process produced SiO_2 films with lowest leakage current and highest breakdown strength; 200°C the worst

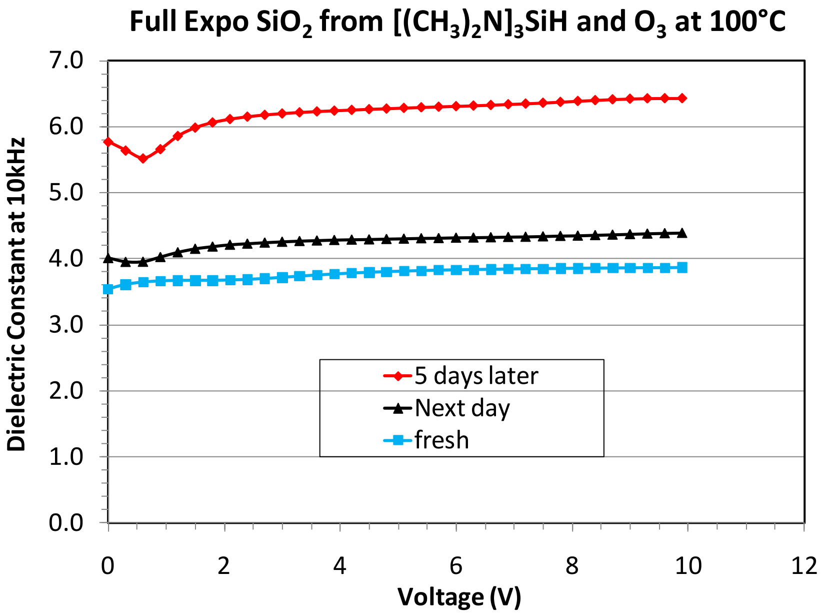


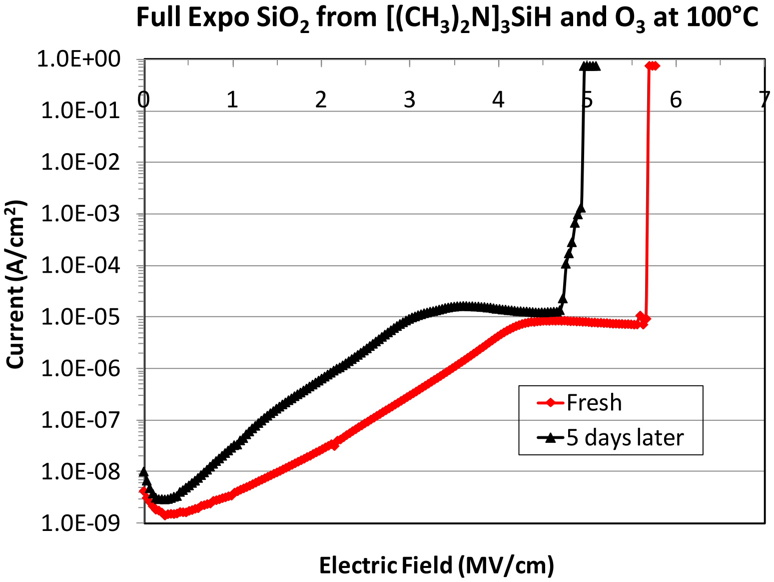


SiO_2 films absorb H_2O in air

Change in Dielectric Constant, Leakage Current and Breakdown Field with Time

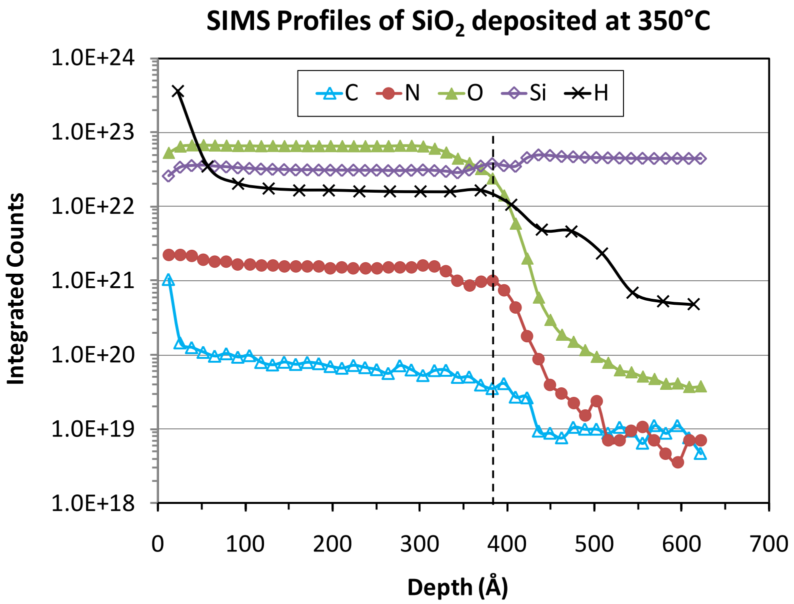
- Dielectric constant of fresh 100°C SiO_2 close to ideal value of 3.9
- It increased with air exposure time until reached a saturated state

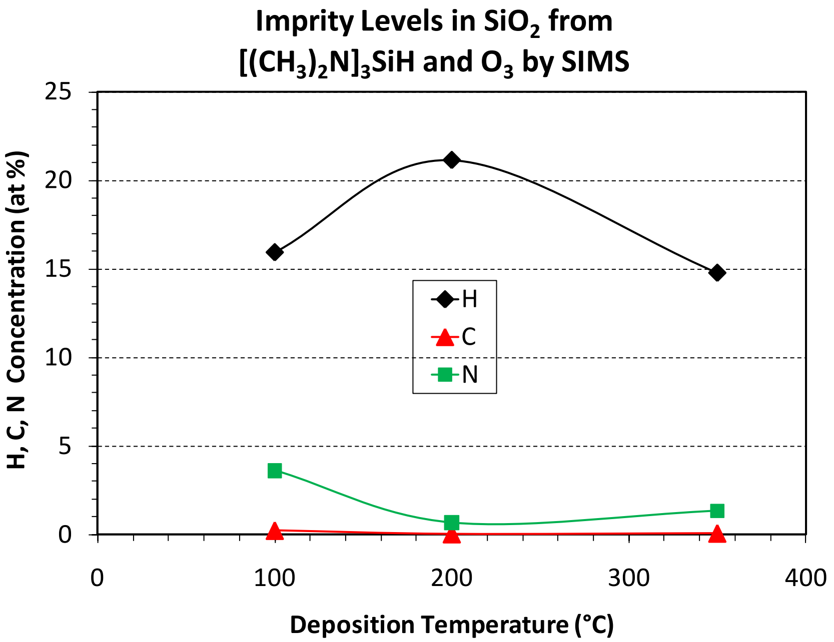




SIMS Analysis

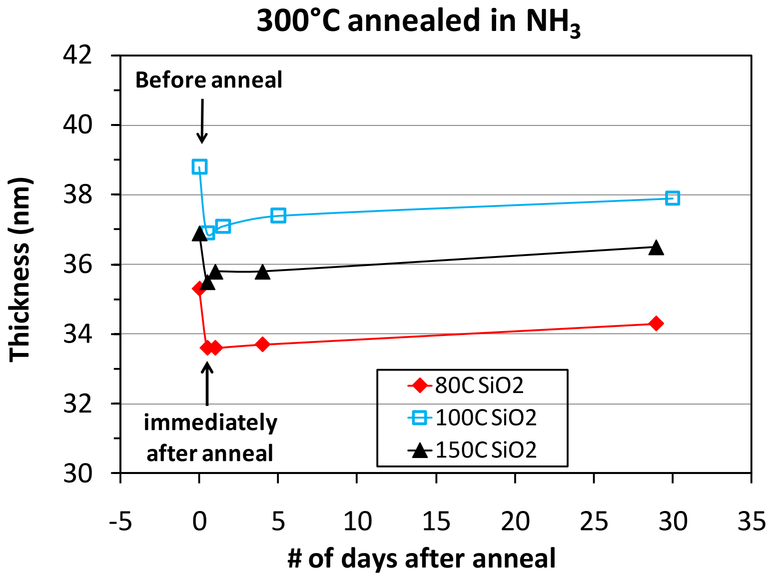
- Very Low C impurity (highest at 0.2 at% with 100°C SiO_2)
- Low N at high temperatures (highest at 3.6 at% with 100°C SiO_2)
- High concentrations of H (highest with 200°C SiO_2)

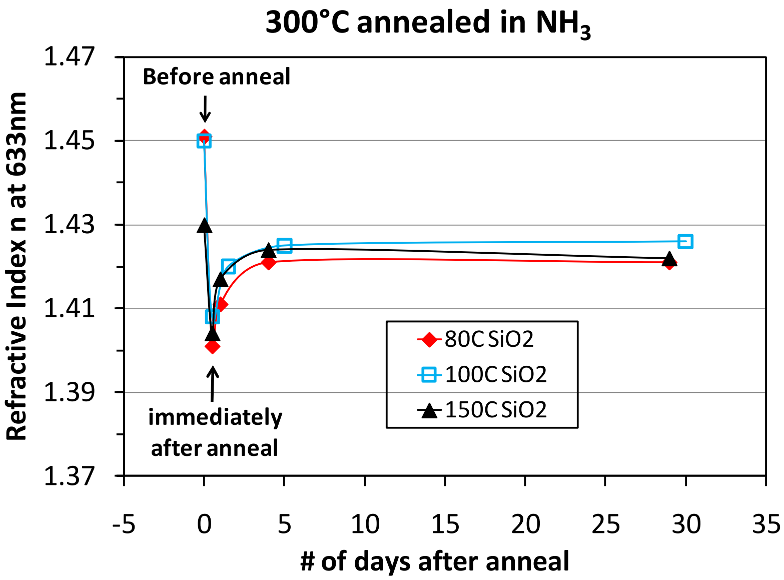

SIMS Profiles of SiO_2 deposited at 350°C


Imprity Levels in SiO_2 from $[(CH_3)_2N]_3SiH$ and O_3 by SIMS

H_2O-saturated SiO_2 films: annealing in vacuum or NH_3

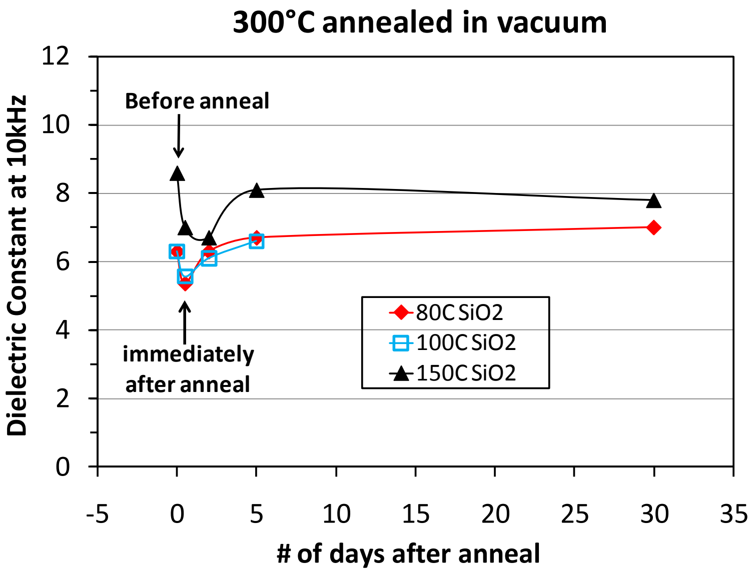
- Annealing at ≥300°C led to 3-5% decrease in thickness and a slight drop in refractive index
- Refractive index partially reversible upon re-exposure to air

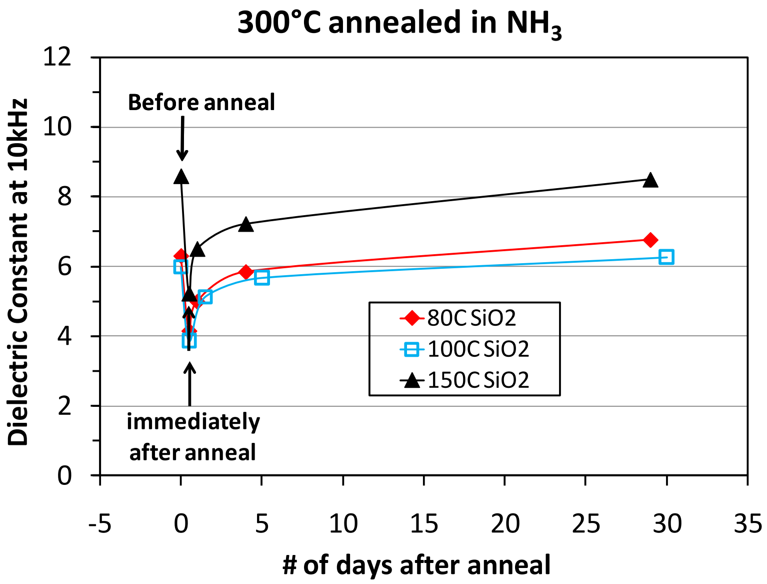




H_2O-saturated SiO_2 films: annealing in vacuum or NH_3

- 300°C anneal in NH_3 was more effective than vacuum anneal
  Dielectric constant dropped to 3.9 for NH_3-annealed 80-120°C SiO_2
- NH_3 facilitates removal of OH groups?
- Reversible dielectric constant with re-exposure to air


300°C annealed in vacuum


300°C annealed in NH_3

Summary

- TDMAS-O_3 a good ALD process for SiO_2
- Full exposure mode helps growth saturation
- 80-120°C SiO_2 films have better electrical properties
- Uncapped ALD SiO_2 absorbs H_2O in air
- Annealing of H_2O-absorbed SiO_2 films in NH_3 at 300-350°C restores electrical properties