

# **Process Characterization for BTBAS Films**

**Work Performed by Jim Ellenberger  
Presentation by Dr. Robert Herring**

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San Jose, California  
May 2001

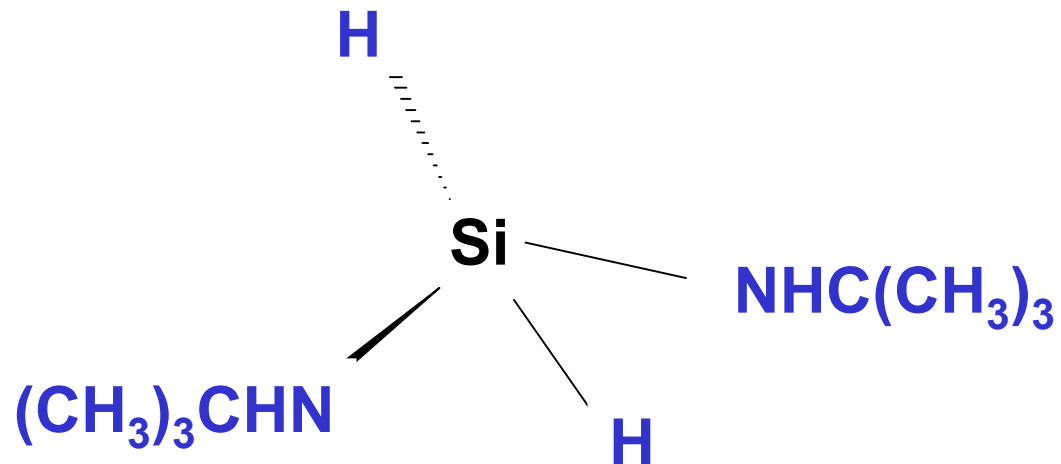
# Outline

- BTBAS Background / Properties
- Silicon Nitride
- Silicon Oxide
- Phosphorous doped silicon oxide (PSG)
- Silicon Oxynitride

# BTBAS Background

- Developed by Schumacher
- BTBAS = Bis (tertiarybutylamino) silane
- Objective: Lower temperature replacement for Dichlorosilane (without chlorine)
- Testing in the SVG Applications Lab since Jan. 1999
- Dedicated vertical furnace system for BTBAS films
- Several DOE's completed
- Processed wafers for several customer applications

# BTBAS Molecule

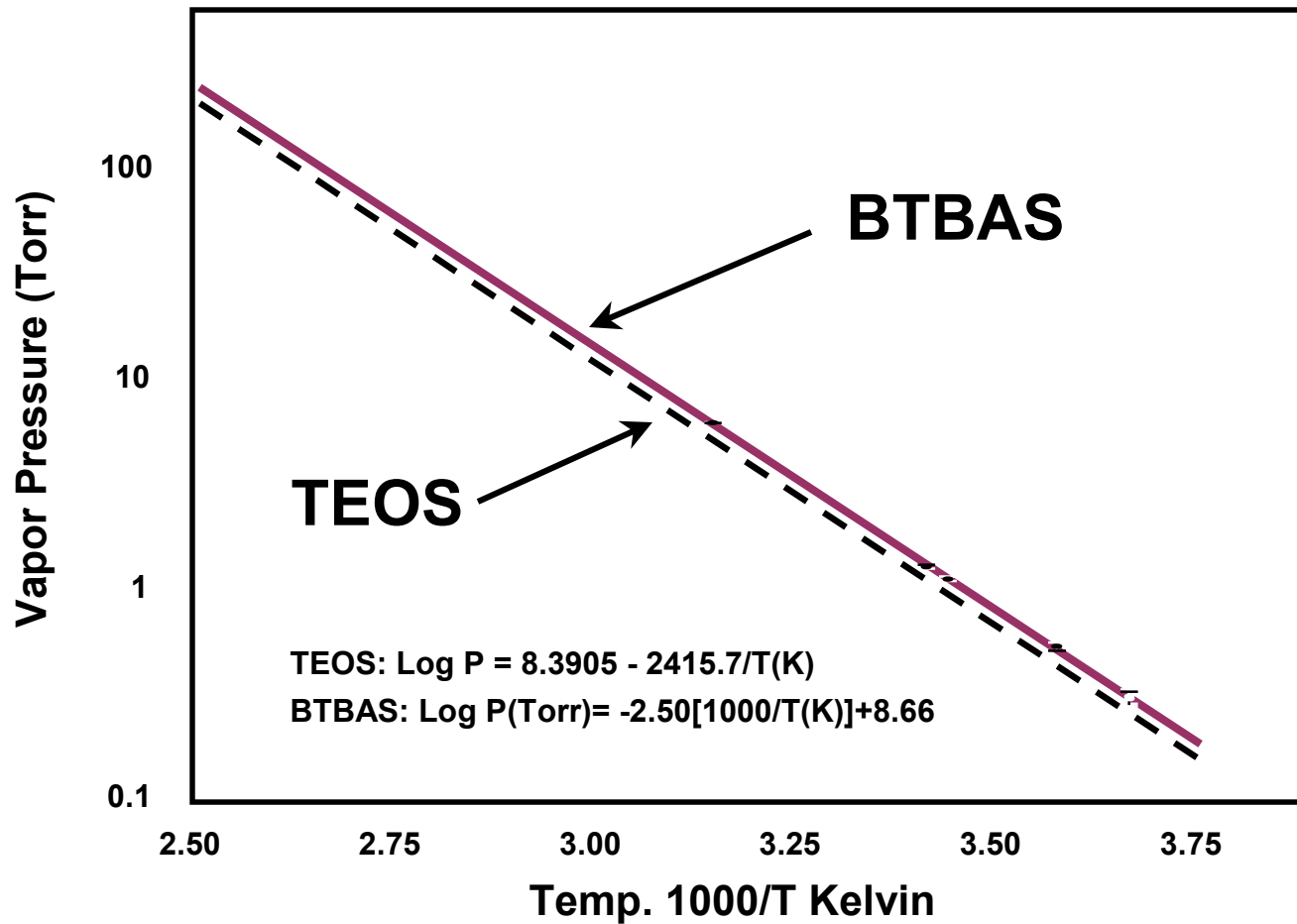


## Bis (TertiaryButylAmino) Silane

# Physical Properties of BTBAS

<b>Chemical Formula</b>	<b>C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Si</b>
<b>Molecular Weight</b>	<b>174.3</b>
<b>Vapor Pressure @ 20°C</b>	<b>1.15 Torr</b>
<b>Specific Gravity @ 22°C</b>	<b>0.816 g/ml</b>
<b>Boiling Point @ 760mm Hg</b>	<b>167°C</b>
<b>Viscosity @ 22°C</b>	<b>&lt; 1.5 cPs</b>
<b>Flash Point</b>	<b>30°C</b>
<b>LEL (% in air)</b>	<b>0.5%</b>
<b>UEL (% in air)</b>	<b>Not Available</b>

# Vapor Pressure BTBAS and TEOS



# BTBAS Applications

Objectives: Decrease of process thermal budget

- Sidewall spacers
  - lower process temperatures
- Etch stop layers
  - Self aligning contacts
- Trench Structure Fill or Liners
  - STI fill (3:1-6:1 aspect ratio)
  - Deep trench liners (>20:1 aspect ratio)

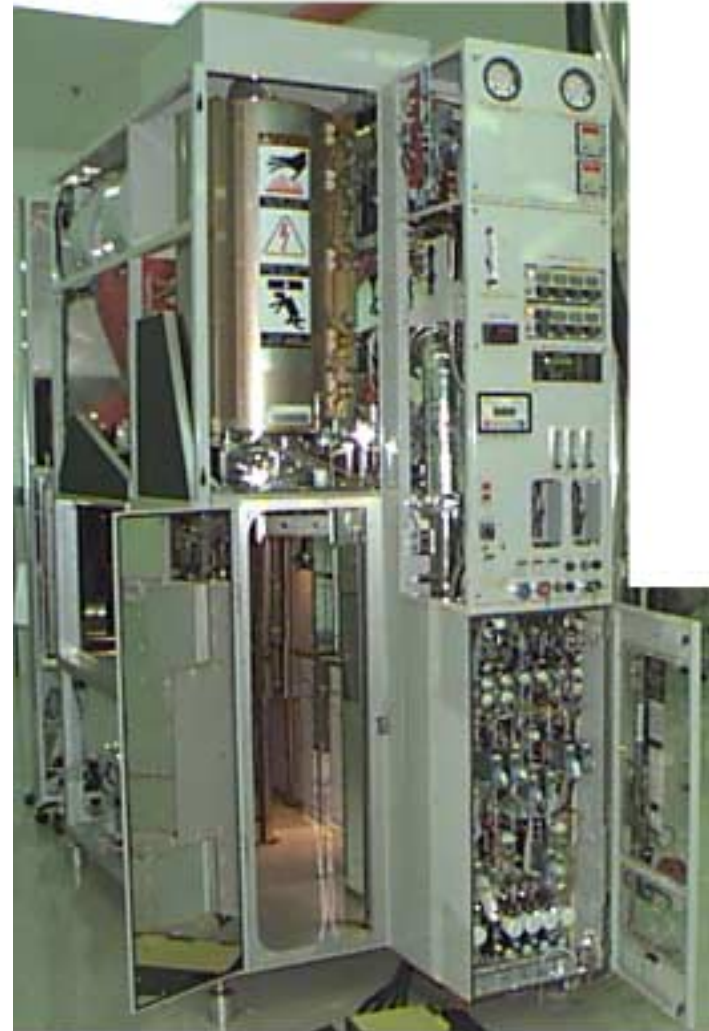
# BTBAS Films

- Films Studied
  - Silicon Nitride
  - Silicon Dioxide
  - Phosphorus Doped Oxides
  - Oxynitrides

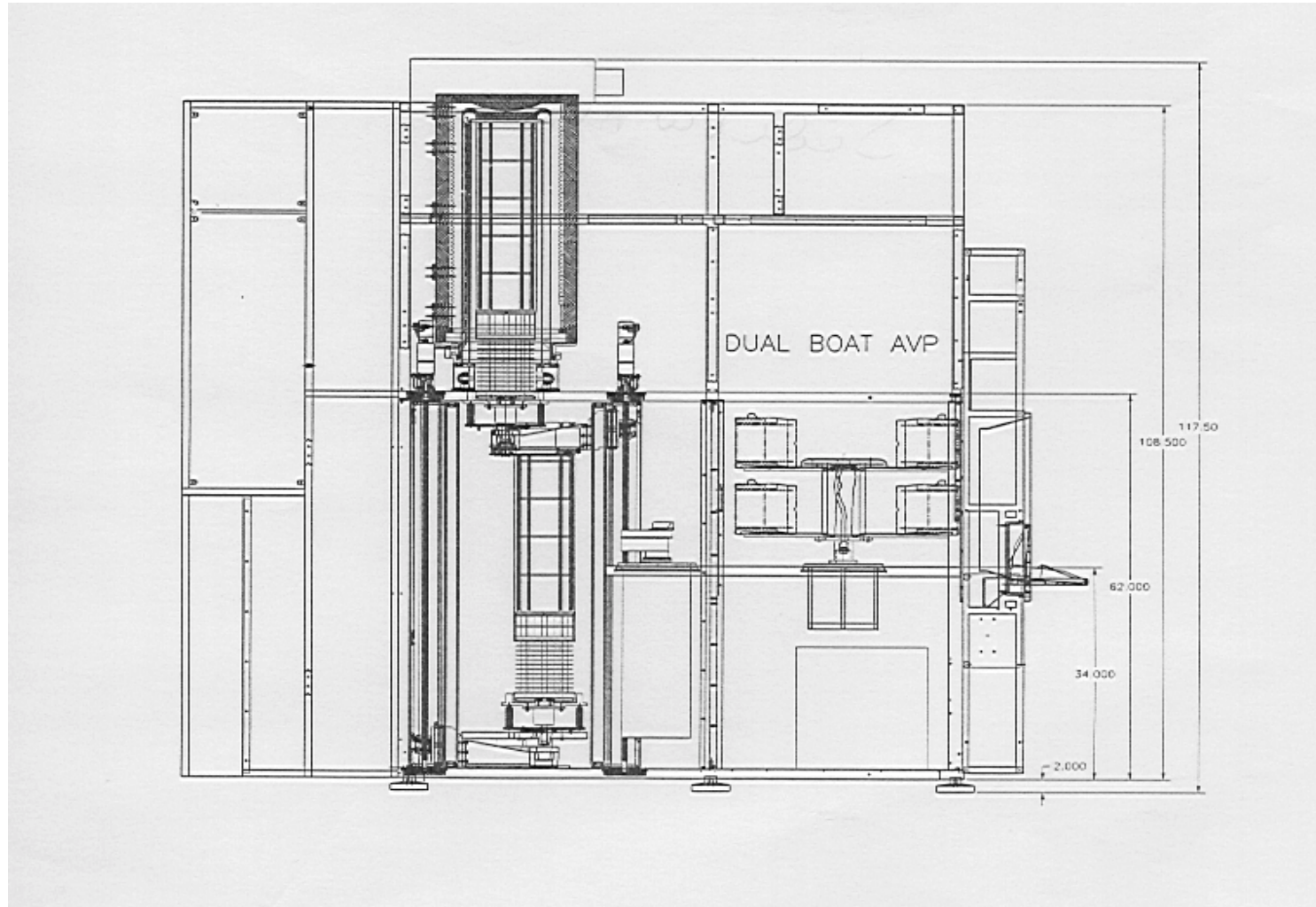
# BTBAS Films

- Test Methods and Equipment
  - All tests used 200-mm wafers
  - SVG Vertical LPCVD Furnace
    - series 8000 AVP
  - Measured thickness and refractive index by ellipsometry

# Front and Rear Views of AVP



# Side View AVP Dual Boat System



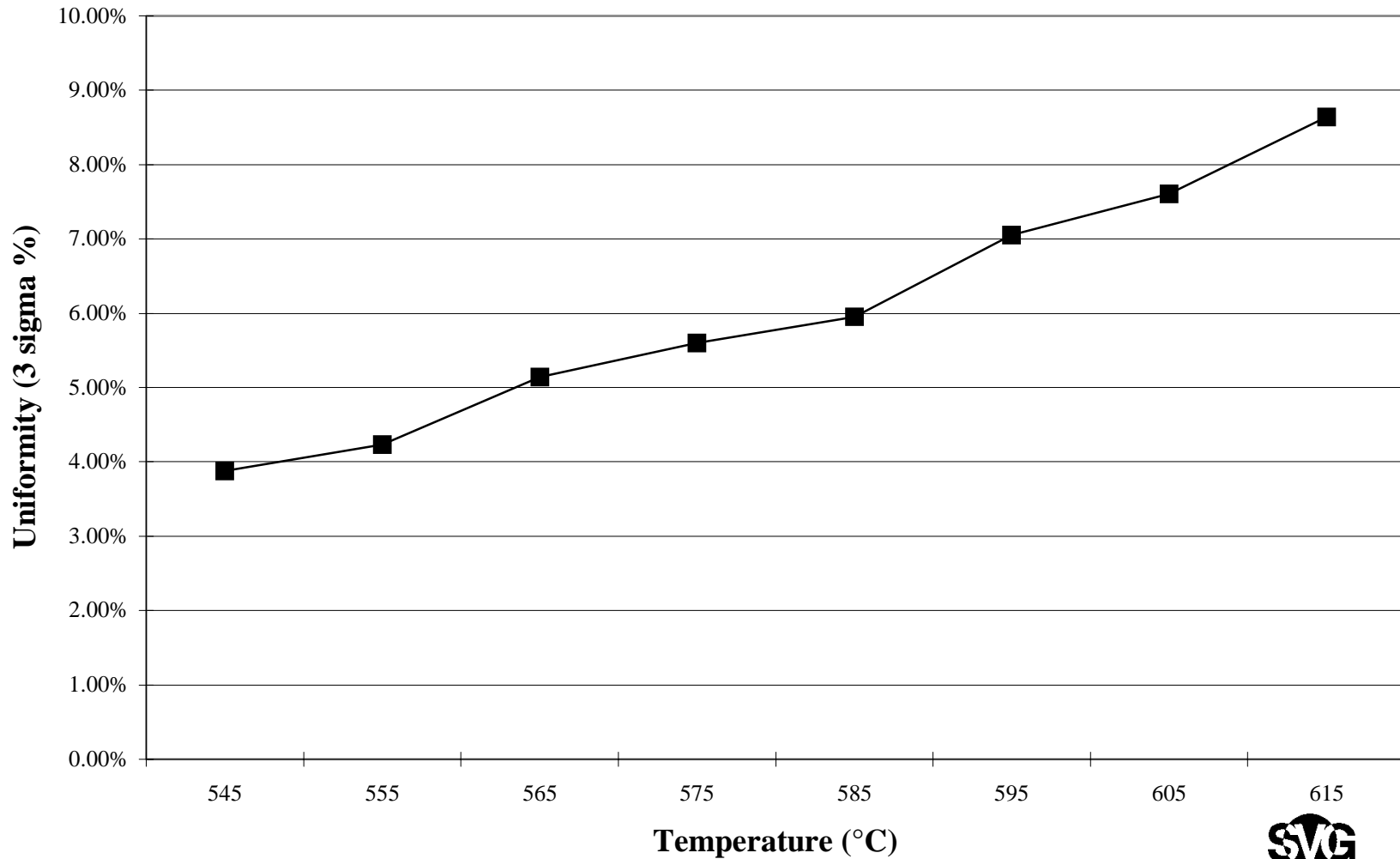
# BTBAS Films

- Silicon Nitride
  - BTBAS and Ammonia ( $\text{NH}_3$ )
- Silicon Dioxide
  - BTBAS and Oxygen ( $\text{O}_2$ )
- Phosphorus Doped Silicon Dioxide (PSG)
  - BTBAS, Oxygen, 10% Phosphine in Nitrogen
- Oxynitride
  - BTBAS. Ammonia, Oxygen
  - Or
  - BTBAS, Ammonia, Nitrous Oxide ( $\text{N}_2\text{O}$ )

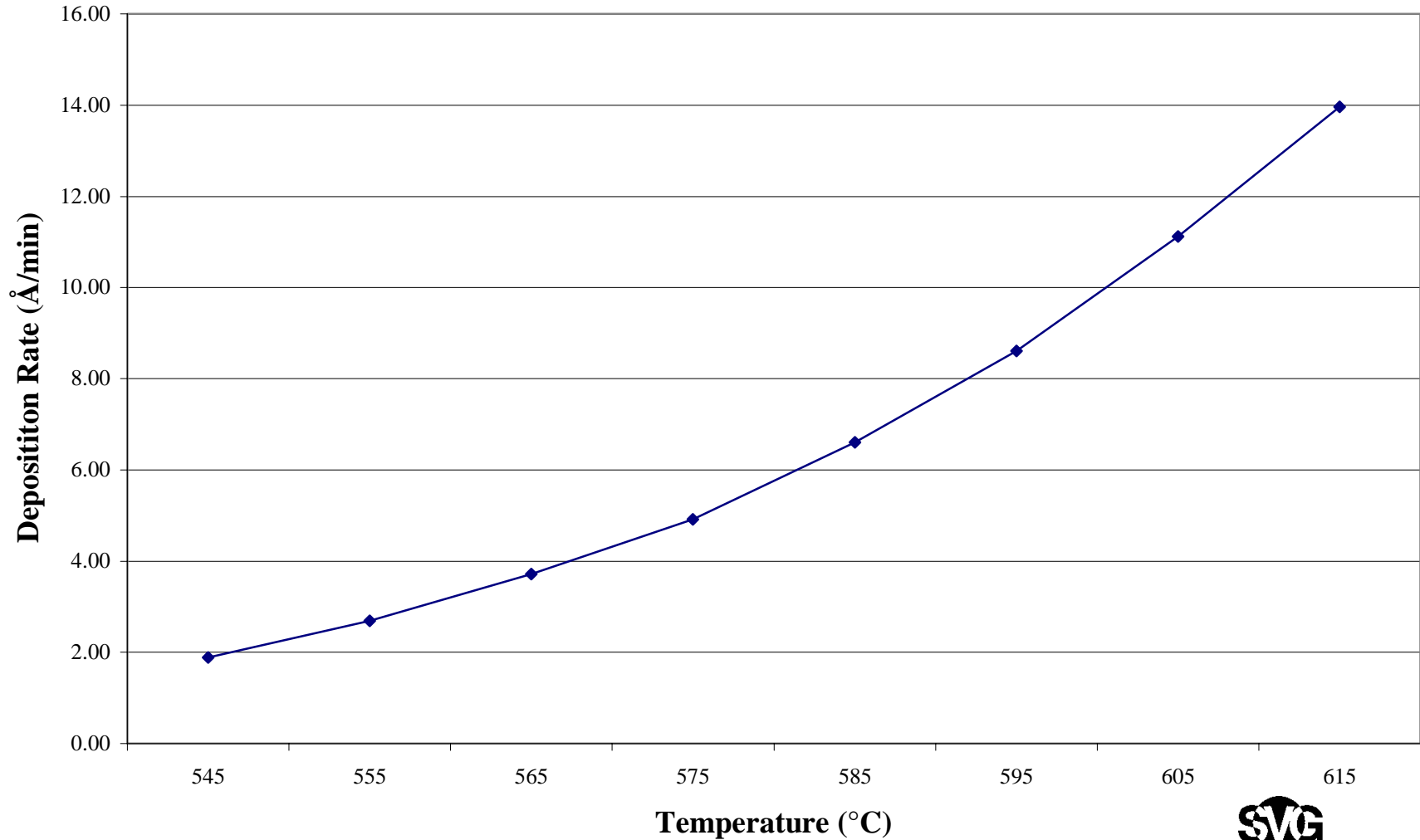
# Silicon Nitride BTBAS Films

- Primary Process Window
  - Temperature 500 to 625°C
  - Total Flow 100 to 300 sccm
  - NH<sub>3</sub>: BTBAS Ratio 1:1 to 12:1
  - Pressure 100 to 600 mT

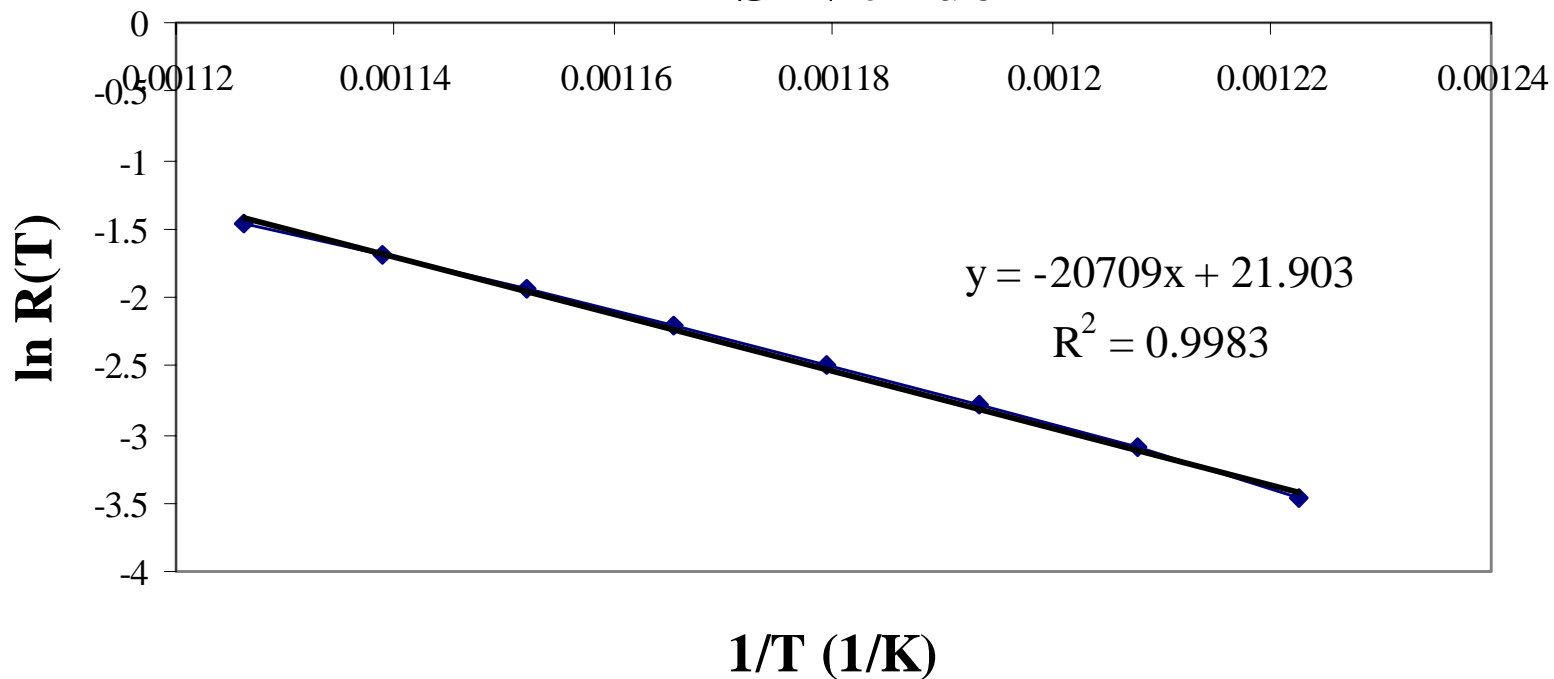
**Figure 1 - BTBAS Nitride**  
**Temperature vs Within Wafer Uniformity for 0.5" Spacing,**  
**100 mTorr, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**



**Figure 2 - BTBAS Nitride**  
**Temperature vs Deposition Rate for 0.5" Spacing,**  
**100 mTorr Pressure, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**

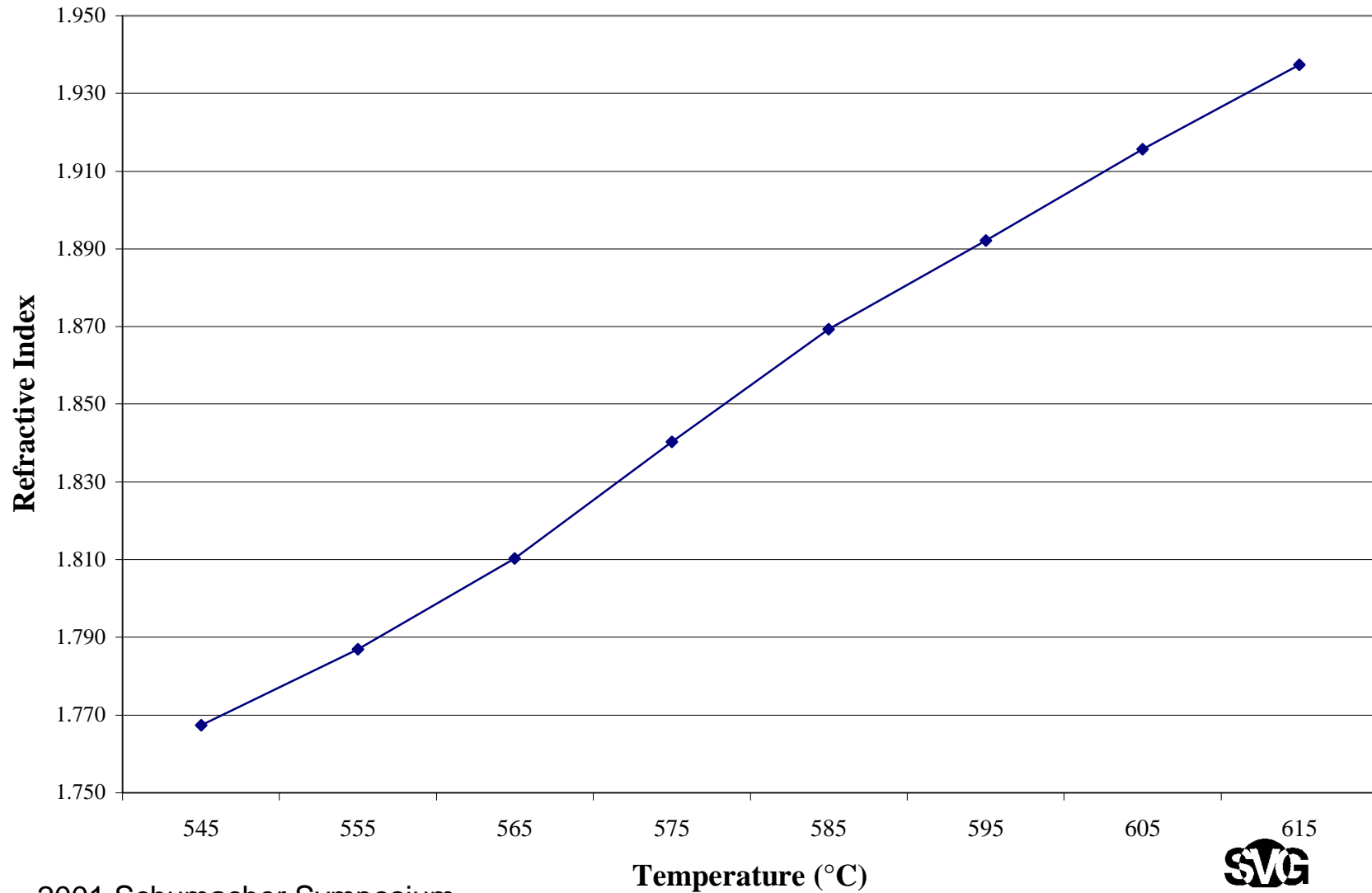


### Figure 3 - Arrhenius Plot for BTBAS Nitride

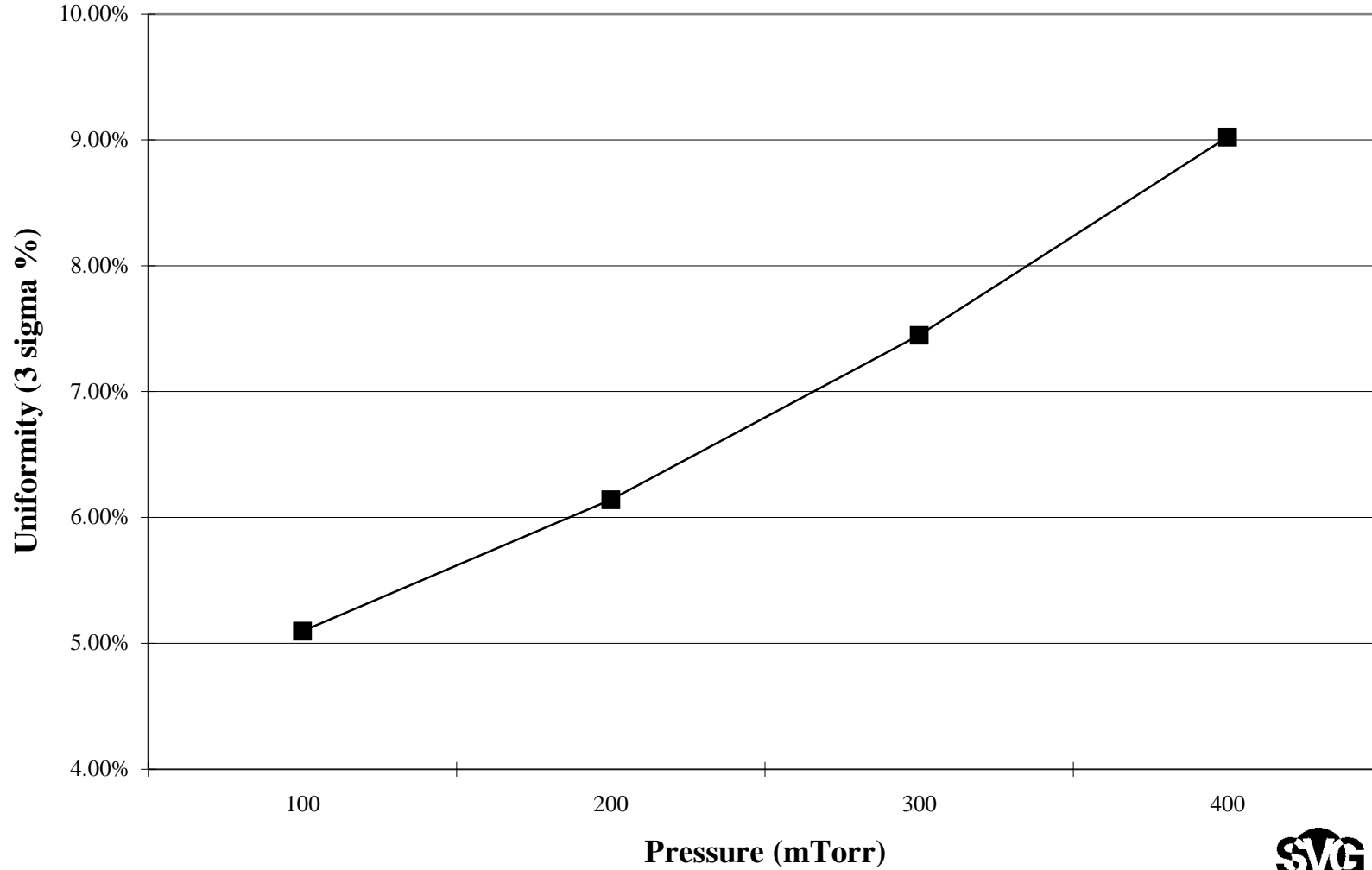


Activation energy = 1.5489 eV  
= 149.46 kJ/mol

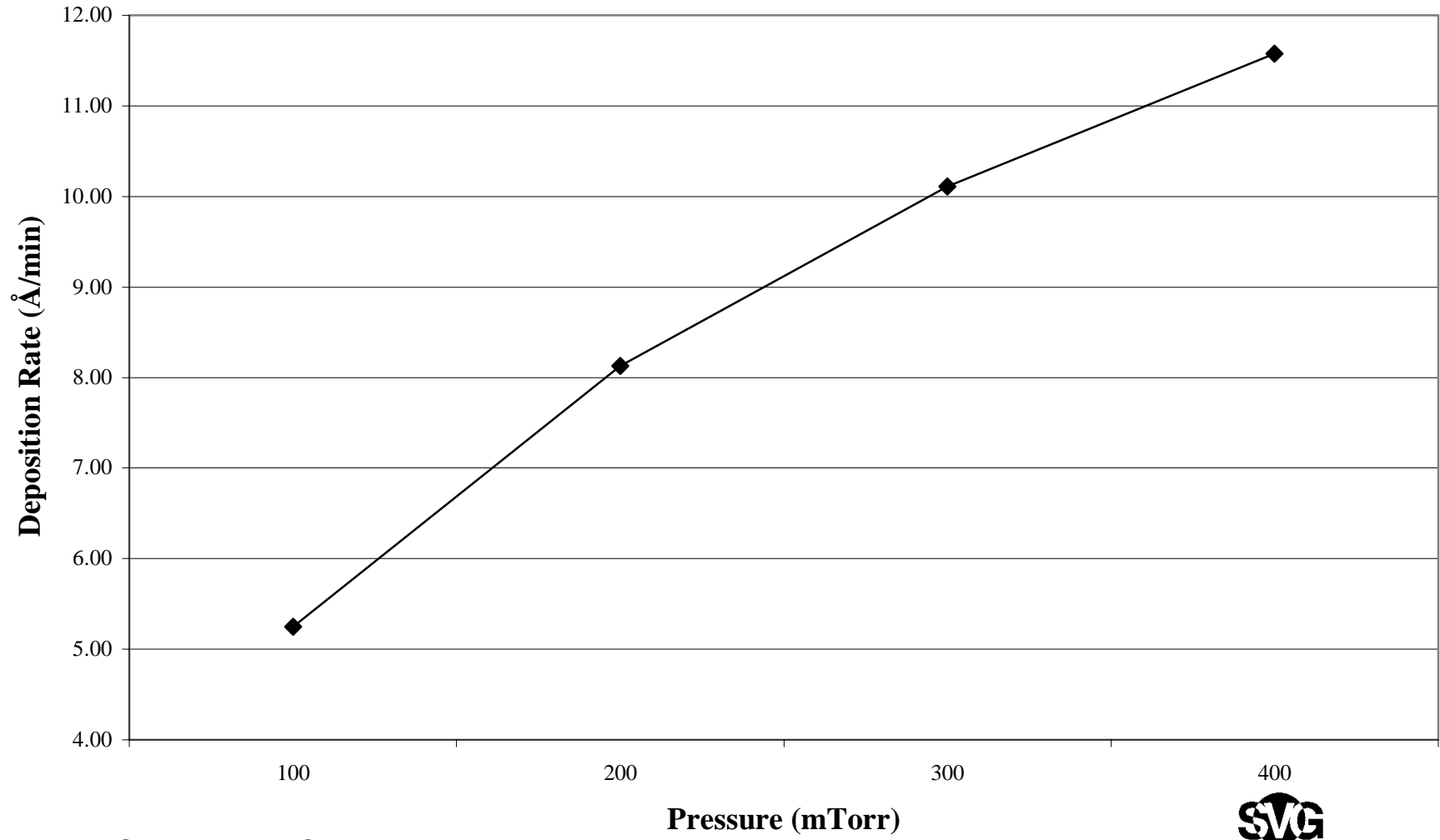
**Figure 4 - BTBAS Nitride  
Temperature vs Refractive Index for 0.5" Spacing,  
100 mTorr Pressure, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**



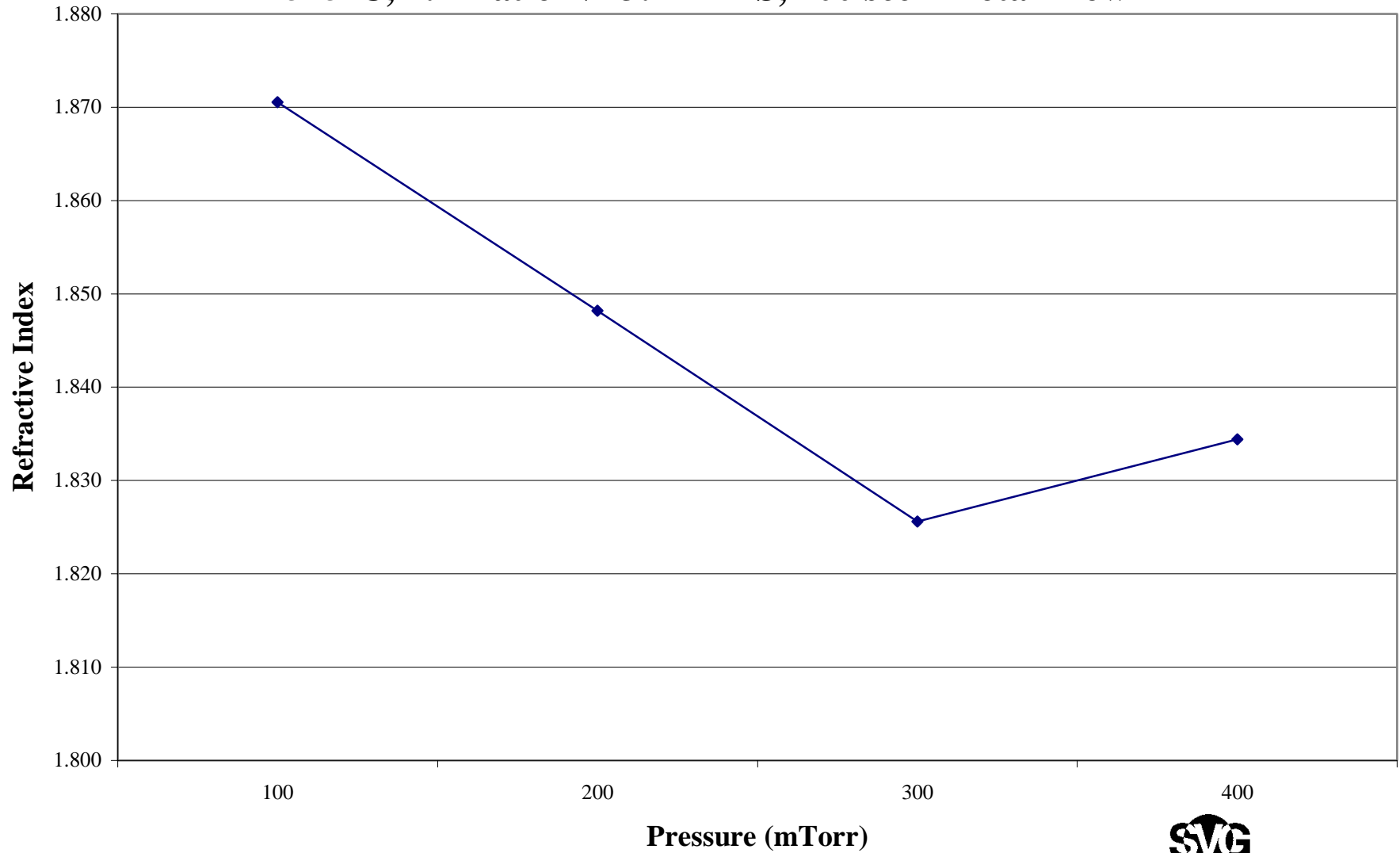
**Figure 5 - BTBAS Nitride  
Pressure vs Within Wafer Uniformity for 0.5" Spacing,  
575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**



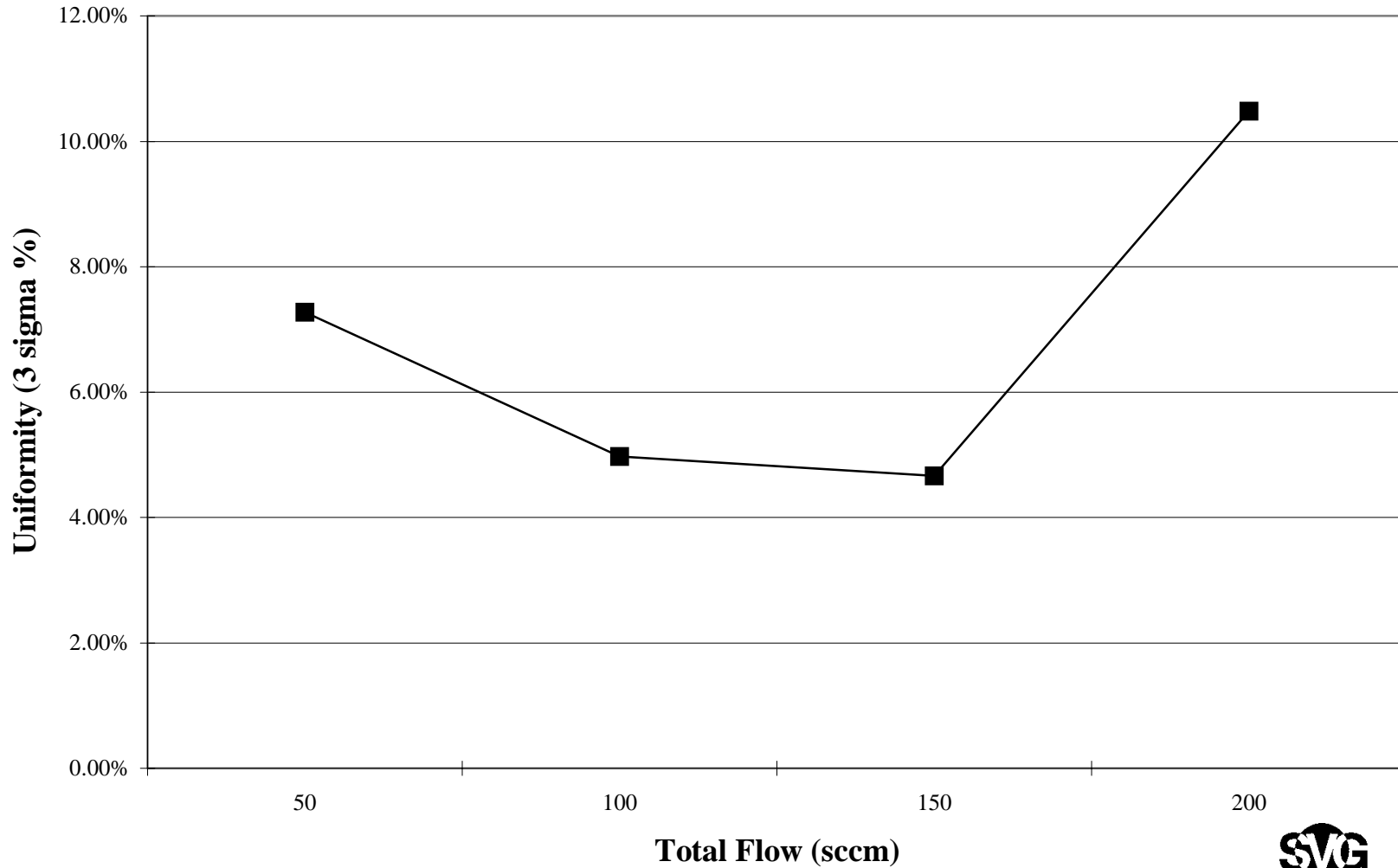
**Figure 6 - BTBAS Nitride  
Pressure vs Deposition Rate for 0.5" Spacing,  
575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**



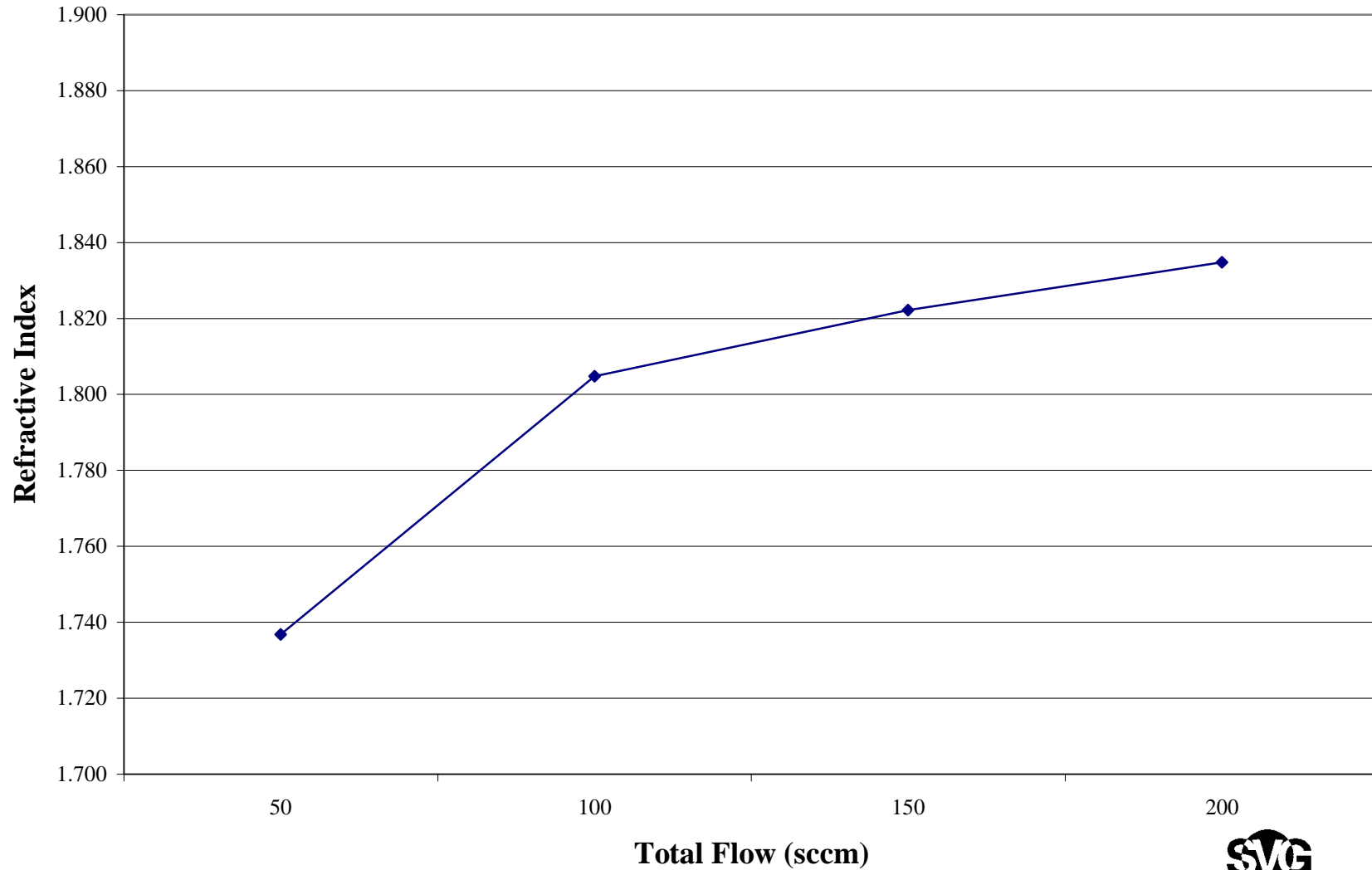
**Figure 7 - BTBAS Nitride  
Pressure vs Refractive Index for 0.5" Spacing,  
575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 200 sccm Total Flow**



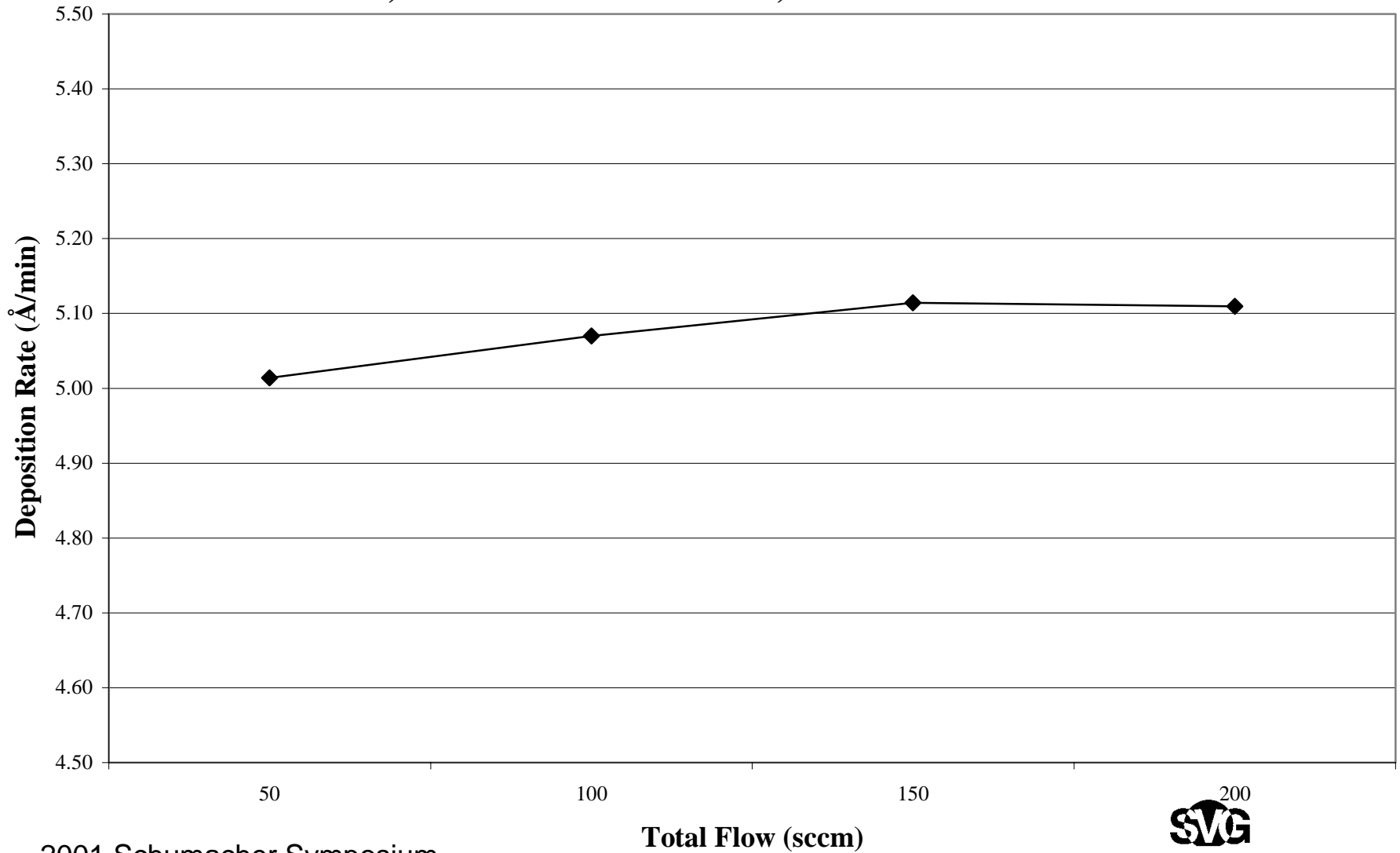
**Figure 8 - BTBAS Nitride**  
**Total Flow vs Within Wafer Uniformity for 0.5" Spacing,**  
**575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 100 mTorr Pressure**



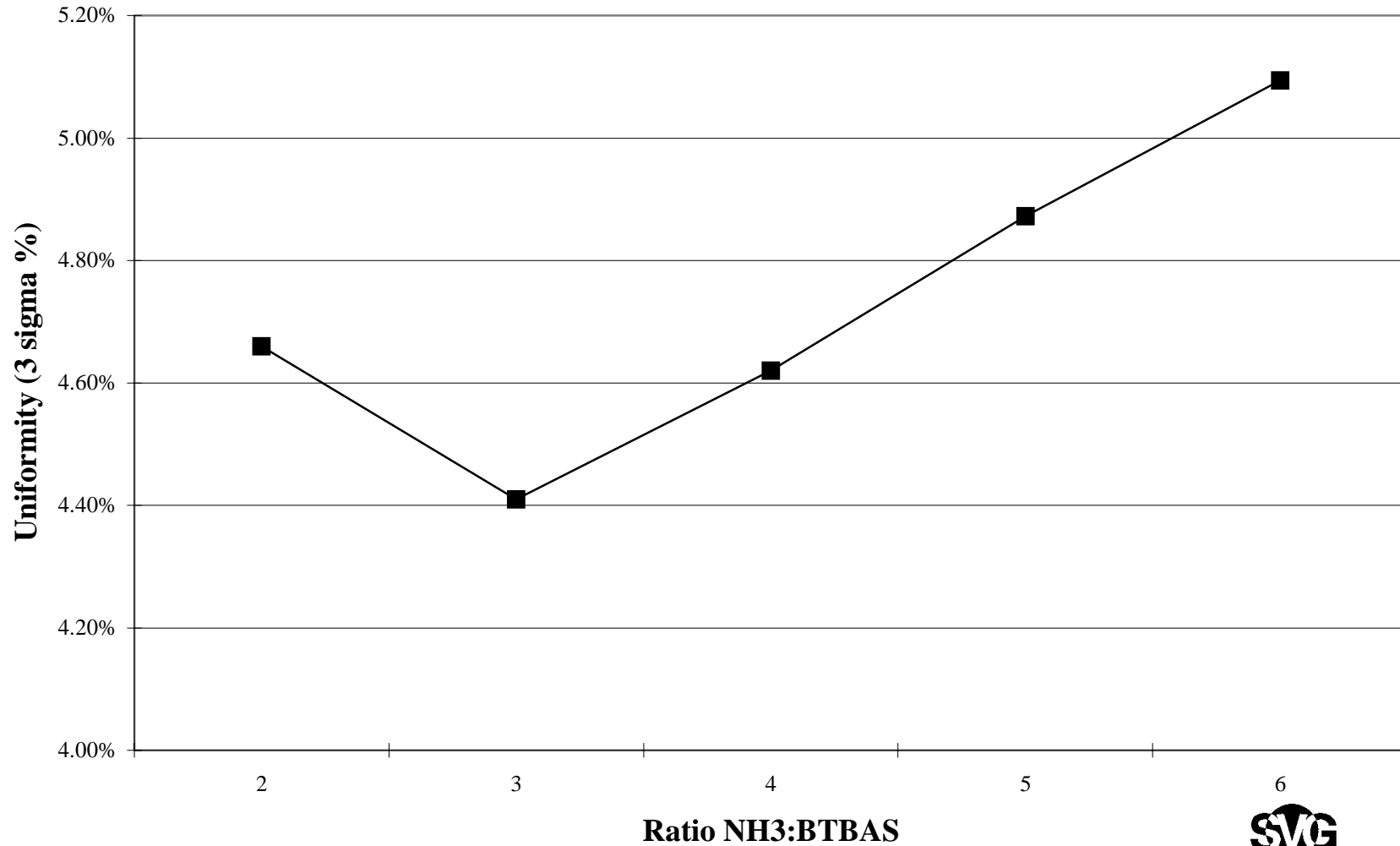
**Figure 8 - BTBAS Nitride**  
**Total Flow vs Refractive Index for 0.5" Spacing,**  
**575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 100 mTorr Pressure**



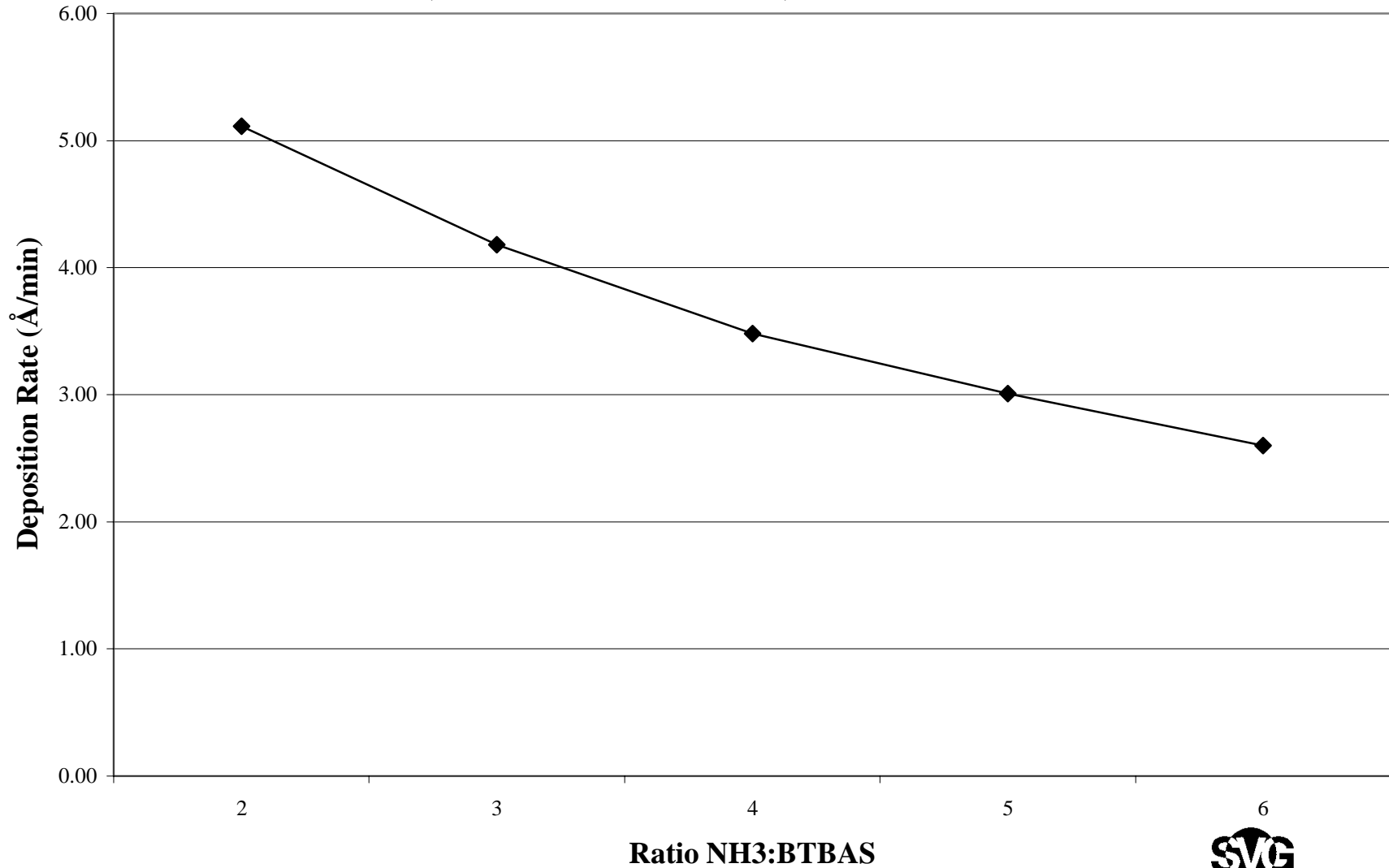
**Figure 10 - BTBAS Nitride**  
**Total Flow vs Deposition Rate for 0.5" Spacing,**  
**575°C, 2:1 Ratio NH<sub>3</sub>:BTBAS, 100 mTorr Pressure**



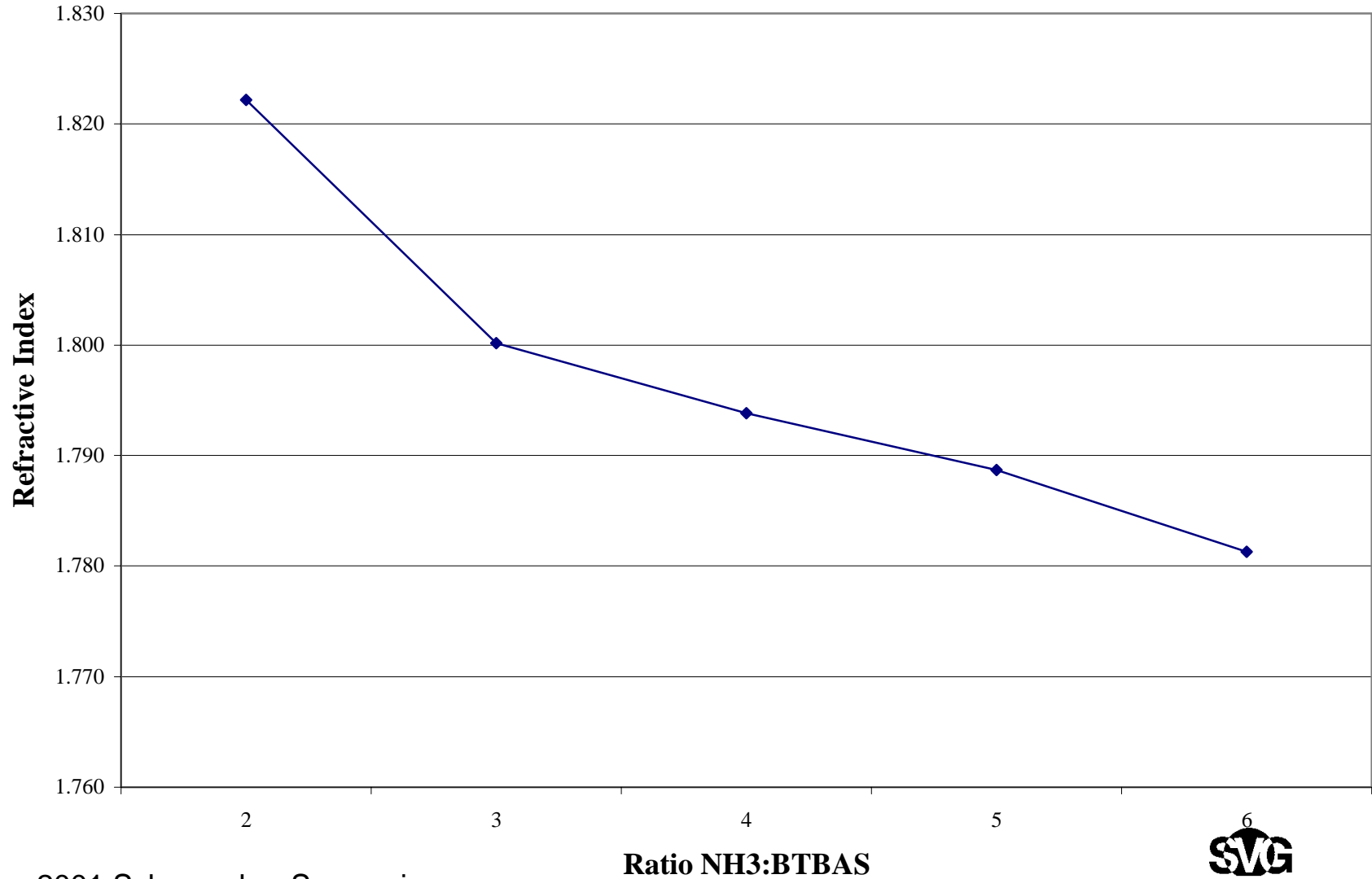
**Figure 11 - BTBAS Nitride**  
**Ratio NH<sub>3</sub>:BTBAS vs Within Wafer Uniformity for 0.5" Spacing,**  
**575°C, 100 mTorr Pressure, 150 sccm Total Flow**



**Figure 12 - BTBAS Nitride**  
**Ratio NH<sub>3</sub>:BTBAS vs Deposition Rate for 0.5" Spacing,**  
**575°C, 100 mTorr Pressure, 150 sccm Total Flow**



**Figure 13 - BTBAS Nitride  
Ratio NH<sub>3</sub>:BTBAS vs Refractive Index for 0.5" Spacing,  
575°C, 100 mTorr Pressure, 150 sccm Total Flow**

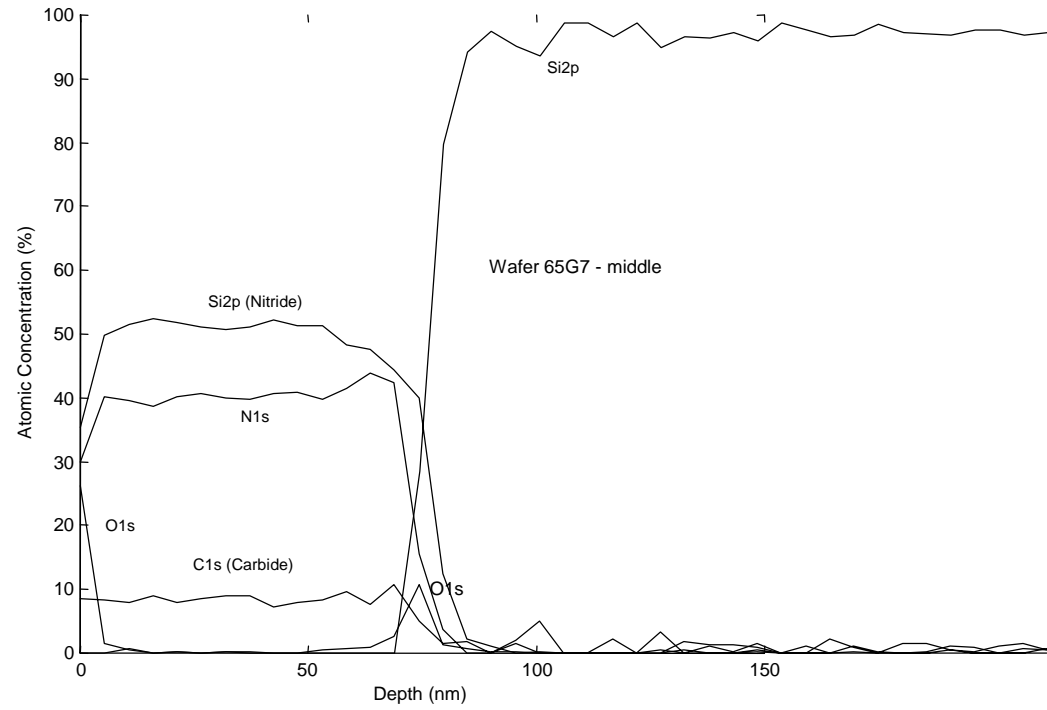


# BTBAS Nitride 100 Wafer Loads (0.25 inch Wafer Pitch)

- Using previous knowledge from 0.5 inch wafer pitch tests
- Added new reduced diameter tube liner (240mm ID)
- Added Boat Rotation to improve uniformity within wafer
- “Best Process Conditions”
  - Temperature 560°C
  - Pressure 100 mT
  - Flows 150 BTBAS, 150 NH<sub>3</sub>
- Best Results:
  - Within Wafer <5% 3 $\sigma$
  - Wafer to Wafer <3% 3 $\sigma$
  - Refractive Index 1.91 to 1.93
  - Deposition Rate 3.3 Å/minute

# Figure 14 X-ray Photoelectron Spectroscopy

01167005.pro: Nitrisw: Nitride  
2001 Mar 29 Al mono 49.4 W 100.0  $\mu$  45.0° 58.70 eV  
Si2p/Point5: 65G7 - Middle  
01167005.pro



# X-ray Photoelectron Spectroscopy

- Films deposited at 560°C and 610°C
- Thin oxide layer at the Si-SiN interface.
- Surface of the films have a thin oxide layer
  - may be adsorbed surface oxygen
- Si:N ratio in all the samples is near 5:4
  - films are silicon rich
- ~10% Carbon detected in all the SiN films
  - Carbon is present as a carbide (probably SiC)

# BTBAS Nitride Advantages

- Liquid source
- Similar to TEOS - delivery, handling
- Vapor pressure of ~ 6.5 Torr at 45°C
- Reacts with Ammonia to form Silicon Nitride
- Temperature of deposition 550°C to 650°C
- More conformal than DCS or SiH<sub>4</sub> Silicon Nitride

# BTBAS Nitride Limitations

- Best within wafer uniformities at lower temperatures
- Lower temperature = lower deposition rates
- Spacing is important -
  - (wafer pitch and wafer edge to liner)

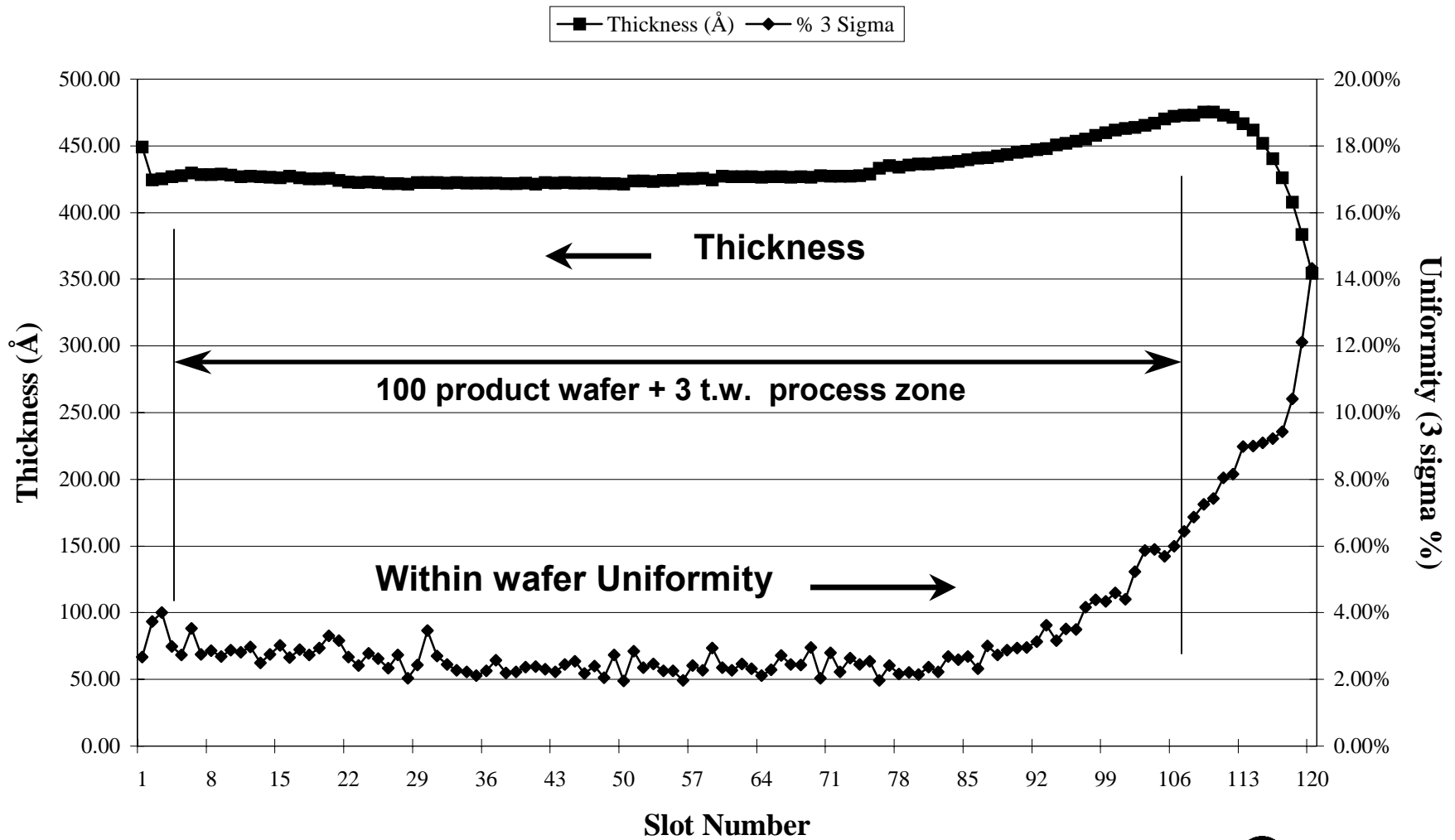
<u>Wafer pit</u>	<u>Loadsize</u>	<u>WIW Uniformity</u>
0.50 inch	50 product	< 4.5 % $3\sigma$ (std. Liner)
0.25 inch	100 product	< 6.5 % $3\sigma$ (std. Liner)
0.25 inch	100 product	< 5.0 % $3\sigma$ (reduced liner)

- Refractive Index 1.8-1.95 typical in these tests
- Refractive index decreases toward better WIW Unif.

# Silicon Dioxide BTBAS Films

- Primary Process Window
  - Temperature 500 to 600°C
  - Total flow 200 to 500 sccm
  - O<sub>2</sub>: BTBAS Ratio 2:1 to 10:1
  - Pressure 150 to 450 mT
- Area of best results
  - Temperature 500°C
  - Total Flow 200 sccm
  - O<sub>2</sub>: BTBAS Ratio 2:1
  - Pressure 150 mT

**Figure 15 - BTBAS Oxide - 120 Wafer Load (0.25" Spacing)  
- Not Optimized**



# BTBAS Oxide

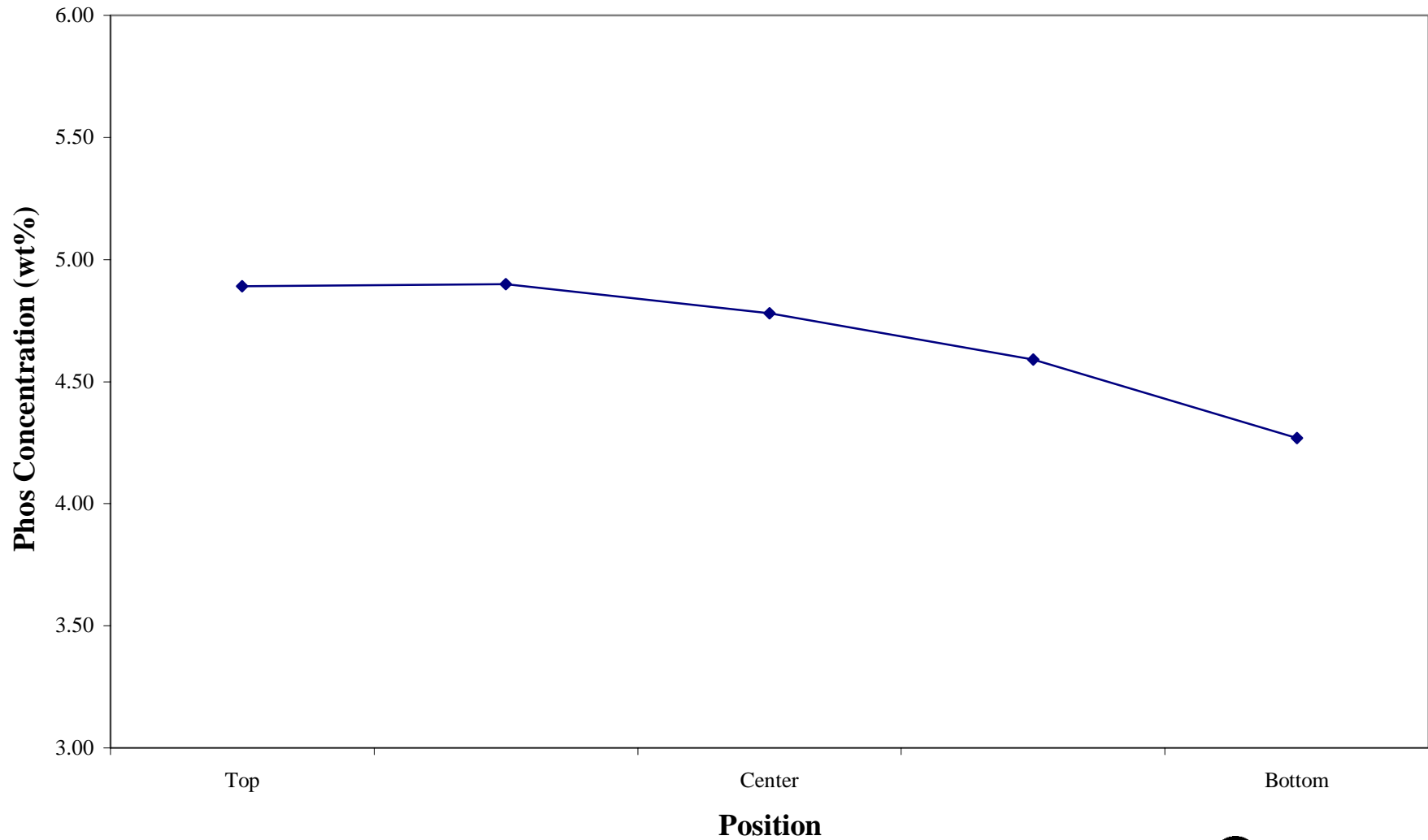
## Etch Rate Comparison – 40:1 BOE

Run	Etch Rate Å/minute	Relative to Thermal Oxide	Deposition Temperature °C
BTBAS Ox1	6.17	2.32	575
BTBAS Ox5	6.18	2.32	575
BTBAS Ox7	6.00	2.25	575
TEOS	6.80	2.55	650
TEOS	6.50	2.44	650
Thermal Ox	2.66	1.00	NA

# Phosphorus Doped Silicon Dioxide BTBAS Films

- Primary Process Window
  - Temperature 450 to 500°C
  - Total Flow 525 to 1600 sccm
  - O<sub>2</sub>: BTBAS Ratio 2:1
  - PH<sub>3</sub> mole ratio 1.4 to 5.0 E-2
  - Pressure 300 to 1000 mT
  - Phosphine Mixture 10% PH<sub>3</sub> in N<sub>2</sub>

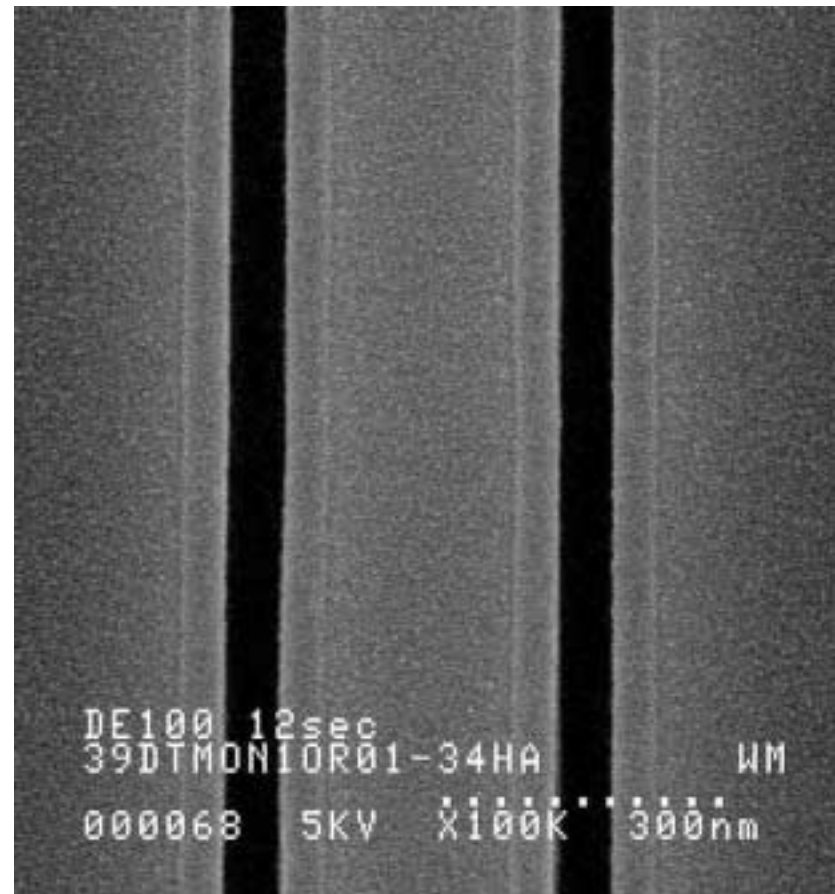
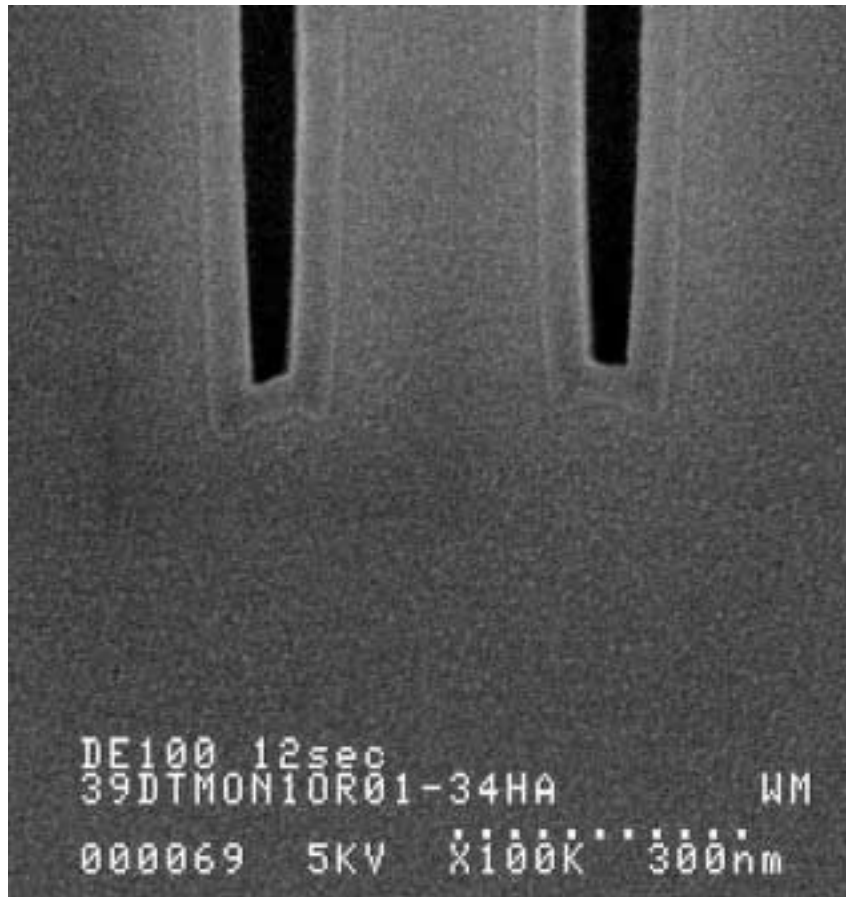
**Figure 16 - Phosphorus Concentration Down Load For BTBAS Oxide**



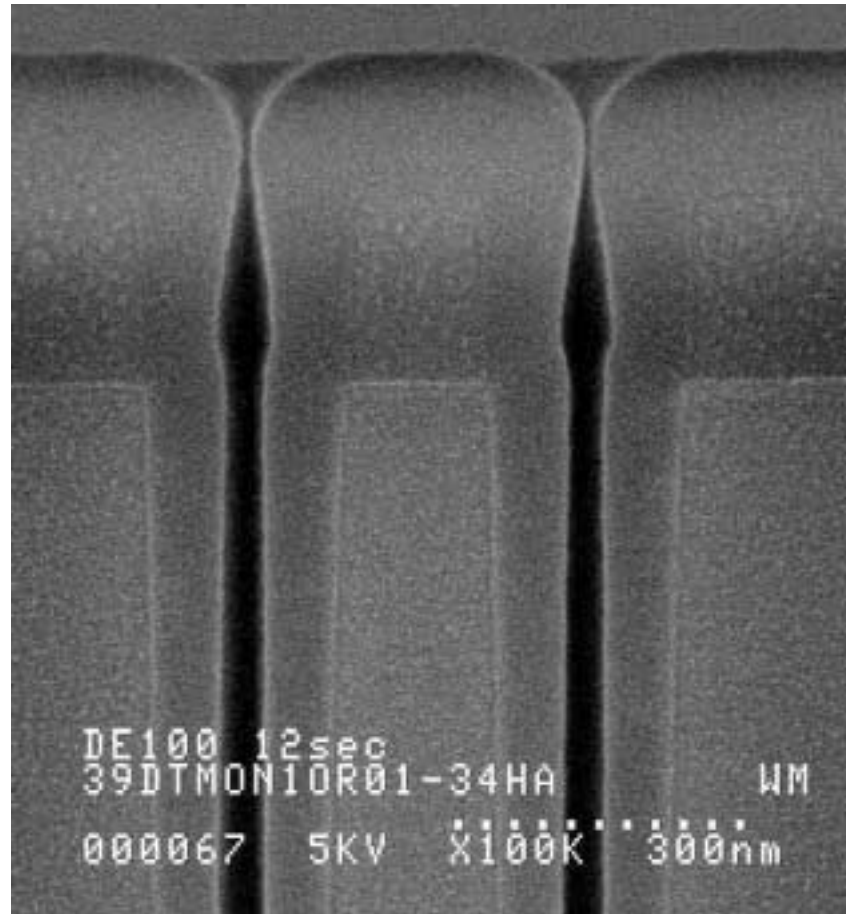
# BTBAS Phos Doped Oxide Etch Rate Comparison – 40:1 BOE

Run	Etch Rate Å/minute	Relative to Thermal Oxide	Deposition Temperature °C
4.3 Wt%	7.84	2.94	500
5.5 Wt%	8.85	3.32	500
4.8 Wt%	10.48	3.94	475
6.4 Wt%	10.01	3.76	475
Thermal Ox	2.66	1.00	NA

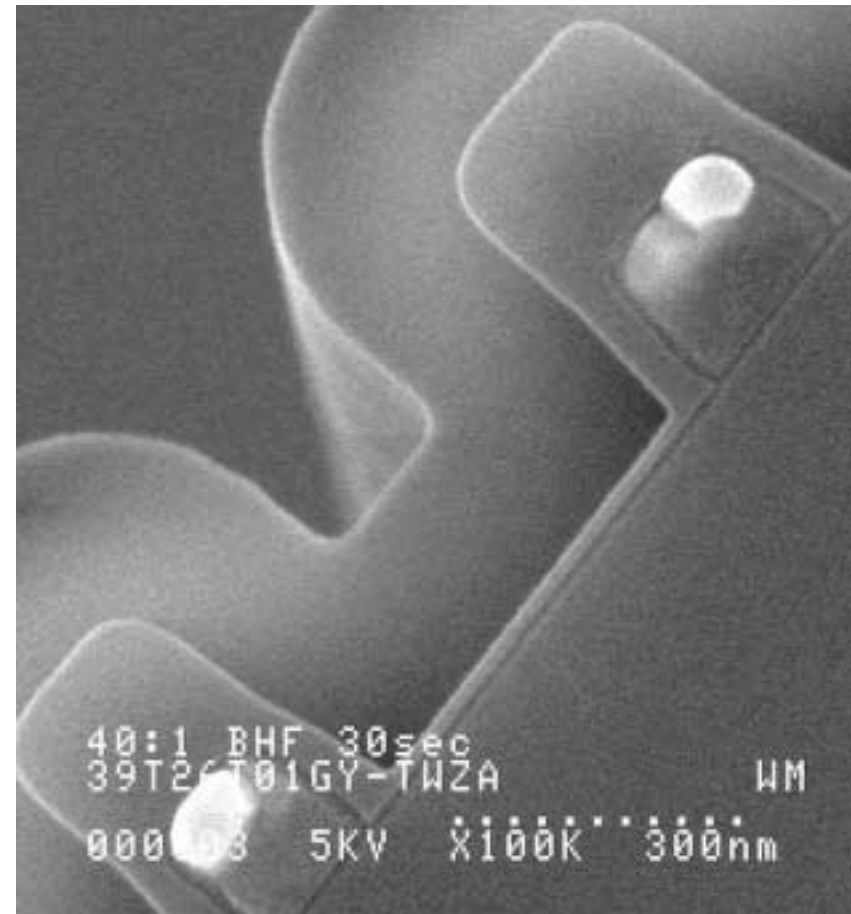
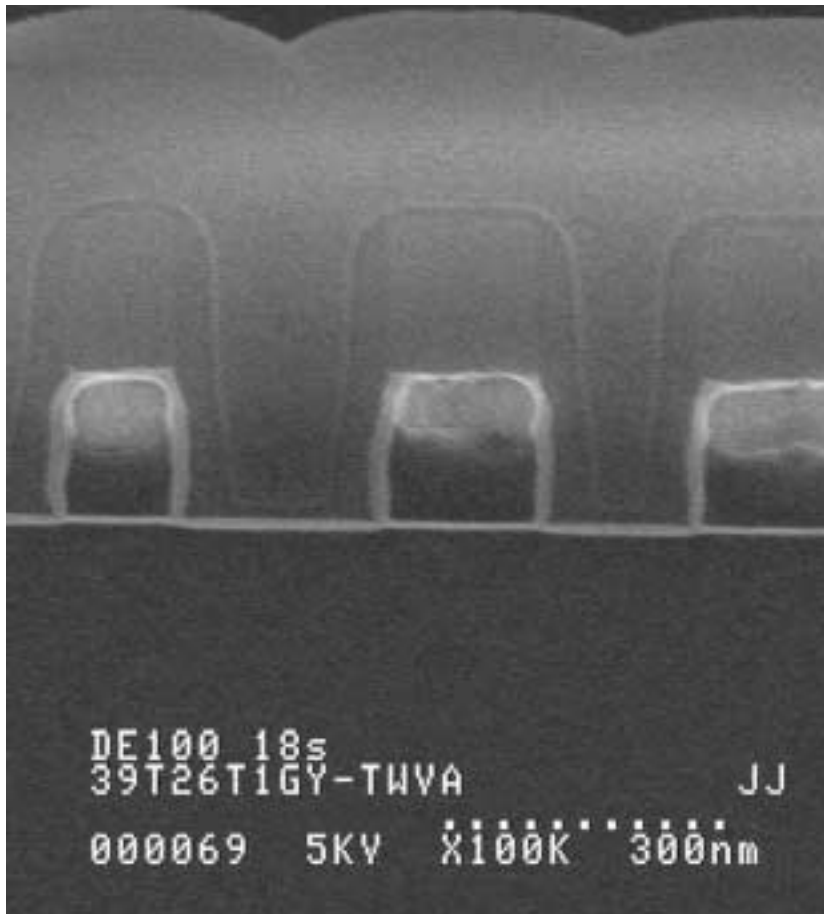
# BTBAS Oxide Step Coverage Deep Trench Oxide Liner



# Step Coverage – Deep Trench



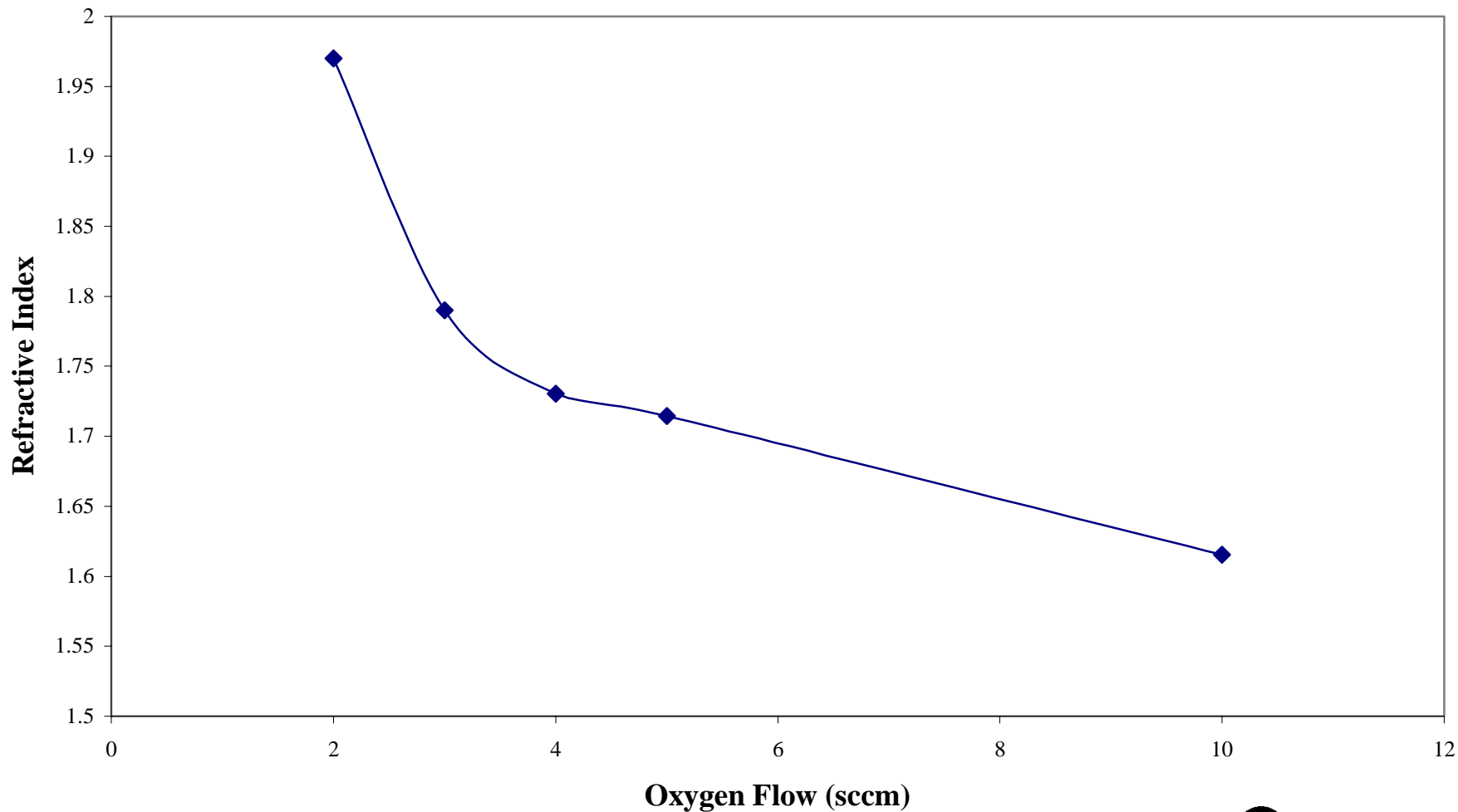
# Step Coverage – Shallow Trench Isolation BTBAS Oxide



# BTBAS Oxynitride

- BTBAS + NH<sub>3</sub> + O<sub>2</sub> or N<sub>2</sub>O
- Tests run with O<sub>2</sub> only
  - N<sub>2</sub>O not currently available on our system
- Standard BTBAS/NH<sub>3</sub> flows
  - Added very small amounts of O<sub>2</sub> (2 to 10 sccm)
- Pressure at 150 mTorr
- Refractive index = 1.62 to 1.97
- Index Uniformity = < 3% 3σ all points
- Wafer pitch = 0.5 inch
- Using Boat Rotation

**Figure 17 - BTBAS Oxynitride Refractive Index vs Oxygen Flow**  
**2:1 NH<sub>3</sub>:BTBAS, 560°C, 150 mT**



# Conclusions

- **BTBAS films:**
  - **Nitrides, Oxides, Phosphorus Doped Oxides, and Oxynitrides can be produced in a Vertical Batch Furnace with good load size and uniformity**
- **Many device applications can be developed**
- **The SVG Apps Lab has a system dedicated to BTBAS film process demonstration and application development.**
- **We are willing to work with interested companies on potential device applications.**

# Acknowledgements

We thank --

- Dr. David Brown at AMD Austin for XPS work on nitride
- BJ Park at IBM for Oxide and PSG etch rate and dopant analysis results
- Helen Marsh at the San Jose Applications Lab for running most of the experiments and making the film measurements