a clear edge

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Abatement of N_2O from Semiconductor Manufacturing

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Overview – N_2O Abatement

- N_2O is a Greenhouse Gas
- N_2O can be abated
  - N_2O lab tests
    - Byproducts
- Caveats
  - Emission factors
  - Complex process recipes

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N_2O Emissions from the Fab

- Nitrous oxide (N_2O) is used as a process gas in CVD and diffusion
  - Benign and stable
  - A Greenhouse Gas that accumulates in the atmosphere
- N_2O accounts for ~5% of all process-related GHG emissions from US Semi manufacturing*
- N_2O by-products include NO, NO_2
  - NOx leads to acid rain

*In tons of CO_2 equivalents

Source: Per EPA 2012 GHG emissions summary. N_2O 100 yr GWP 298 (vs. CF_4, 7390; SF_6, 22,800)

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N_2O Abatement Project - SEMATECH sponsored

- – Can N_2O be abated?
  - – Excellent DRE in lab
    - N_2O flow at 10 slm
- Edwards Atlas Kronis abatement
  - – Porous ceramic inward-fired combustor
  - – CH_4 and/or O_2 added as needed for process recipe
    - Configurable based on application
  - – Integrated water scrubber
- Abatement of N_2O is not straightforward

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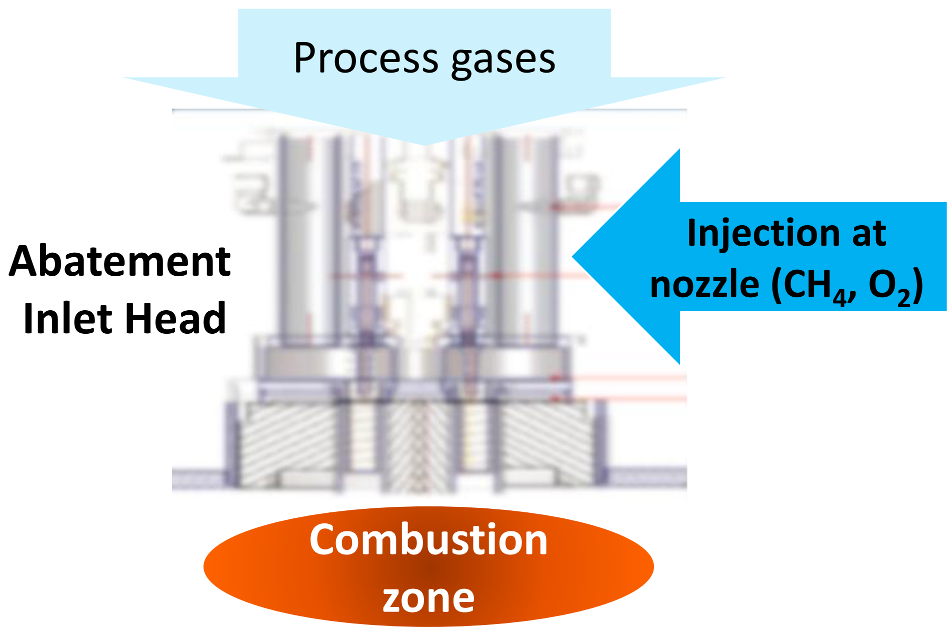
Abatement Process Modes for Effective Abatement

Mode	Injection At nozzle	Combustion chemistry	Application	By product Concerns
"Clean"	None	Reducing	NF_3	NOx
"Deposition"	O_2, CH_4	Oxidizing	Low k, NH_3	PICs, NOx, VOCs
"Reducing"	CH_4	Reducing	N_2O	PICs



Edwards abatement combustor can be modified to most effectively destroy targeted process gases

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N_2O Abatement – Lab Results

- 10 slm N_2O from MFC
  - 50 slm N_2 purge from vacuum pump

Test	SiH_4	Fuel	N_2O in	N_2O out	N_2O %DRE
	slm	slm	ppm	ppm	
1	0	0	166,667	19,124	0.0
2	1	0	163,900	17,369	9.2
3	2	0	161,300	12	99.9
4	0	3	158,700	17599	8.0
5	0	4	156,300	14197	25.8
6	0	5	153,800	6886	64.0
7	0	6	151,500	3478	81.8
8	0	7	149,300	2233	88.3

- Added reducing agents, as N_2O is an oxidizer
  - SiH_4, CH_4

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- With no additional reducing agents, N_2O is unabated

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- Addition of 2 slm SiH_4 abates N_2O better

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- Addition of natural gas works pretty well too

Addition of SiH_4 or Fuel Abates N_2O

- If only it were that easy …

How Much Fuel to Add?

- More fuel gives better DRE
  - 10 slm N_2O is abated to 99% with 2 slm added silane
    - Mimics process recipes where SiH_4 flows with N_2O

Test	SiH_4	Fuel	NO out	NO_2 out	CO out	N_2O %DRE
	slm	slm	ppm	ppm	ppm	
1	0	0	40	22	108	0.0
2	1	0	387	27	76	9.2
3	2	0	1,481	47	58	99.9
4	0	3	210	59	2231	8.0
5	0	4	523	73	1655	25.8
6	0	5	795	36	725	64.0
7	0	6	803	27	405	81.8
8	0	7	732	29	432	88.3

How Much Fuel to Add?

- Methane addition at low flows is less expensive
  - Poor DRE, high CO generation
    - Inadequate methane – below LFL – does not combust cleanly

Test	SiH_4	Fuel	NO out	NO_2 out	CO out	N_2O %DRE
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  - Similar behavior is seen with low k precursors
    - Incomplete DRE in absence of adequate fuel (Semicon West 2002, 2004)

How Much Fuel to Add?

- High methane addition gives better DRE
  - Lower CO
  - Higher NO, not as high as with SiH_4

Test	SiH_4	Fuel	NO out	NO_2 out	CO out	N_2O %DRE
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  - Good performance

How Much Fuel to Add?

- Step 1: Fuel based on N_2O flow
- Step 2: Generate Look-up Table for fuel vs. N_2O
  - Example:

N_2O In	Fuel added	Expected Emissions			
slm	slm	N_2O DRE	CO, ppm	NO, ppm	NO_2, ppm
2	1	98	xxx	yyy	zzz
4	---	---	---	---	---
6	+++	+++	+++	+++	+++
8	---	---	---	---	---
10	+++	+++	+++	+++	+++
15	---	---	---	---	---
20	+++	+++	+++	+++	+++
25	---	---	---	---	---

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Assigning the Correct Fuel Flow to Abate N_2O

- If only it were that easy …

Reaction of N_2O in the Process Chamber

- N_2O is not passive in the process chamber
  - Reacts with TEOS, SiH_4, low k …
- N_2O + Plasma or Heat → NO, NO_2, N_2, O_2
  - In varying proportions
- Emissions Factors (EFs) for N_2O virtually nonexistent
  - Hundreds of etch processes
  - Dozens of NF_3-based cleans
- Fuel look-up table is useless without EFs

N_2O Decomposition Byproducts

- N_2O + Plasma or Heat → NO, NO_2, N_2, O_2
- QMS required to measure N_2 and O_2
  - N_2 and O_2 are not IR-active (cannot use FTIR)
  - N_2 is used for various purges
    - Pre-pump QMS is very difficult
  - N_2 and O_2 are atmospheric gases
    - Minor leaks in high vacuum of QMS have large effect
- 20 slm N_2O in - maybe 15 slm N_2O in exhaust
  - Or 12 slm, or 10 slm, or 8 slm
- **Cannot select fuel setting without EFs**

QMS *– quadrapole mass spectrometer*
FTIR *– Fournier Transfer InfraRed (spectrometer)*

N_2O Decomposition Byproducts

- NO : NO_2 ratio changes
  - NOx abated in strongly reducing environment
    - More fuel
  - Significant Products of Incomplete Combustion (PICs) – CO, CH_4
    - Less fuel
- NO and NO_2 formation in the abatement?
  - NOx levels can increase in oxidizing combustor
- EFs are required to evaluate NOx from abatement
  - Differentiate process NOx from abatement NOx

Varying Flows of N_2O During Recipe

- Some recipes have widely-ranging N_2O flows
  - High N_2O setup produces PICs at low N_2O
  - Low N_2O setup produces poor DRE high N_2O

- No generalized setting for N_2O abatement
  - Interactive abatement systems that respond to N_2O flows
  - Need tie in to process gas flows and EFs for best performance

- Process gases can affect N_2O DRE
  - E.g. TEOS makes ethanol and CO
    - These act as fuels

NF_3 – Based Chamber Cleans

- NF_3 abatement has different abatement requirements
  - Fuel injection used for N_2O
  - High fuel on NF_3 chamber clean ($2\ NF_3 \rightarrow 3\ F_2 + N_2$) makes CF_4
    - $CH_4 + 4\ F_2 \rightarrow CF_4 + 4\ HF$
    - This has been well-documented
  - Need interface to indicate clean step

- Tool interface <u>required</u> for N_2O and NF_3
  - Only way to optimize both Dep and Clean steps
    - Else you make more CF_4 (high GWP) than you save by abating N_2O

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Summary for N_2O Abatement

Good News

- **N_2O is readily abated using combustion to > 95% DRE**
  - Proper combustor chemistry (CH_4, O_2) critical
  - Minimize NOx and CO emissions

More Work

- Need for emission factors for N_2O processes
- Need interfacing with tool to indicate process gas flows
- Expand to evaluate all N_2O processes