Off-gassing from III-V Wafer Processing -- A Collaboration of SEMATECH and IMEC

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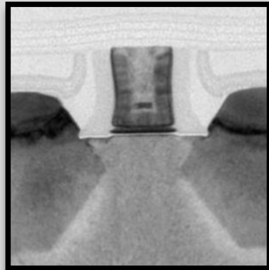
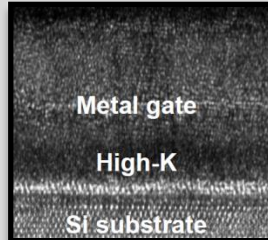
Technology Outlook

Manufacturing **Development** **Research**

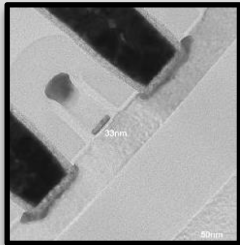
- SiGe Stressors
- High-κ/Metal Gate
- Bulk FinFETs / FD-SOI



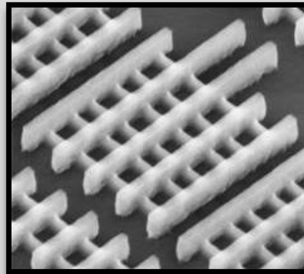
SiGe Stressors: INTEL



High-κ/Metal Gate: TSMC

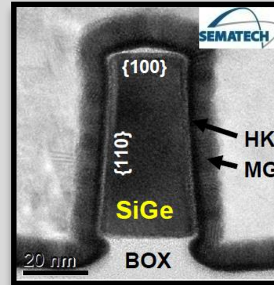


FD-SOI: GLOBALFOUNDRIES

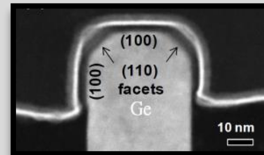


Bulk FinFETs: INTEL

- SiGe Channels
- Ge Channels
- ET-SOI

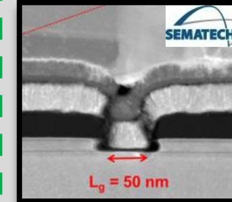


SiGe Channel: SEMATECH

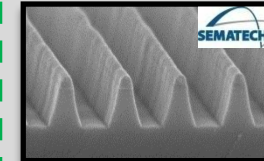


Ge FinFET: TSMC

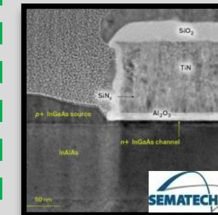
- Ge/III-V FinFETs
- Vertical NW
- TFET



III-V FET: SEMATECH

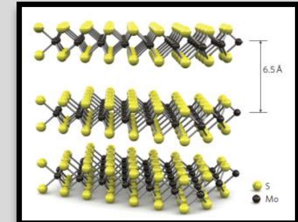


III-V Fins: SEMATECH

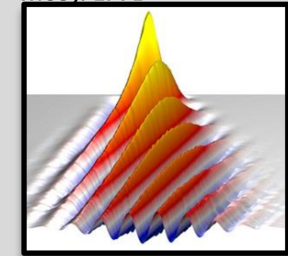


TFET: SEMATECH

- 2D
- Spin



MoS_2: EPFL



Spintronics: IBM

45 nm / 32 nm / 22 nm **14 nm / 10 nm** **7 nm / 5 nm / 3 nm**

Experiment Goals

- **CMP polishing:**
  - Quantify and identify species off-gassing during CMP using analytical instrumentation.
    - CM4® has been used in the past – but analytical instrumentation adds considerably more information
    - Differences in off-gassing due to III-V layer composition?
    - Off-gassing influenced by slurry composition?
  - Evaluate whether off-gassing of III-V CMP wafers is a health & safety issue

- **Wafer off-gassing in FOUP environment:**
  - Can we identify off-gassing of III-V layers in FOUPS?
  - Is there any ESH concern or issue?

Experiment Goals

- Evaluate off-gassing of III-V wafers: InP, GaAs, and InGaAs.

- Off-gassing testing for two activities/areas:
  - In Front Opening Unified Pods (FOUPs)
  - During CMP polishing process at a CMP tool
  - Joint experiment was performed at IMEC in Leuven, Belgium in November 2014.

FTIR and CM4 Techniques

- Identify the species of the off-gassing by using Fourier Transform Infra Red Spectroscopy (FTIR) as the analytical tool.
  - MKS 2030 FTIR

FTIR Detection Limits			
	AsH_3 (ppmv)	PH_3 (ppmv)	SiH_4 (ppmv)
Runs 1,2,3	0.011	0.117	0.010
Runs 4,5	0.010	0.119	0.012

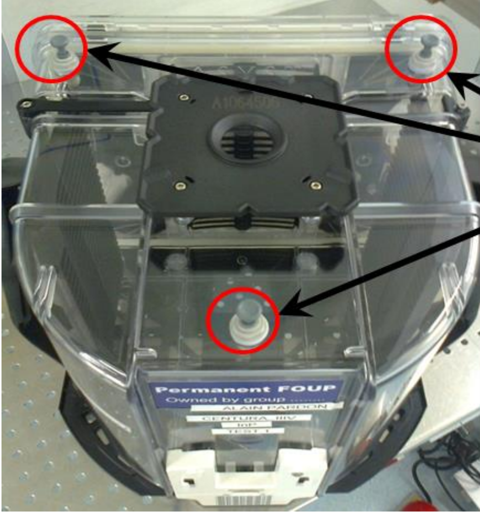
- CM4® gas monitor was used as a monitoring instrument during the tests.

Off-gassing in FOUPs

Objective:

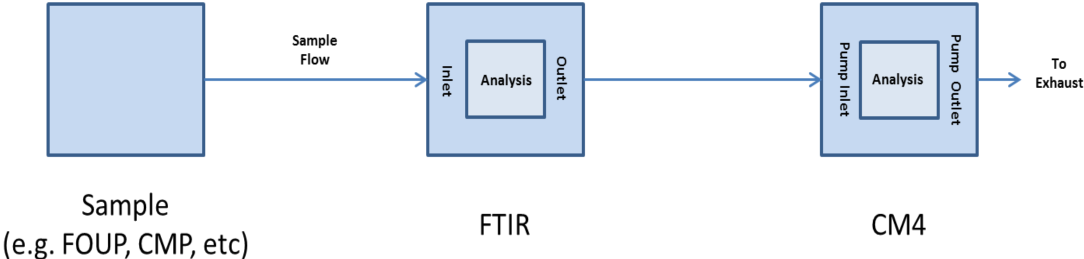
- Evaluate PH_3 and AsH_3 emissions off InP and GaAs wafers in wafer FOUPs after MOCVD deposition
- Evaluate off-gassing recurrence over time

Port Configuration on the Modified FOUPs



Three, one-touch, quick-connect, ¼” FOUP Ports arranged in a triangular pattern on the top surface of the FOUP. Pictured here with plugs inserted.

General Sampling Configuration



FOUP Test Setup and Description

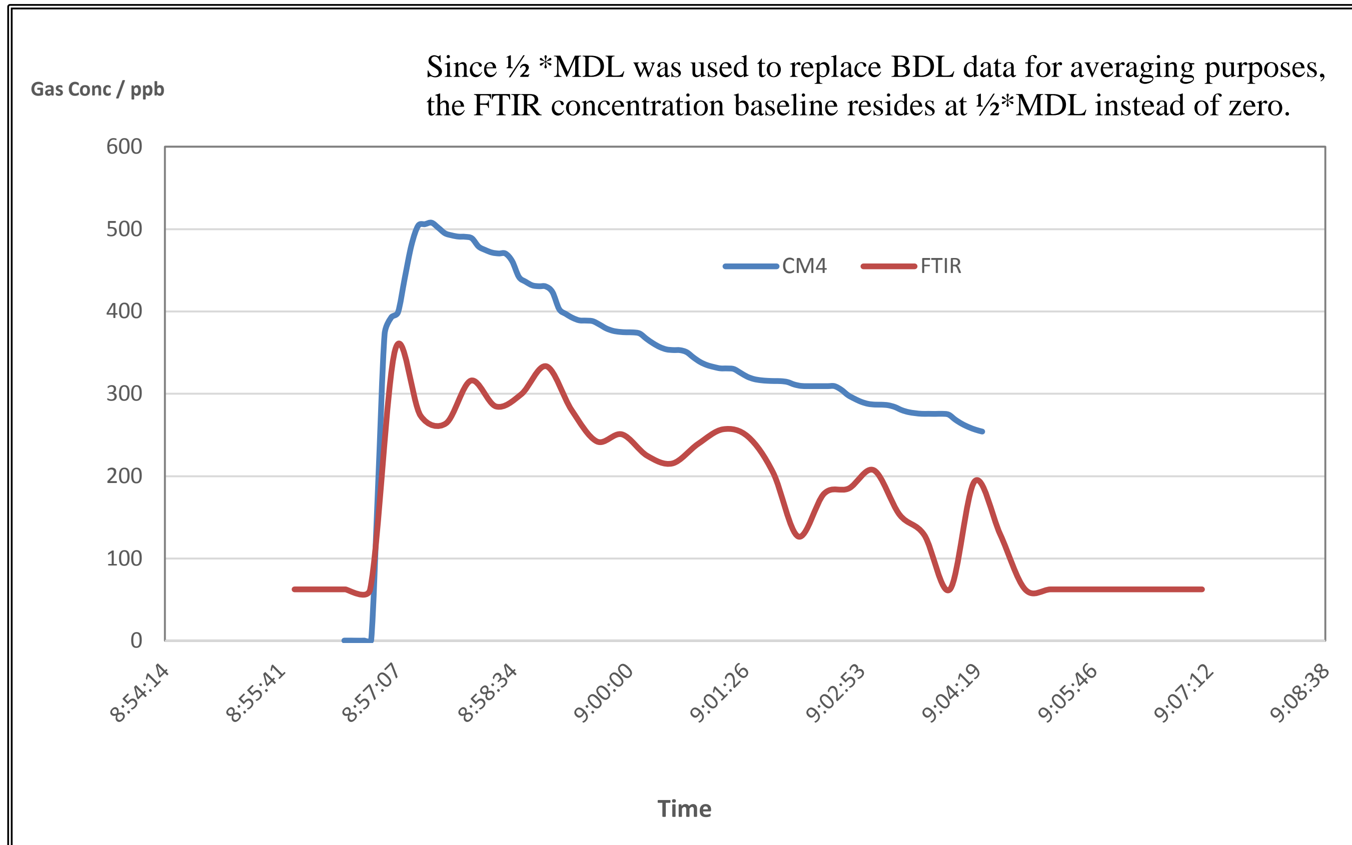
Test Name	FOUP ID	Wafer Substrate	Test Description	Gas	Content (# Wfrs)	Experimental Setup
Test 1	2	InP	1st InP (fresh wafers)	Ambient Air	3	Extractive via CM4® pump
Test 2	1	GaAs	1st GaAs (fresh wafers)	Ambient Air	3	Extractive via CM4® pump
Test 3	2	InP	2nd InP (Same wafers as Test #1, 24-hrs later)	Ambient Air	3	Extractive via CM4® pump
Test 4	2	InP	3rd InP (same wafers as Test #3, 48-hrs later)	Ambient Air	3	Extractive via CM4® pump
Test 5	3	InP	4th InP (Fresh InP wafers)	Ambient Air	10	Extractive via CM4® pump

FOUP Test Results

Test Name	Wafer Substrate	Test Description	Concentration Statistic	Arsine	Phosphine	Phosphine	Silane	
				By-FTIR (ppmv)	By-FTIR (ppmv)	By-CM4® * (ppmv)	By-FTIR (ppmv)	
Test 1	InP	Extractive	Minimum	BDL	BDL	0.0001	BDL	
			Maximum	BDL	0.432	0.457	BDL	
			Average	BDL	0.176	0.219	BDL	X
			MDL	0.014	0.117	NA	0.016	
Test 2	GaAs	Extractive	Minimum	BDL	BDL	NA	BDL	
			Maximum	BDL	BDL	NA	BDL	
			Average	BDL	BDL	NA	BDL	
			MDL	0.012	0.104	NA	0.014	
Test 3	InP	Extractive (24 hours after Test #3)	Minimum	BDL	BDL	0.0001	BDL	
			Maximum	BDL	0.218	0.199	BDL	
			Average	BDL	0.088	0.106	BDL	X
			MDL	0.01	0.091	NA	0.014	
Test 4	InP	Extractive (24 hours after Test #5)	Minimum	BDL	BDL	0.037	BDL	
			Maximum	BDL	BDL	0.139	BDL	
			Average	BDL	BDL	0.089	BDL	X
			MDL	0.009	0.125	NA	0.017	
Test 5	10 Fresh InP Wfrs	Fresh InP wafers	Minimum	BDL	BDL	0.0002	BDL	
			Maximum	BDL	0.358	0.508	BDL	
			Average	BDL	0.203	0.316	BDL	
			MDL	0.009	0.125	NA	0.017	

*** CM4® was set to interpret the chemical tape's response as phosphine.**

FOUP Test 5 – 10 Fresh InP Wafers – CM4® and FTIR



Concentrations of PH_3 from a previously sealed FOUP containing 10 Fresh InP wafers measured via CM4® and FTIR.

Summary - Off-gassing from FOUP

- AsH_3 was below FTIR detection limit of 11 ppb during the FOUP off-gassing tests, and below the CM4 ® detection limit
- The presence of PH_3 off-gassing inside the FOUP is detected by FTIR at a level of >>300ppb
  - Off-gassing of PH_3 from the InP wafers was observed after 24 hours of setting time.
- The off-gassing of the wafers appears to dissipate over time; the off-gassing issue in the manufacturing process needs ESH attention.
- Further studies are on-going.

Off-gassing during CMP

Objective: Evaluate hydride off-gassing during III-V CMP

- Slurries with different pH values and different hydrogen peroxide concentrations

- III-V layered wafers (GaAs, InGaAs, InP)

Off-gassing during CMP

Run 1:

- Parameters: **Slurry A**, 150 ml/min, pH4, additive 1.5% H_2O_2

Run	Material	Polishing Time[s]
1	InP	150
1	InP	150
1	InP	150
1	oxide	60
1	oxide	60
1	InGaAs	120
1	InGaAs	120
1	oxide	60
1	oxide	60
1	GaAs	180
1	GaAs	180
1	oxide	60
1	oxide	60
1	Si	120
1	Si	120
1	Si	120

Off-gassing during CMP

Run 1:

- Parameters: **Slurry A**, 150 l/ml, pH4, additive 1.5% H_2O_2
- Test results:

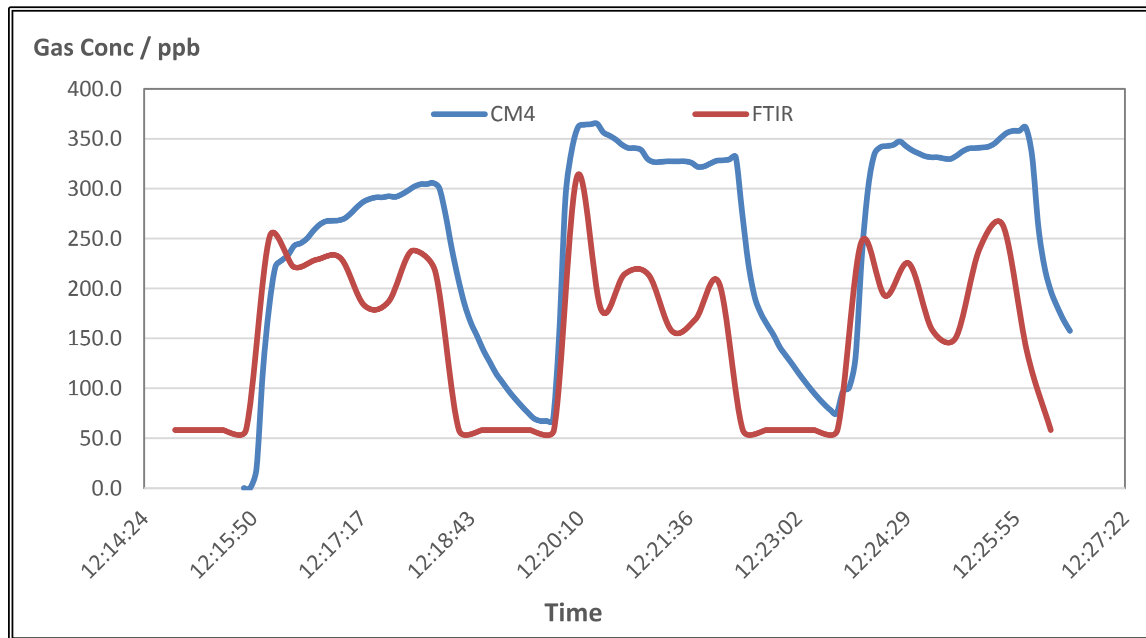
		Run 1 FTIR Concentration Summary (ppmv)								
Wafer Type	Wafer Number	AsH3 (ppmv)			PH3 (ppmv)			SiH4 (ppmv)		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
InP	1	BDL	BDL	BDL	BDL	0.252	0.176	BDL	BDL	BDL
	2	BDL	BDL	BDL	BDL	0.313	0.153	BDL	BDL	BDL
	3	BDL	BDL	BDL	BDL	0.263	0.162	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	0.276	0.164	BDL	BDL	BDL
InGaAs	6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GaAs	10	BDL	0.024	0.008	BDL	BDL	BDL	BDL	0.016	0.007
	11	BDL	0.019	0.007	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	0.022	0.008	BDL	BDL	BDL	BDL	0.016	0.007
Si	14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.016	0.009
	16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.019	0.010
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.017	0.010
Oxide	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

over-polishing to silicon layer

Off-gassing during CMP

Run 1:

- InP Wafer Off-gassing Readings: CM4® and FTIR



FTIR (blue) and CM4® (red) concentration readings of PH_3 during CMP Run 1 using InP wafers (wafers 1, 2, and 3)

Off-gassing during CMP

Run 2:

- Parameters: **Slurry A**, 150 ml/l, pH4, additive 3% H_2O_2

Run	Material	Polishing Time[s]
2	oxide	60
2	oxide	60
2	oxide	60
2	oxide	60
2	InP	150
2	InP	150
2	InP	150
2	oxide	60
2	oxide	60
2	InGaAs	120
2	InGaAs	120
2	oxide	60
2	oxide	60
2	GaAs	90
2	GaAs	90
2	oxide	60
2	oxide	60
2	Si	60
2	Si	60
2	Si	60

Off-gassing during CMP

Run 2:

- Parameters: **Slurry A**, 150 ml/l, pH4, additive 3% H_2O_2
- Test results:

Wafer Type	Wafer Number	Run 2 FTIR Concentration Summary								
		AsH3 (ppmv)			PH3 (ppmv)			SiH4 (ppmv)		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
InP	1	BDL	BDL	BDL	BDL	0.168	0.118	BDL	BDL	BDL
	2	BDL	BDL	BDL	BDL	0.199	0.130	BDL	BDL	BDL
	3	BDL	BDL	BDL	BDL	0.178	0.101	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	0.182	0.116	BDL	BDL	BDL
InGaAs	6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GaAs	10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si	14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Oxide	22	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	23	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	24	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	25	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Off-gassing during CMP

Run 3:

- Parameters: **Slurry B**, 150 ml/l, pH8, additive 1.5% H_2O_2

Run	Material	Polishing Time[s]
3	oxide	60
3	oxide	60
3	oxide	60
3	oxide	60
3	InP	180
3	InP	180
3	InP	180
3	oxide	60
3	oxide	60
3	InGaAs	120
3	InGaAs	120
3	oxide	60
3	oxide	60
3	GaAs	120
3	GaAs	120
3	oxide	60
3	oxide	60
3	Si	120
3	Si	120
3	Si	120

Off-gassing during CMP

Run 3:

- Parameters: **Slurry B**, 150 ml/l, pH8, additive 1.5% H_2O_2
- Test results:

Wafer Type	Wafer Number	Run 3 FTIR Concentration Summary								
		AsH3 (ppmv)			PH3 (ppmv)			SiH4 (ppmv)		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
InP	1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
InGaAs	6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GaAs	10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	11	BDL	0.015	0.006	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	0.015	0.006	BDL	BDL	BDL	BDL	BDL	BDL
Si	14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Oxide	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Off-gassing during CMP

Run 4:

- Parameters: **Slurry C**, 150 ml/l, pH10, additive 1.5% H_2O_2

Run	Material	Polishing Time[s]
4	oxide	60
4	oxide	60
4	oxide	60
4	oxide	60
4	InP	180
4	InP	180
4	InP	180
4	oxide	60
4	oxide	60
4	InGaAs	120
4	InGaAs	120
4	oxide	60
4	oxide	60
4	GaAs	120
4	GaAs	120
4	oxide	60
4	oxide	60
4	Si	120
4	Si	120
4	Si	120

Off-gassing during CMP

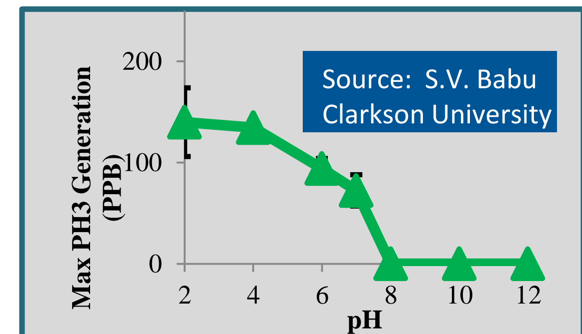
Run 4:

- Parameters: **Slurry C**, 150 ml/l, pH10, additive 1.5% H_2O_2
- Test results:

Wafer Type	Wafer Number	Run 4 FTIR Concentration Summary								
		AsH3 (ppmv)			PH3 (ppmv)			SiH4 (ppmv)		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
InP	1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
InGaAs	6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GaAs	10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si	14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Oxide	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Average	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Summary – Off-gassing during CMP

- Significant level of PH_3 (with peaks of 170 – 300 ppb) was detected during InP wafer polishing with Slurry A (@pH 4).
- Significant level of AsH_3 was detected during GaAs wafer polishing with Slurry A (24 ppb @pH 4) and Slurry B (15 ppb @pH 8).
- Hydride evolution depends on slurry pH, slurry type, and the concentration of H_2O_2.
- The presence of increased H_2O_2 concentration tends to reduce the off-gassing rate of III-V hydride gases.
- Hydride off-gassing during III-V CMP polishing needs ESH attention.



Industry Exposure Thresholds

	OSHA PEL (8-hr TWA)	ACGIH TLV (8-hr TWA)	NIOSH IDLH
Arsine (AsH_3)	0.05 ppm; 0.2 mg/m^3	0.005 ppm	3 ppm
Phosphine (PH_3)	0.3 ppm; 0.4 mg/m^3	0.3 ppm	50 ppm

Summary

- Wafer off-gassing of PH_3 from InP layer has been observed inside a sealed FOUP, in contrast to GaAs which did not show AsH_3 off-gassing
  - Off-gassing of PH_3 can continue even 24 to 48 hours after wafer enclosure in FOUP
  - Solutions need to be developed to ensure off-gassing is completed in a shorter time-frame to allow ESH-compatible manufacturing
- Significant level of PH_3 release was detected during CMP process of InP wafers under low pH conditions.
  - InGaAs wafers did not show AsH_3 gas evolution under conditions where GaAs CMP showed AsH_3 evolution
  - Addition experimental confirmation of AsH_3 gas evolution during GaAs CMP is recommended
- FTIR has the capability of identifying the species and the concentrations of the hydride gases
- Quantitative CM4® data was of limited analytical use without prior knowledge of a gas mixture's composition, or a way to differentiate the various gas constituents beforehand

THANK YOU