Novel Reactive Chemistry Sources for Surface Passivation of Future Generation Channel Materials

Presented by
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Overview

- Challenges for passivation of new channel materials
- Why Hydrogen Peroxide & Hydrazine?
- RASIRC BRUTE™ Technology
- Passivation approach to InGaAs(001)
- Passivation approach to SiGe(110)
- Conclusions

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Challenges for Passivation on InGaAs and SiGe Channel Materials

- In Situ methods are desired
- Passivate surface dangling bonds
- Maintain an electrically unpinned surface Fermi Level ready for subsequent high-K gate oxide nucleation
- Passivation layer must prevent atomic migration into subsequent layers
- Underlying substrate must not be damaged
- Low thermal budget constraints (<400C)

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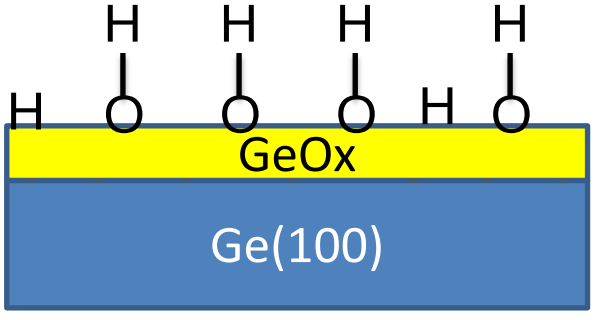
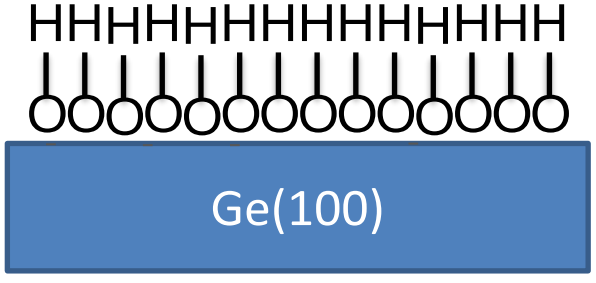
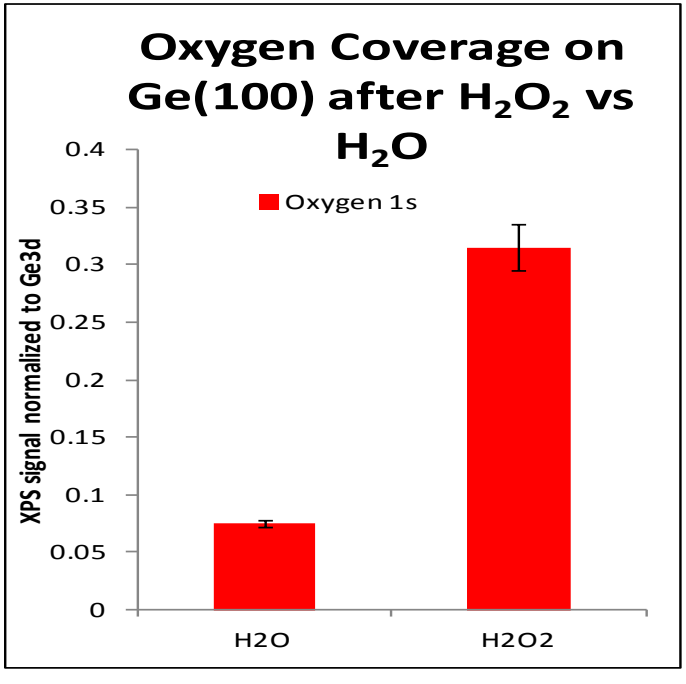
Why Gas Phase Hydrogen Peroxide?



Versus



- Ge dosing experiments
- $HOOH/H_2O$ will nucleate the surface more efficiently than H_2O



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Why Gas Phase Hydrazine?

- Weakness of the N-N bond strength leads to high reactivity on Metal surfaces
- New Channel Materials have limited thermal budgets (typical <400C)
- Early studies (1992) by Slaughter and Gland show H_2NNH_2 to be more reactive than NH_3 on an Si(100) surface

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Challenges

- Anhydrous Hydrogen Peroxide liquid is difficult to handle and may rapidly decompose leading to explosion

$$HOOH_{(l)} \rightarrow H_2O_{(g)} + O_{2(g)}$$

- Anhydrous Hydrazine has a low flash point of 37C and is highly toxic
  - Current commercial sources lack sufficient purity

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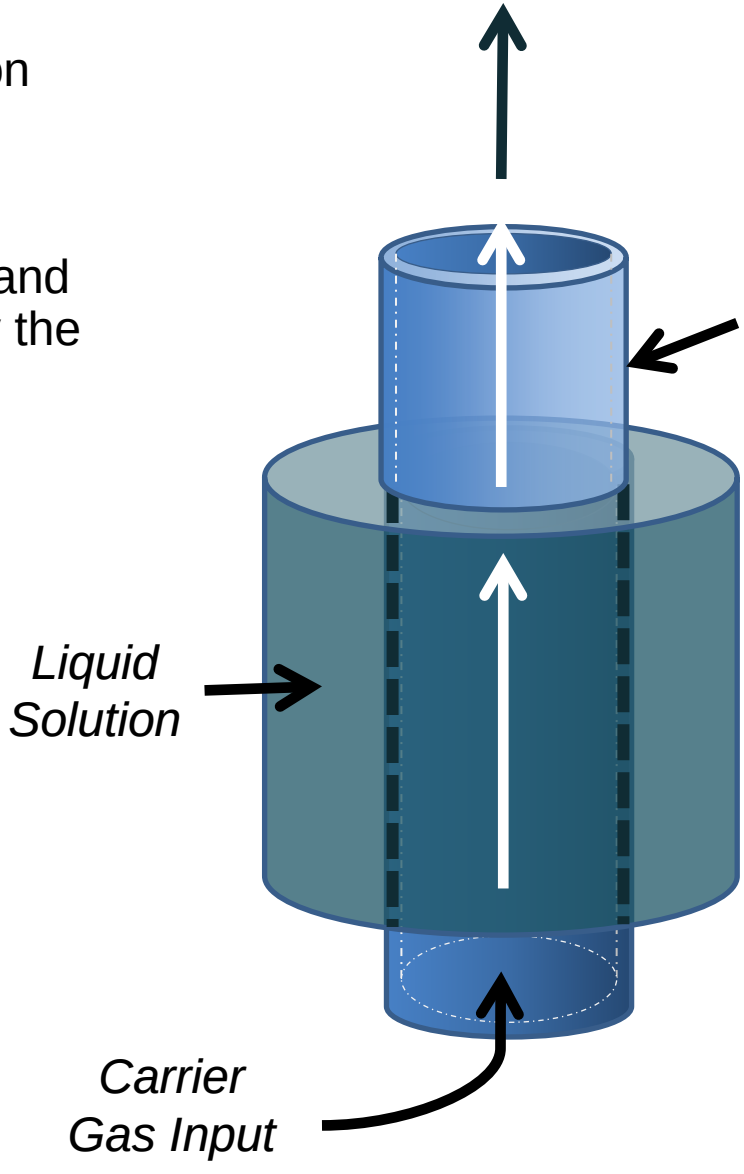
RASIRC Membrane Technology

The liquid (solution surrounds the membrane tubes, passes thru the membrane walls and gets picked up by the carrier gas



- Custom extruded and chemically modified by RASIRC
- Membrane has 10 to 50 nm pores, ionically charged
- Only polar molecules can pass through

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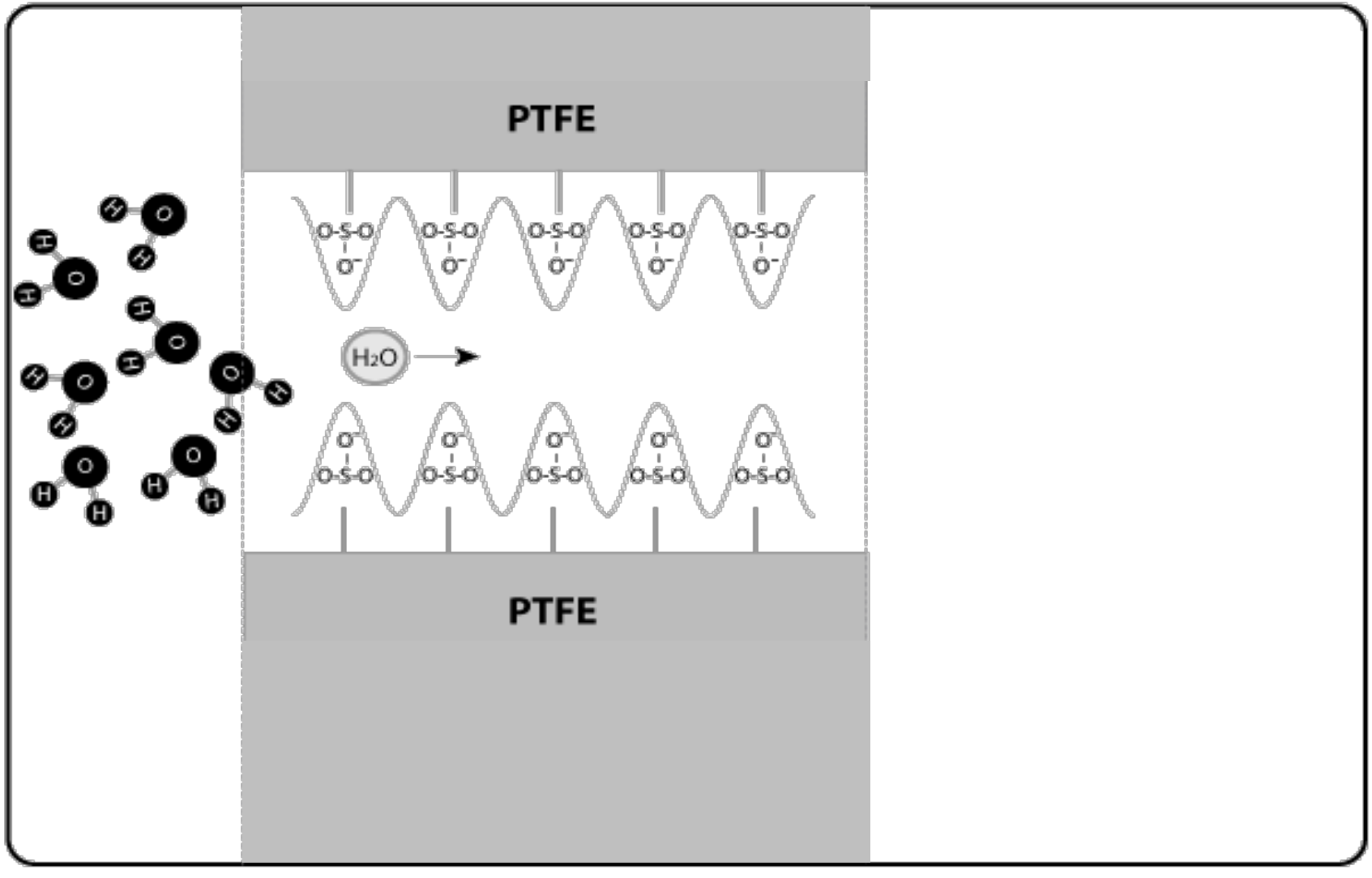
Ionically Charged Channels



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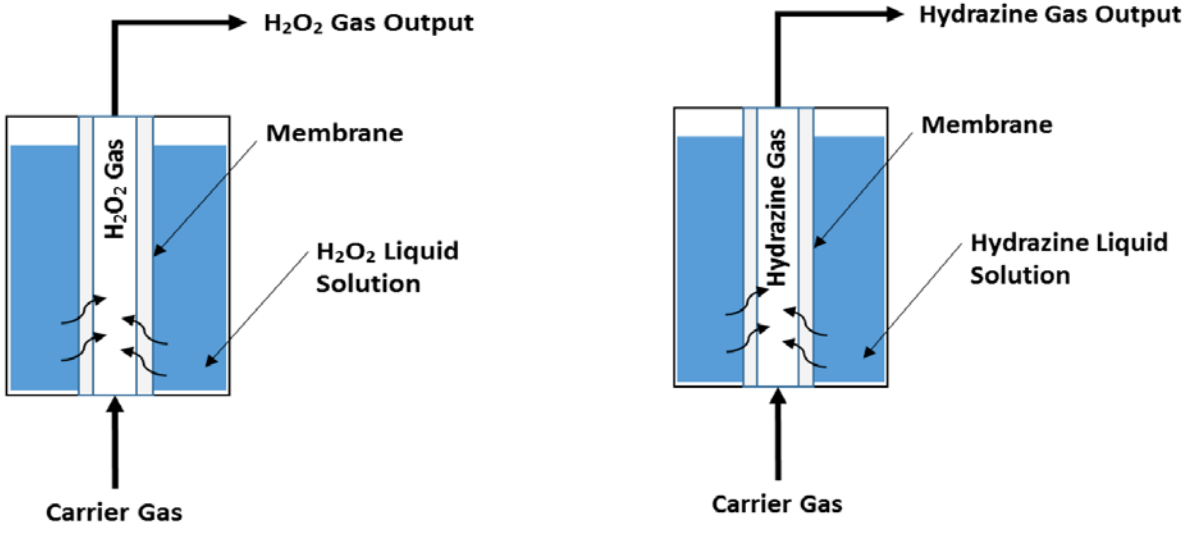
Approach to Anhydrous Delivery



- Purify and Isolate Ultra High Purity Anhydrous HOOH (l) or H2NNH2 (l)
- Reactive chemical is stabilized by mixing with a proprietary solvent
- Tubular Membrane/Carrier Gas
  - Selective for Hydrogen Peroxide or Hydrazine molecules
- Desired Molecule permeates membrane and is delivered to process
- Solvent remains on liquid side of membrane & does not enter gas stream

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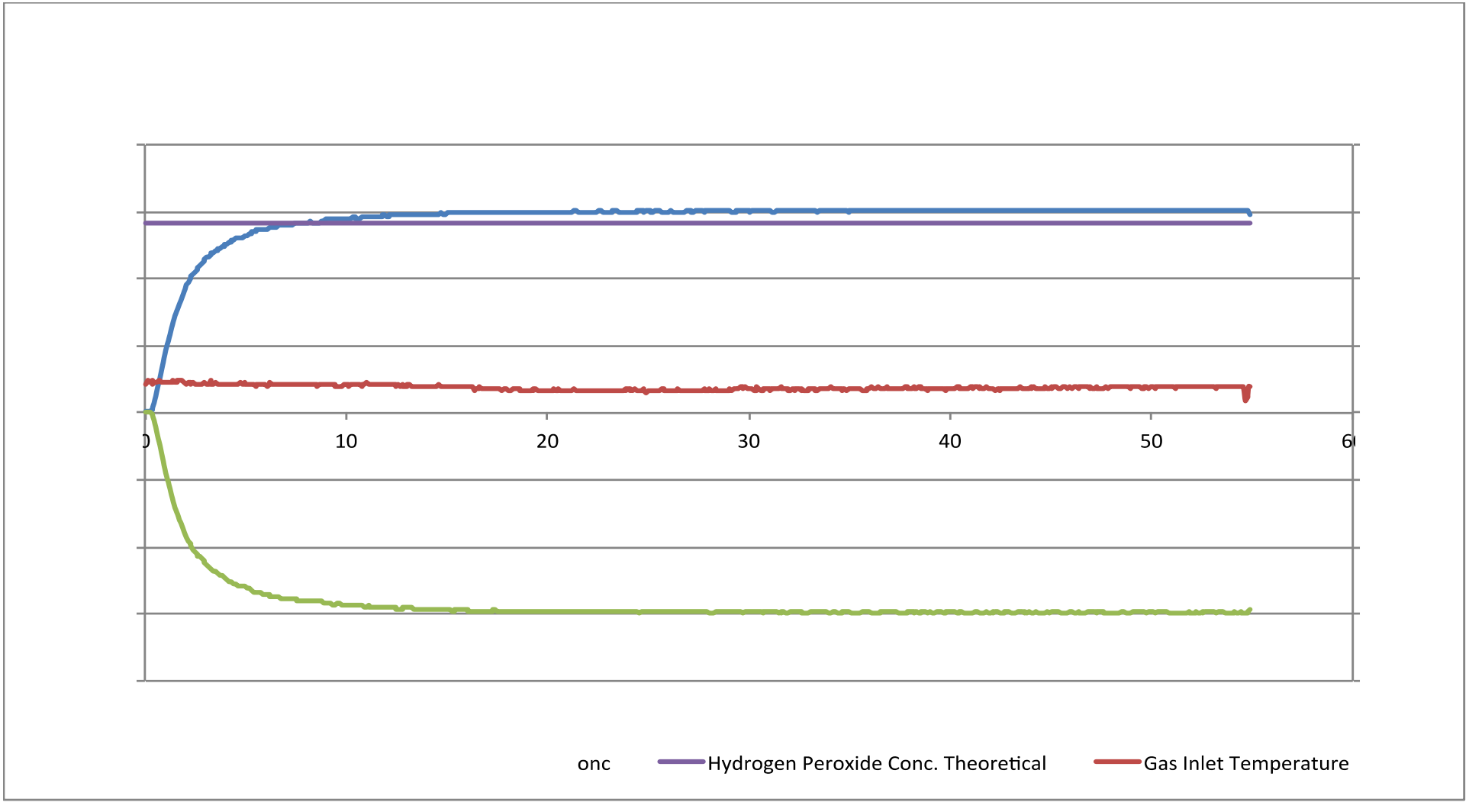
Anhydrous Peroxide

H_2O_2 in Solvent



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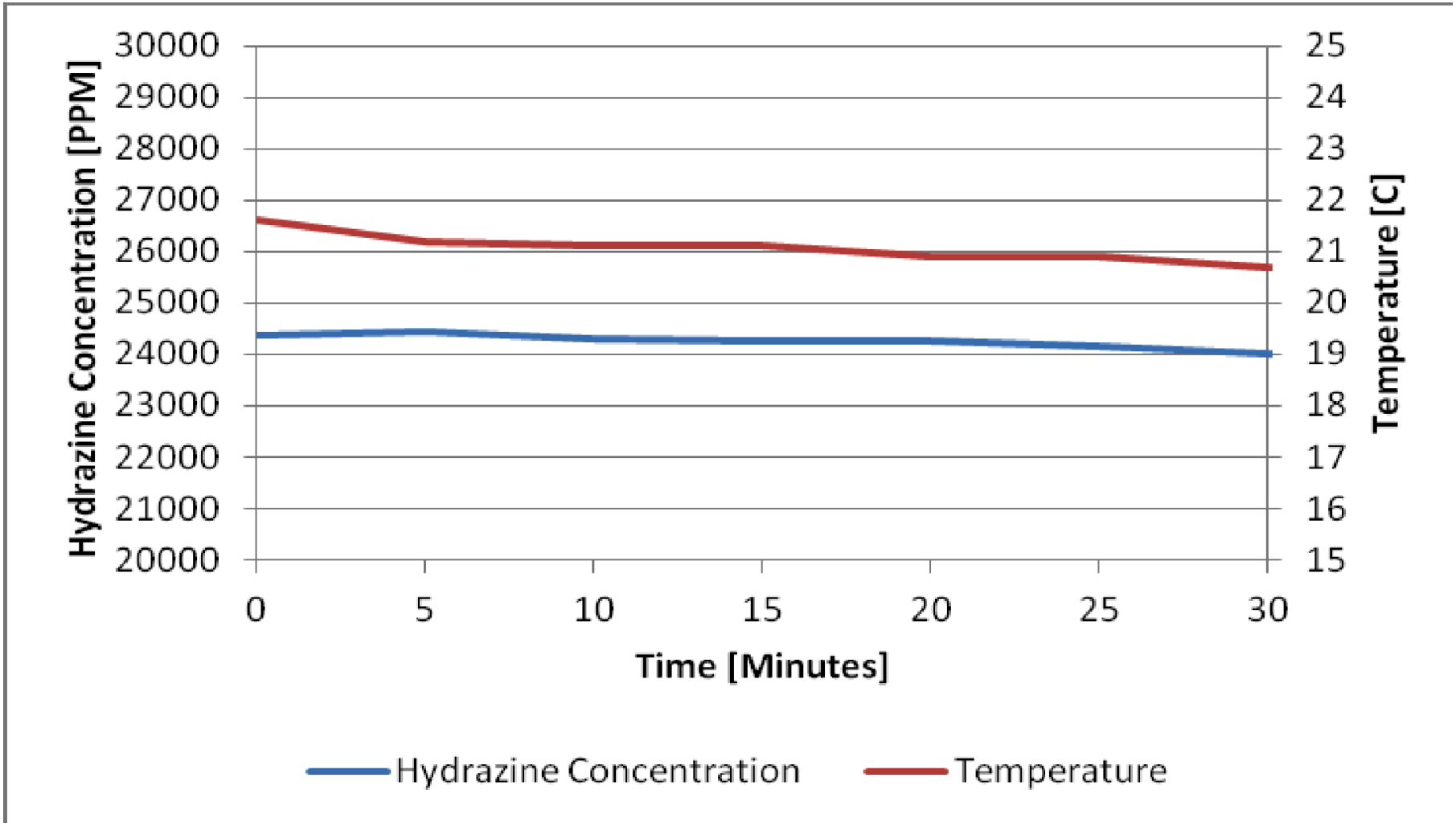
H_2NNH_2 in Solvent



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Approach to InGaAs Passivation/Functionalization

- Decapped InGaAs surface
- InGaAs + Si_2Cl_6 → InGaAs/Si + $GaCl_3$
- InGaAs/Si + HOOH → InGaAs/Si(O)OH
- InGaAs/Si(O)OH + TMA → InGaAs/SiO/Al_2O_3

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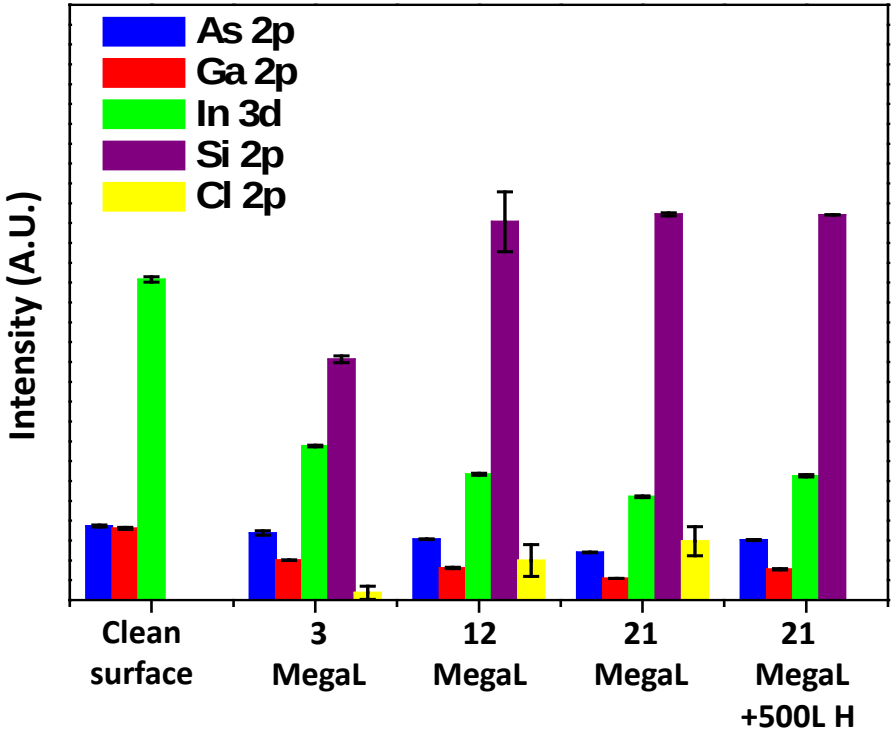
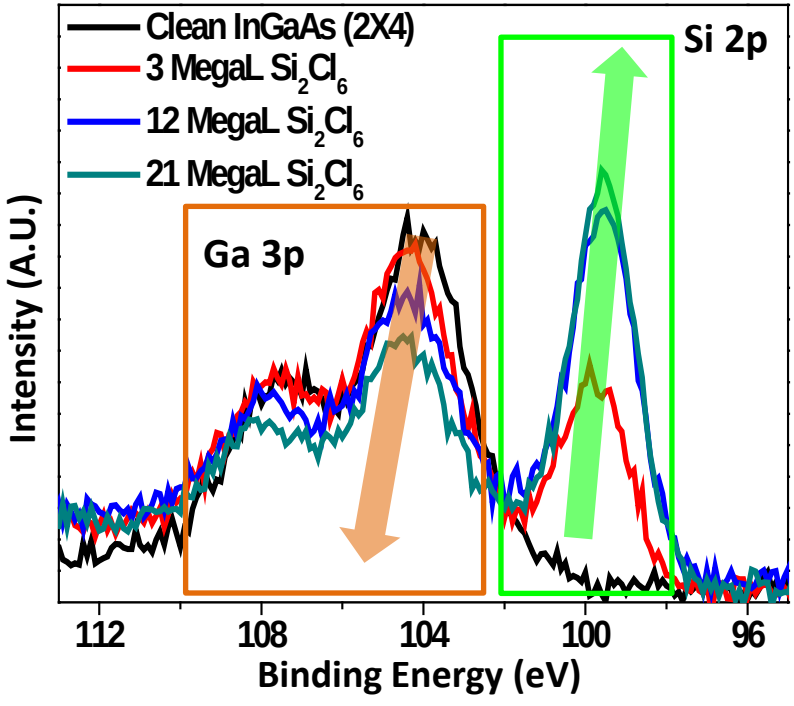
Self Limiting CVD – Si_2Cl_6/InGaAs(001)-(2x4)





Left: XPS Spectra collected at 30° glancing angle. Corrected XPS peak areas for clean (2x4), and following 3, 12, and 21 MegaLangmuir total Si_2Cl_6 doses at 350°C.(Si_2Cl_6 dosed at 10 second pulses of 0.025 Torr).

Right: Raw XPS peak areas for Ga 3p and Si 2p on clean InGaAs(2x4), and following 3, 12, and 21 MegaLangmuir total Si_2Cl_6 doses at 350°C.

- **Desorption limited CVD of Si_2Cl_6 at 350°C until no clean InGaAs surface sites available**

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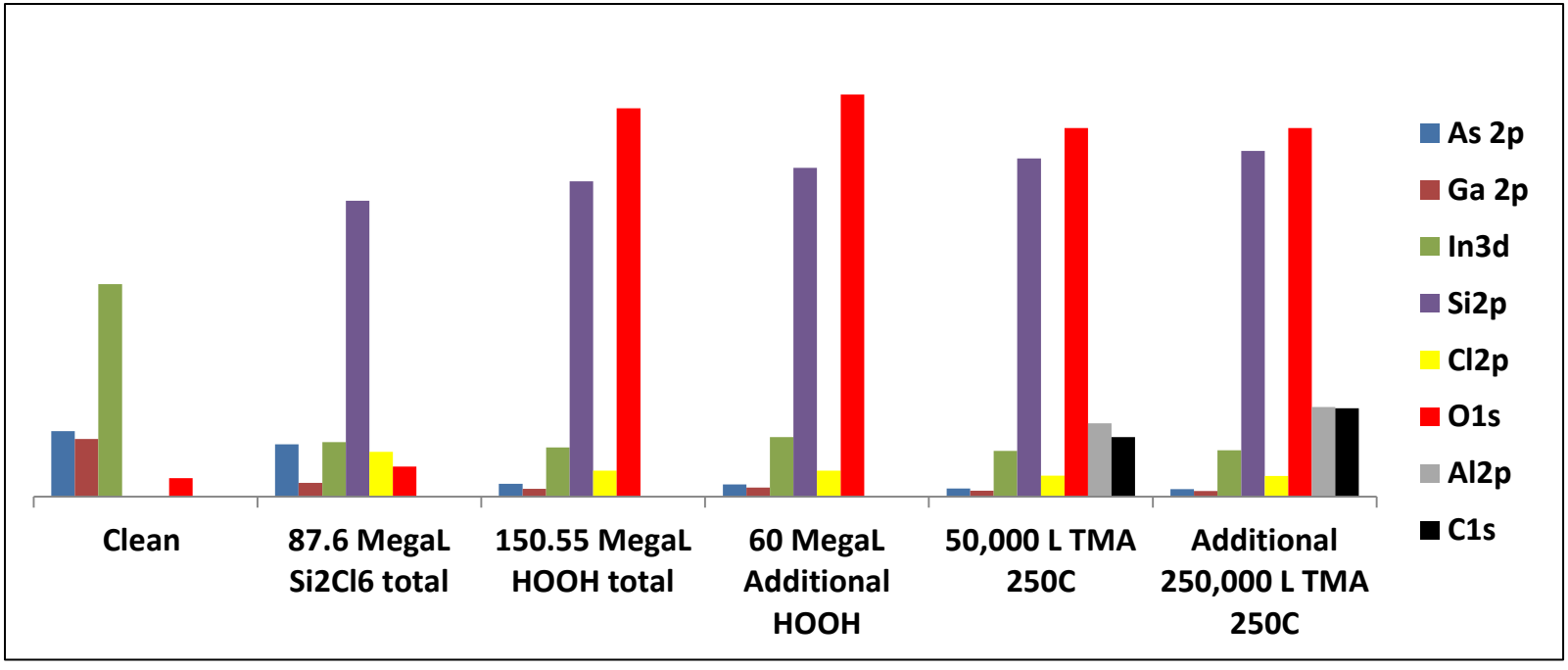
Self Limiting CVD – SiO_x/InGaAs(001)-(2x4)



XPS Spectra collected at 30° glancing angle. Corrected XPS peak areas for clean (2x4), and following 87.6 MegaLangmuir Si_2Cl_6 at 350°C, 150.55 MegaLangmuir HOOH at 350°C, 60 MegaLangmuir additional HOOH at 350°C, 50,000 L TMA at 250°C, and additional 250,000 L TMA at 250°C. Si_2Cl_6 pulses at 2.5x10^-2 Torr . HOOH pulses at 1x10^-2Torr . TMA pulses at 5x10^-3 Torr .

- **Anhydrous HOOH does not diffuse through SiOx layer and does not attack substrate**
- **TMA reacts and saturates on the saturated HOOH surface at 250C**
  - SiO_x control layer on InGaAs nucleates high-K gate oxide growth

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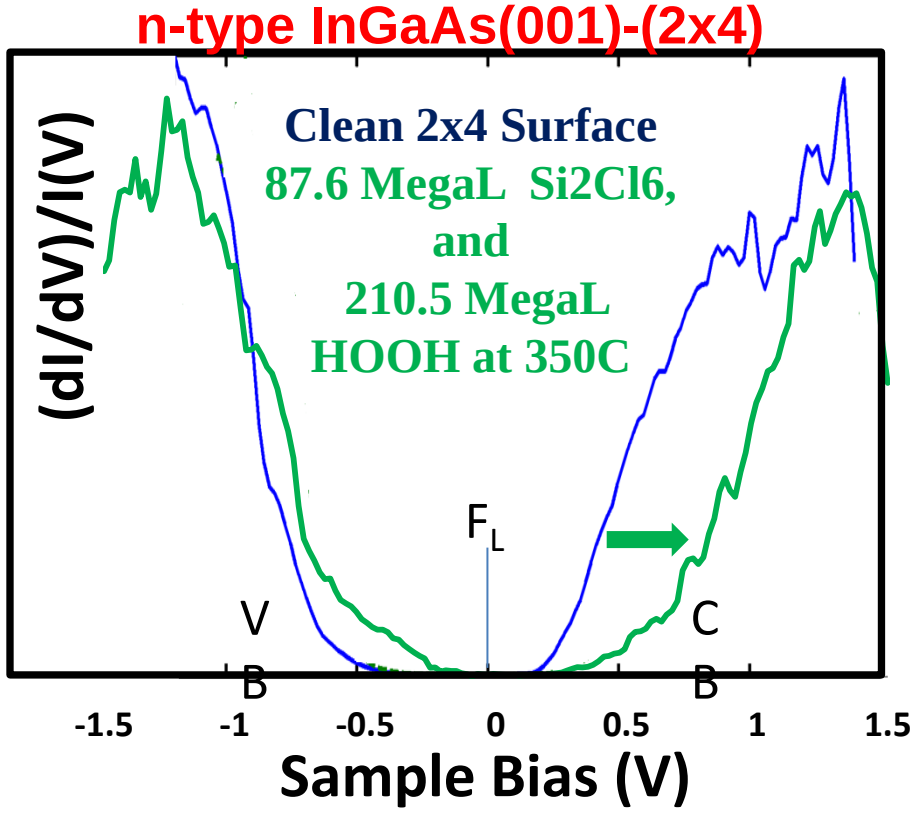
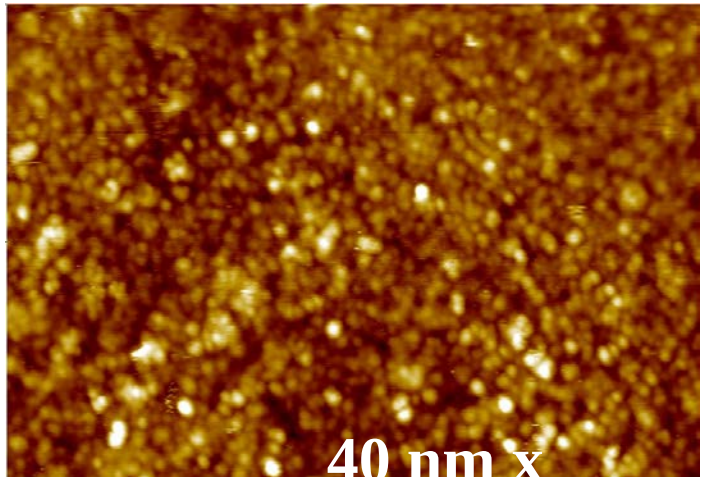
Self Limiting CVD – SiO_x/InGaAs(001)-(2x4)





(Left) STS on n-type InGaAs: clean n-type InGaAs (2x4), : 87.6 MegaL Si_2Cl_6 and 210.5 MegaL anhydrous HOOH at 350C (ave of 7 curves)

Right: Filled State STM image following: 87.6 MegaL Si_2Cl_6 and 210.5 MegaL anhydrous HOOH at 350C on n-type InGaAs(2x4)

- **Surface Fermi level shifts towards valence band from –OH and –O induced surface dipole**

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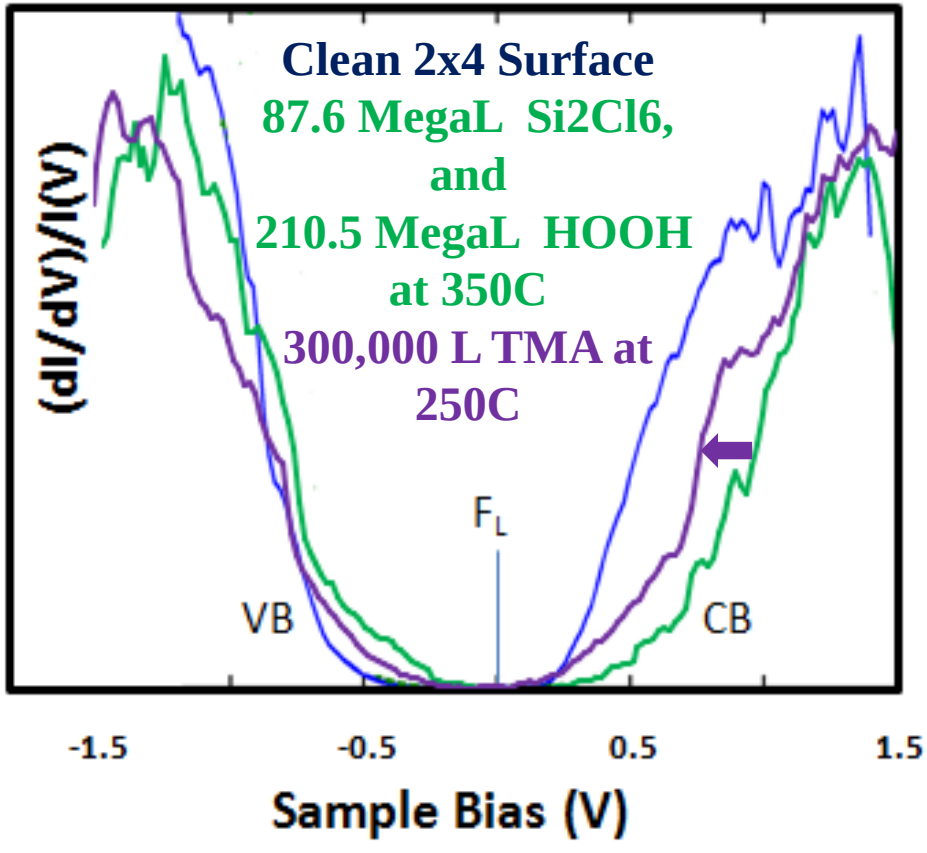
TMA Nucleation on SiO_x/InGaAs(001)-(2x4)

TMA on SiO_x/InGaAs(001)-



Left: **STS on n-type InGaAs: clean n-type InGaAs (2x4), 87.6 MegaL Si2Cl6 + 210.5 MegaL HOOH at 350C (ave of 7 curves), 300,000 L TMA at 250C (ave of 11 Curves)**

- **Surface Fermi Level shifts back near conduction band following TMA dose at 250C**

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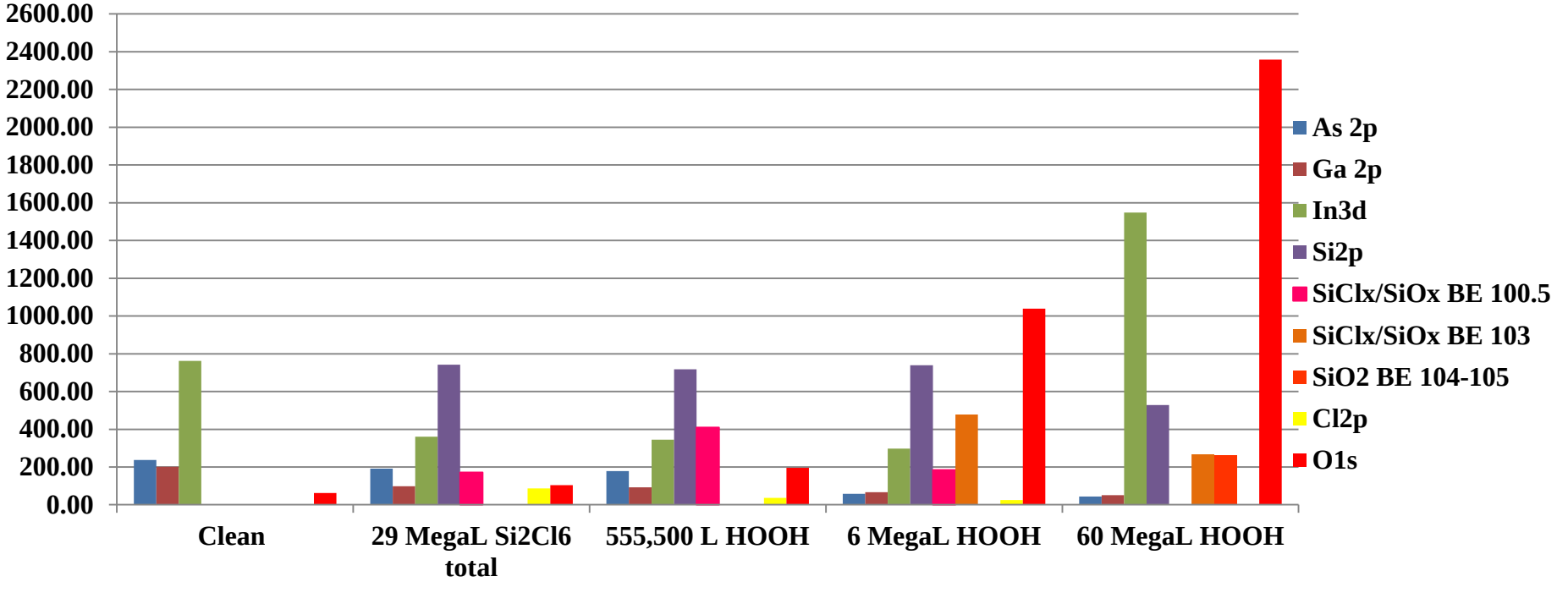
Off-the-Shelf 30% HOOH at 350C



- **29 MegaLangmuir Si_2Cl_6** = Dosed 8 MegaLangmuir total of Si_2Cl_6 at 350°C at P=1x10^-2 Torr and then adjusted dosing conditions and dosed total 21 MegaLangmuir Si_2Cl_6 at P=2.5x10^-2 Torr at 350°C. **About 1.2 Monolayers of Si coverage**
- **555,500 Langmuir HOOH** = 500 L HOOH, additional 5,000 L HOOH, additional 50,000 L HOOH, and then 500,000 L HOOH all at 350°C (1x10^-3 Torr for 500 sec).
- **Additional 6 MegaL HOOH** = 3x10^-2 Torr for 200 seconds at 350°C. **60 MegaL HOOH**= 3x10^-2 Torr for 33 min at 350°C.
- **See no shift in BE of In,Ga,As peaks following 6 MegaL HOOH dose.**
- **See noticeable shift of Si 2p peak to higher BE components: ~101.5 eV and ~103 eV**

➢ **Following 60 MegaL HOOH dose at 350C indium diffuses to surface – large InOx peak seen**

➢ **Going to establish standard Si2Cl6 dose to maintain same SiClx coverage every time**

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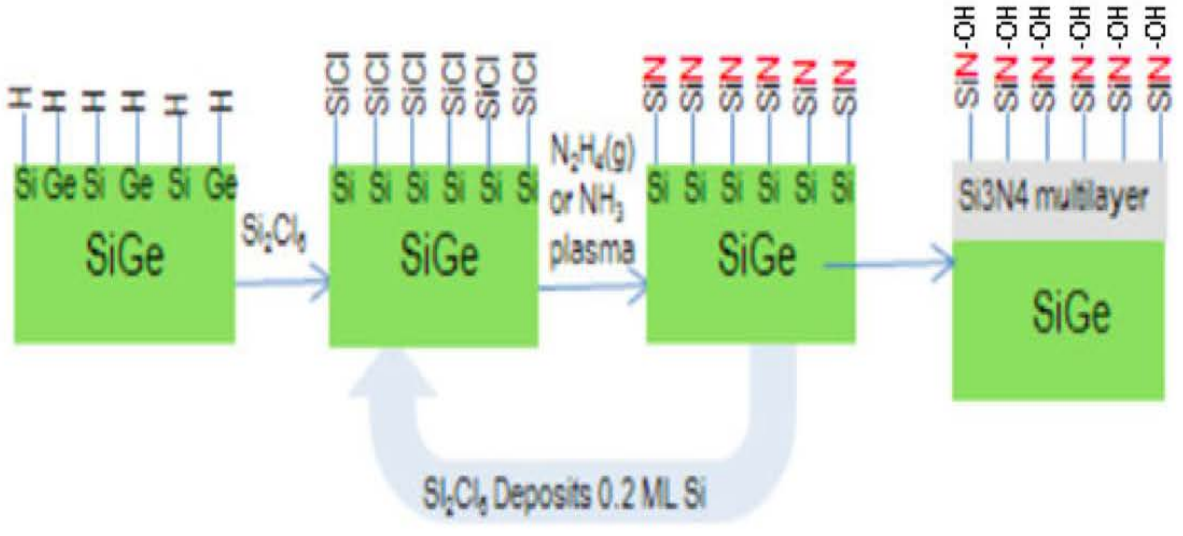
Low Temperature Passivation on SiGe(110) via Plasma Free Process

- Atomic H clean p-type $Si_{0.5}Ge_{0.5}$(110)
- Passivate $Si_{0.5}Ge_{0.}$ (110) dangling bonds with anhydrous hydrazine
- Maintain an electrically unpinned surface Fermi Level ready for subsequent functionalization
- Functionalize the surface and fabricate a MOSCAP with strong performance



- **Subsequent doses of anhydrous hydrazine and hexachlorodisilane can further increase the amount of SiN_x on the surface**
- **Final treatment with HOOH can prepare the surface for High *k* deposition**

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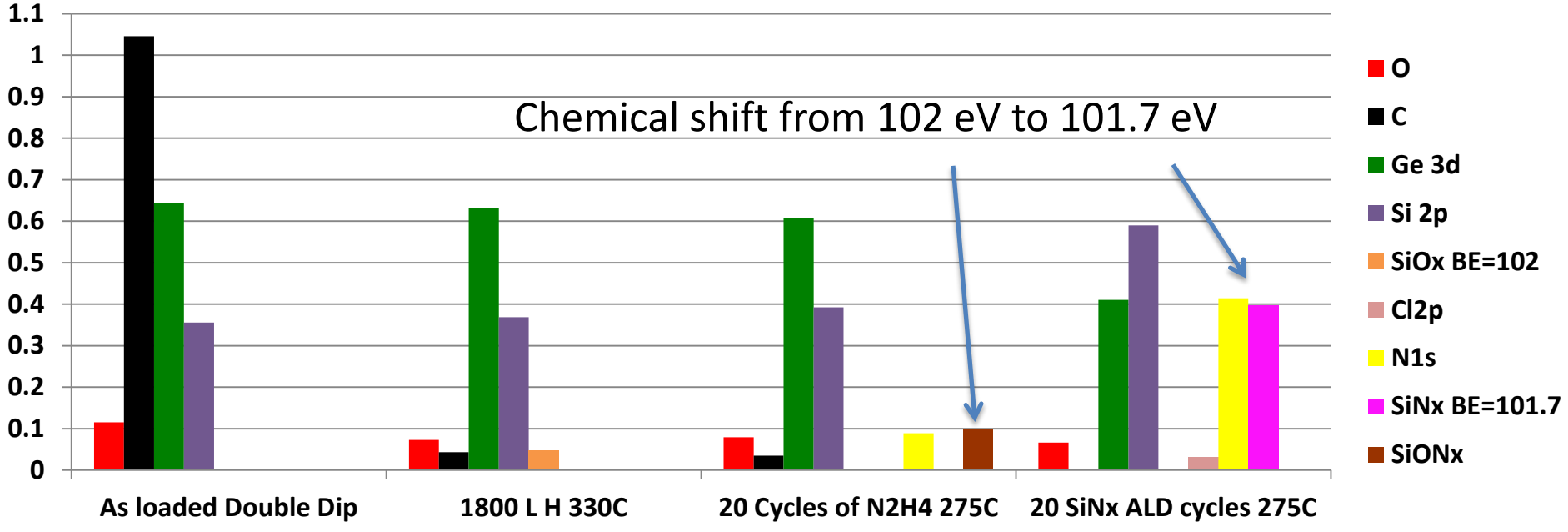
Passivation of SiGe(110) at 275C



- XPS corrected peak areas. $SiGe_{0.5}$(110) p-type sample underwent ex-situ and atomic H cleaning procedures.
- 20 cycles of N_2H_4at 275°C: Each cycle = 20 MegaL N_2H_4 (400MegaL total)
- 20 SiN_x ALD cycles at 275°C: Each cycle = 13.5 MegaL Si_2Cl_6 followed by 20 MegaL N_2H_4

➢ See large SiN_x peak with no increase in oxygen signal with no evidence of contamination in chamber

➢ Higher binding energy silicon peak shift from 102 to 101.7 eV—consistent with Si_3N_4 film growth

➢ Estimated 3-4 monolayers of silicon nitride overlayer

➢ Growth rate of ~0.4 A / ALD cycle

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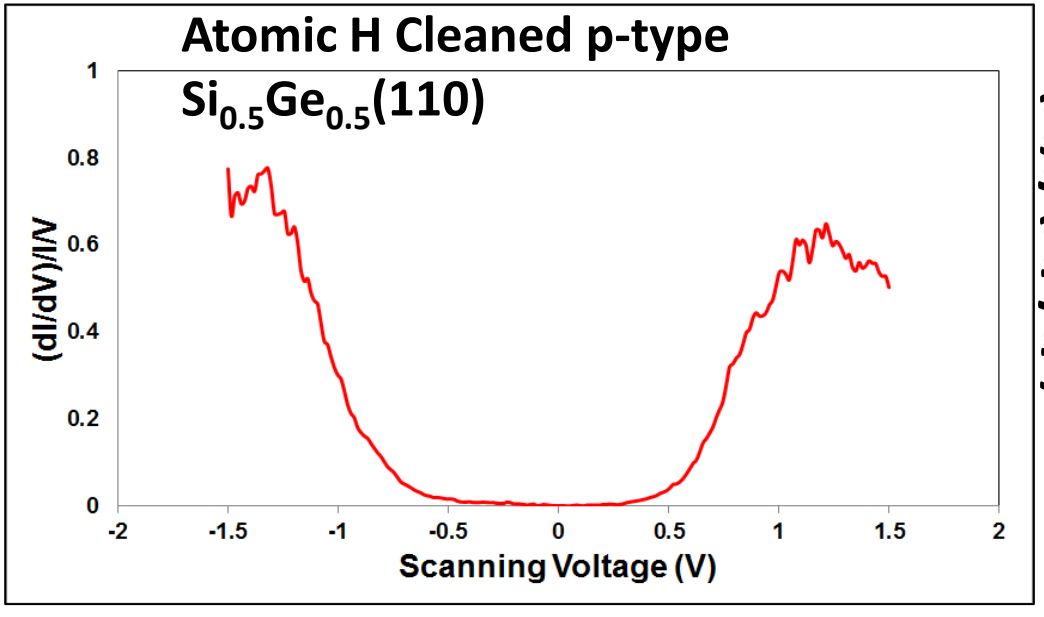
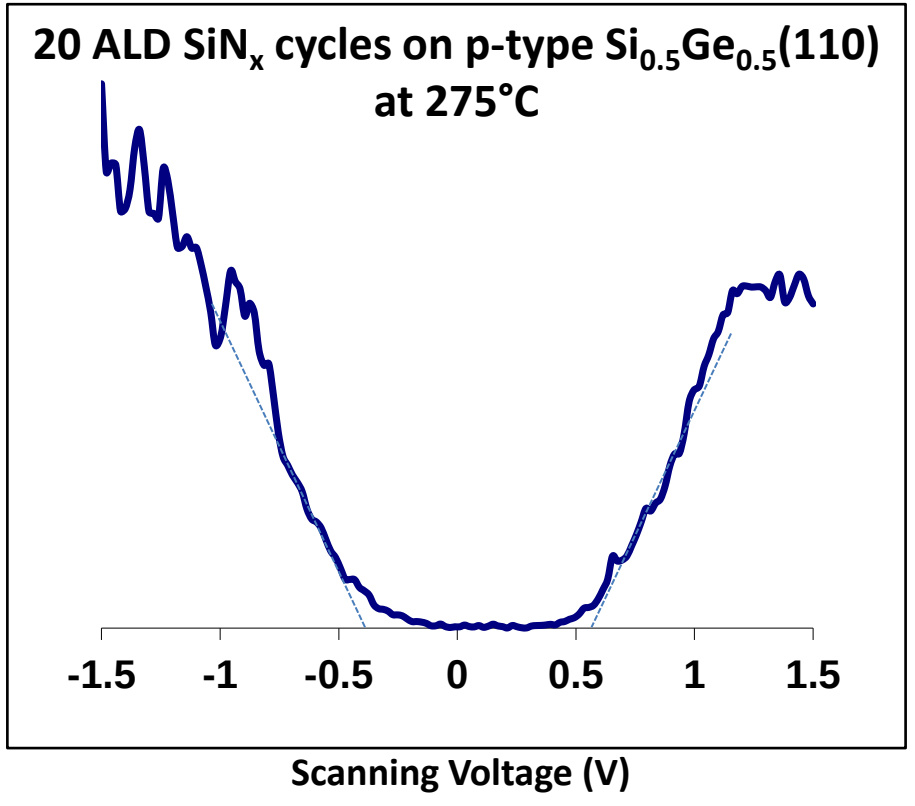
STS of Atomic H vs SiN_x Passivated Surface





Left: STS of Atomic H cleaned p-type $Si_{0.5}Ge_{0.5}(110)$

Right: STS following 20 SiN_x cycles at 275°C on $Si_{0.5}Ge_{0.5}(110)$ p-type sample following 1800L atomic H dose at 330°C and 400 MegaL hydrazine prepulse at 275°C

- Atomic H cleaned surface Fermi level is at the midgap
- SiN_x on SiGe(110) surface still looks slightly more p-type with bandgapsize of ~0.8 – 0.9 eV

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Conclusion

- Demonstrated stable delivery anhydrous hydrogen peroxide
- Demonstrated Si(O)OH passivation of InGaAs(001)
- Underlying InGaAs(001) is not damaged, Si oxidation with HOOH appears to be self-limiting
- Demonstrated low temperature nitride passivation of SiGe(110)
- MOSCAP studies are underway

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Collaborators

- Prof. Andy Kummel – UC San Diego
  - Mary Edmonds
  - Steve Wolf
- Dan Tempel – Matheson Tri-Gas
- Hank Simidzu – Matheson Tri-Gas

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Thank You

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