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

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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
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)
Why Gas Phase Hydrogen Peroxide?

- Ge dosing experiments
- HOOH/H₂O will nucleate the surface more efficiently than H₂O

![Diagram showing GeOx and Ge(100)]

**Oxygen Coverage on Ge(100) after H₂O₂ vs H₂O**

![Bar graph showing XPS signal normalized to Ge3d for H₂O and H₂O₂]
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 <400°C)
- Early studies (1992) by Slaughter and Gland show $\text{H}_2\text{NNH}_2$ to be more reactive than $\text{NH}_3$ on an Si(100) surface
Challenges

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

\[
\text{HOOH} \quad \rightarrow \quad \text{H}_2\text{O} + \text{O}_2
\]

• Anhydrous Hydrazine has a low flash point of 37°C and is highly toxic
  – Current commercial sources lack sufficient purity
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
Ionically Charged Channels
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
H$_2$O$_2$ in Solvent
H₂NNH₂ in Solvent

![Graph showing Hydrazine Concentration and Temperature over time.](image-url)
Approach to InGaAs Passivation/Functionalization

- Decapped InGaAs surface

- \( \text{InGaAs} + \text{Si}_2\text{Cl}_6 \rightarrow \text{InGaAs/Si} + \text{GaCl}_3 \)

- \( \text{InGaAs/Si} + \text{HOOH} \rightarrow \text{InGaAs/Si(O)OH} \)

- \( \text{InGaAs/Si(O)OH} + \text{TMA} \rightarrow \text{InGaAs/SiO/Al}_2\text{O}_3 \)
Self Limiting CVD – $\text{Si}_2\text{Cl}_6$/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 $\text{Si}_2\text{Cl}_6$ doses at 350°C. ($\text{Si}_2\text{Cl}_6$ 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 $\text{Si}_2\text{Cl}_6$ doses at 350°C.

- Desorption limited CVD of $\text{Si}_2\text{Cl}_6$ at 350°C until no clean InGaAs surface sites available.
Self Limiting CVD – SiO$_x$/InGaAs(001)-(2x4)

<table>
<thead>
<tr>
<th>Clean</th>
<th>87.6 MegaL Si$_2$Cl$_6$ total</th>
<th>150.55 MegaL HOOH total</th>
<th>60 MegaL Additional HOOH</th>
<th>50,000 L TMA 250C</th>
<th>Additional 250,000 L TMA 250C</th>
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- XPS Spectra collected at 30° glancing angle. Corrected XPS peak areas for clean (2x4), and following 87.6 MegaLangmuir Si$_2$Cl$_6$ 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$_2$Cl$_6$ pulses at 2.5x10$^{-2}$ Torr. HOOH pulses at 1x10$^{-2}$Torr. 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 250°C
  - SiO$_x$ control layer on InGaAs nucleates high-K gate oxide growth
Self Limiting CVD – SiO$_x$/InGaAs(001)-(2x4)

(Left) STS on n-type InGaAs: clean n-type InGaAs (2x4), 87.6 MegaL Si$_2$Cl$_6$, and 210.5 MegaL anhydrous HOOH at 350C (ave of 7 curves)

Right: Filled State STM image following: 87.6 MegaL Si$_2$Cl$_6$ 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
TMA Nucleation on SiO$_x$/InGaAs(001)-(2x4)

**Left:** STS on n-type InGaAs: clean n-type InGaAs (2x4), 87.6 MegaL Si$_2$Cl$_6$ + 210.5 MegaL HOOH at 350°C (ave of 7 curves), 300,000 L TMA at 250°C (ave of 11 Curves)

- Surface Fermi Level shifts back near conduction band following TMA dose at 250°C
Off-the-Shelf 30% HOOH at 350C

- 29 MegaLangmuir Si$_2$Cl$_6$ = Dosed 8 MegaLangmuir total of Si$_2$Cl$_6$ at 350°C at P=1x10^-2 Torr and then adjusted dosing conditions and dosed total 21 MegaLangmuir Si$_2$Cl$_6$ 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 Si$_2$Cl$_6$ dose to maintain same SiCl$_x$ coverage every time
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$_{0.5}$ (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
Passivation of SiGe(110) at 275°C

- XPS corrected peak areas. SiGe$_{0.5}$(110) p-type sample underwent ex-situ and atomic H cleaning procedures.
- 20 cycles of N$_2$H$_4$ at 275°C: Each cycle = 20 MegaL N$_2$H$_4$ (400MegaL total)
- 20 SiNx ALD cycles at 275°C: Each cycle = 13.5 MegaL Si$_2$Cl$_6$ followed by 20 MegaL N$_2$H$_4$
  - See large SiNx 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$_3$N$_4$ film growth
  - Estimated 3-4 monolayers of silicon nitride overlayer
  - Growth rate of ~0.4 Å / ALD cycle
**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 bandgap size of ~0.8 – 0.9 eV
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
Collaborators

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