X-RAY PHOTOELECTRON SPECTROSCOPY OF NANOMATERIALS
– GRAPHENE AND III-V INTERFACES

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Acknowledgements

- Students
  - Dmitry Zhernokletov, Hong Dong, Rohit Galataage, Santosh K.C.
  - Angelica Azcatl, David Hinojos, Srikar Jandhyala, Greg Mordi, Adam Pirkle (now @ Intel)
- Postdocs
  - Barry Brennan, Stephen McDonnell, Ka Xiong, Li Tao (UT Austin)
- Colleagues
  - K.J.Cho (DFT of interfaces), Chris Hinkle, Jiyoung Kim, Yves Chabal
  - Luigi Colombo (Texas Instruments)
  - Deji Akinwande, Rod Ruoff (UT Austin)
  - Suman Datta (Penn State), Paul Hurley (Tyndall), Eric Vogel (GIT), Peide Ye (Purdue)

NRI

FCRP

NSF

SWAN

South-West Academy of Nanotechnology

NIST

DARPA

MTO

Nanoelectronics • Architectures

MIND

MIDWEST INSTITUTE FOR NANOELECTRONICS DISCOVERY

TMEIC

We drive industry

Outline

- Background and Motivation
- Experimental Methods
- Results
  - In-situ vs. Ex-situ methods
  - Arsenide Studies
  - Phosphide Studies
  - Antimonide Studies
  - Nitride Studies
  - Graphene
- Conclusions

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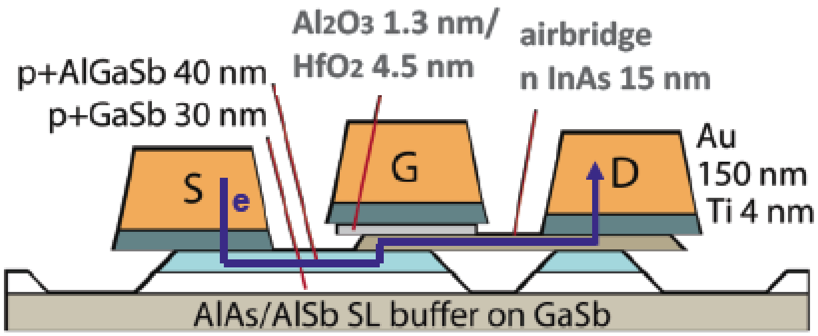
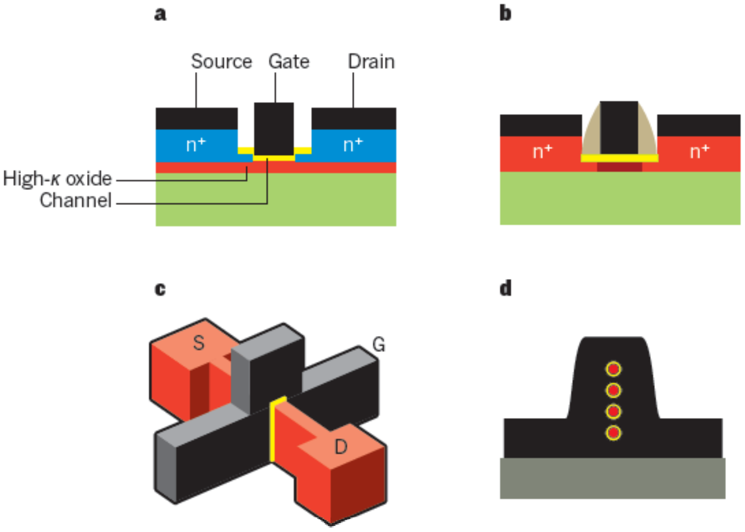
Motivation

- CMOS performance requirements point toward alternative…
  - Materials (e.g., III-V)
  - Structures (planar → 3D Fin FET → Gate all around)
  - Devices (MOSFET → TFET)

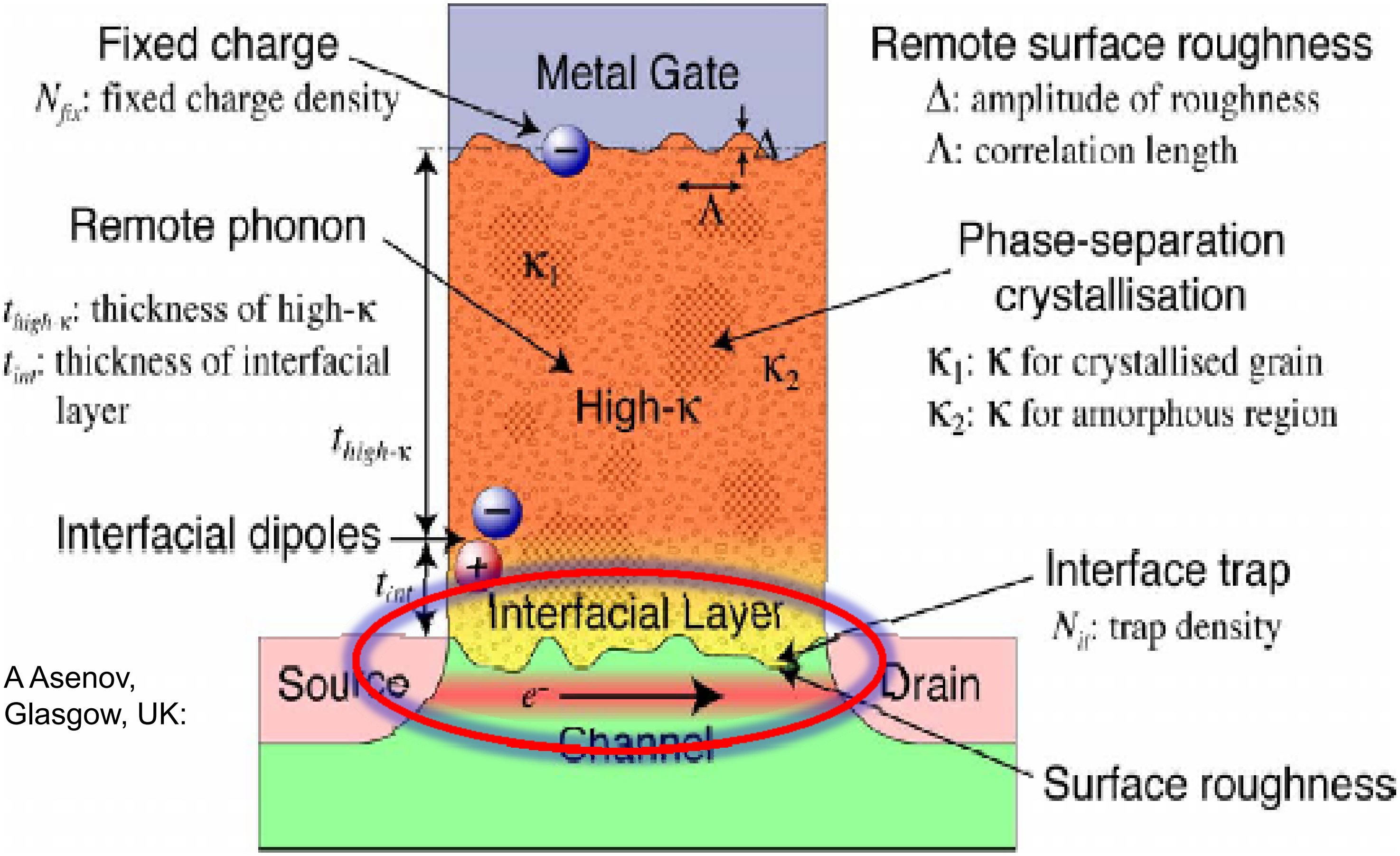


Seabaugh, et al.



Del Alamo Nature (2011)

Interfaces, interfaces….



A Asenov,
Glasgow, UK:

Courtesy A. Kummel

Outline: III-V

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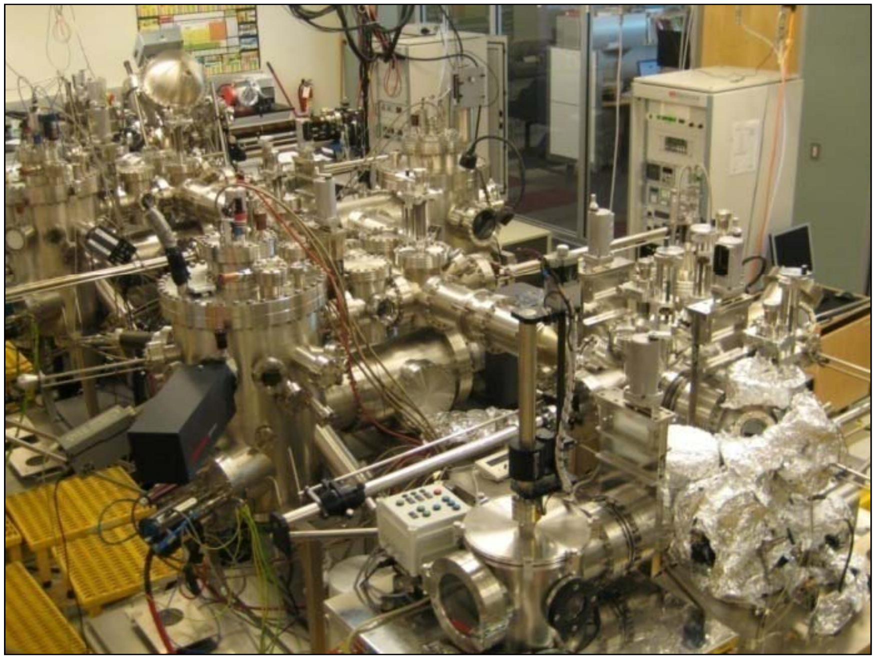
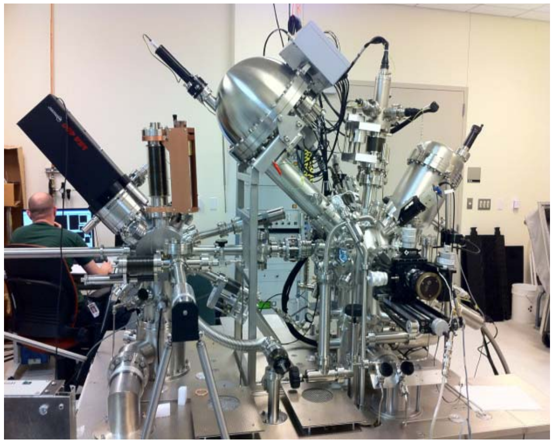
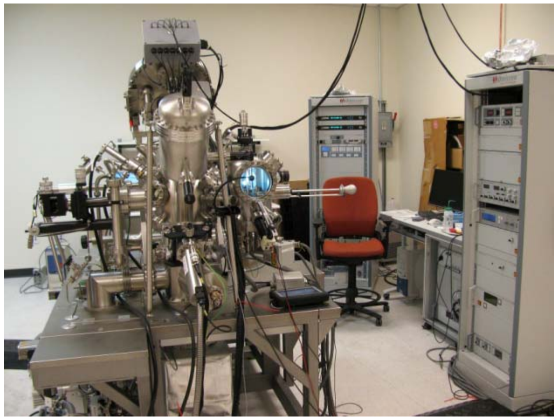
Tools for *in-situ* studies of interfaces…

UHV Surface Science System

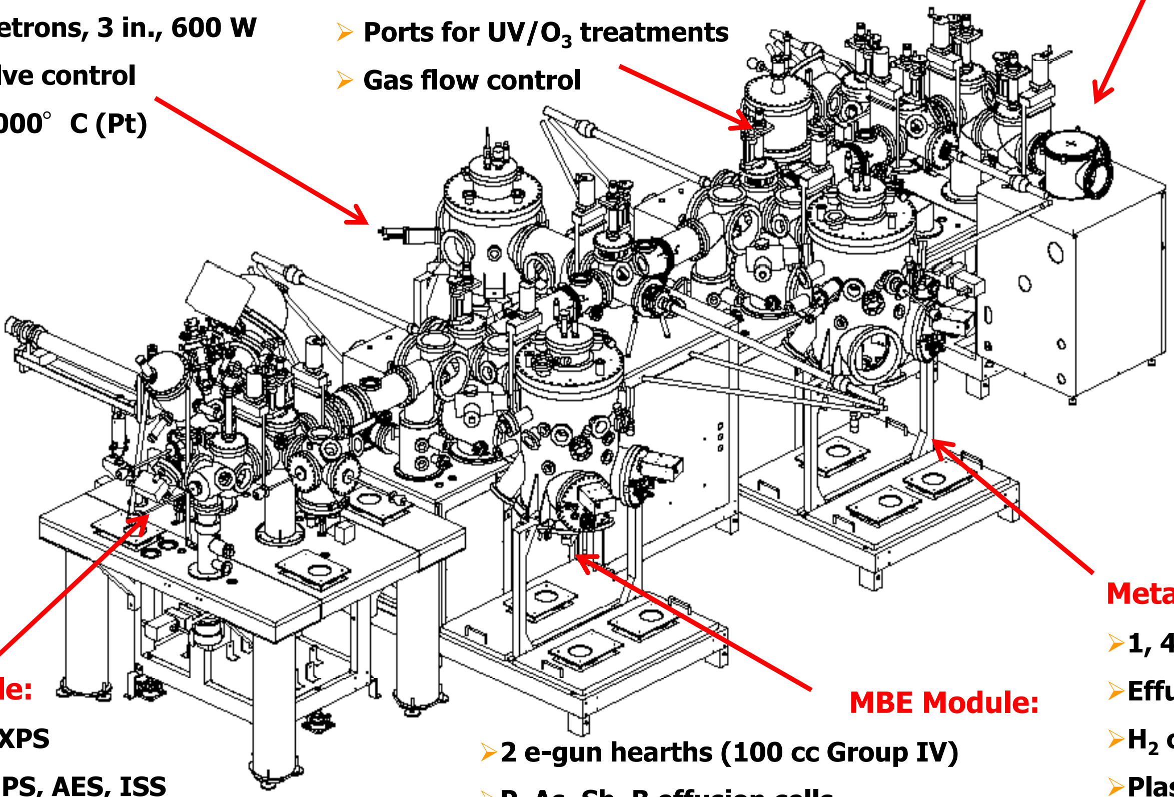






UHV Cluster System

In-situ deposition and analysis system



Sputter Module:

- UHV capable
- 4 – RF Magnetrons, 3 in., 600 W
- Pressure/valve control
- Sample T≤1000° C (Pt)

Annealing Module:

- Custom UHV capable furnace
- 100mm sample, T≤700° C, O_2, 1atm.
- Ports for UV/O_3 treatments
- Gas flow control

ALD Module:

- Hot wall reactor
- Custom UHV transfer system
- 100mm sample, T≤350° C
- Liquid, gas and solid sources
- Gas flow control

Analytical Module:

- Monochromatic XPS
- High Intensity UPS, AES, ISS
- LEED, analysis
- Substrate size flexible
- Heating/cooling
- Sample rotation, ARXPS

MBE Module:

- 2 e-gun hearths (100 cc Group IV)
- P, As, Sb, B effusion cells
- 100mm wafer, T≤1200° C, shutter
- Rotary/mag drive
- QMS (x-beam), quartz microbalance
- RHEED, analysis

Metal MBD Module:

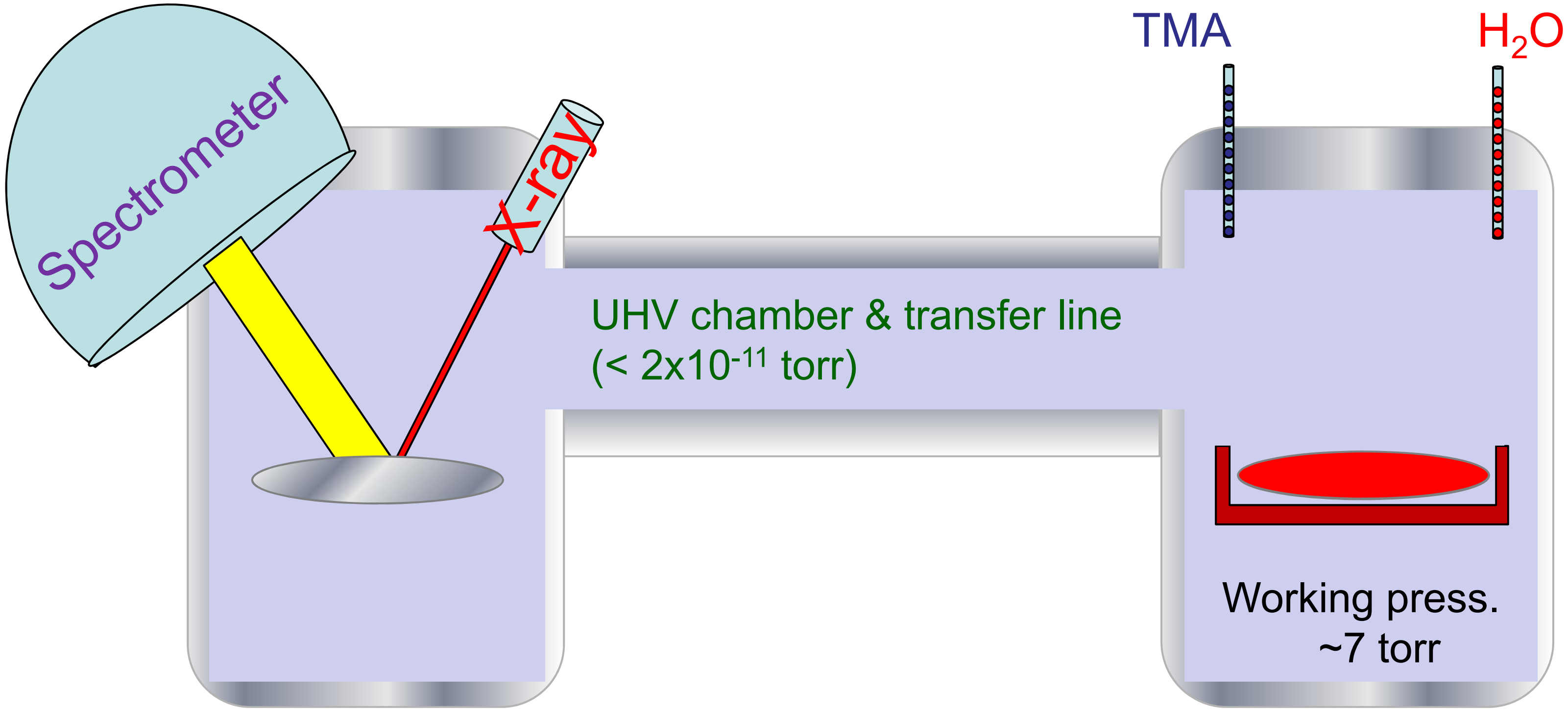
- 1, 4 pocket e-gun hearths (8 cc)
- Effusion cells
- H_2 cracker source
- Plasma source
- Backside metallization
- 100mm sample, T≤1000° C, shutter
- Rotary/mag drive
- Quartz microbalance

ECS Transactions, 16 (5) 255-271 (2008)

In-situ half cycle ALD reactions study by XPS

High Resolution Monochromatic XPS

Picosun ALD
Hot wall and Shower head type



XPS Analysis

Pre-substrate Scan
Analysis after 1st Al pulse
Analysis after 1st H_2O pulse

ALD (Al & H_2O)

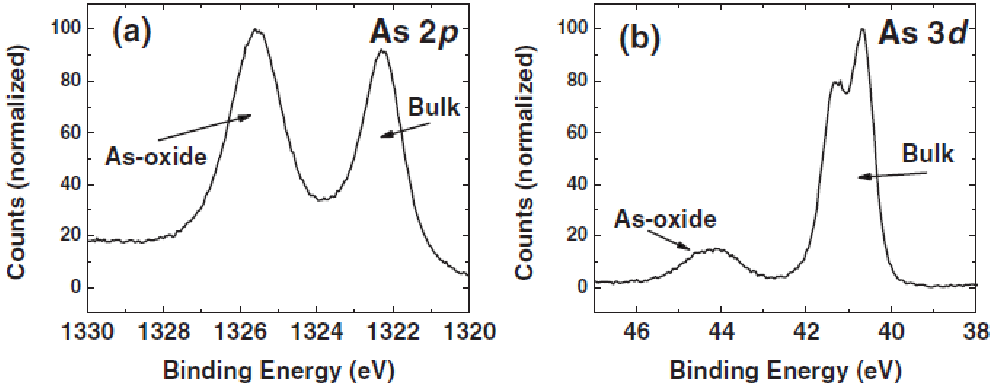
Al pulse
H_2O pulse

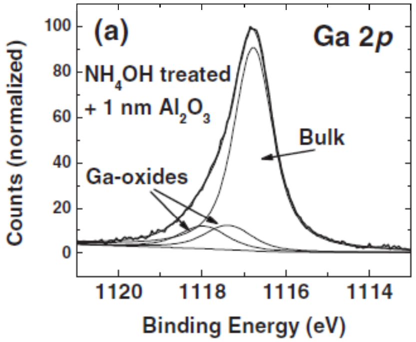
ECS Transactions, 16 (5) 255-271 (2008)

XPS of Arsenides

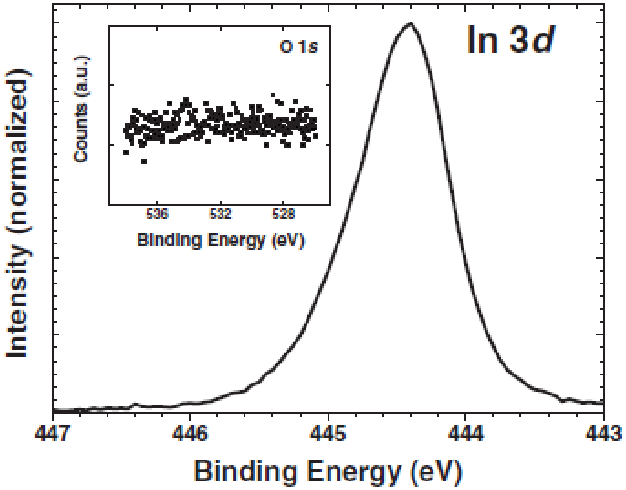
surface sensitive

“bulk” sensitive

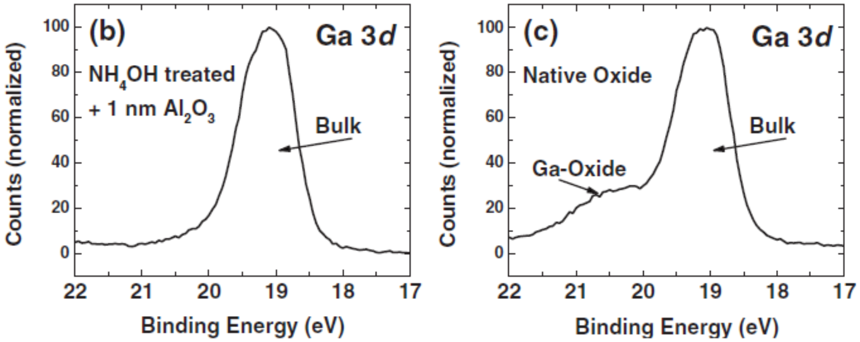




surface sensitive



Asymmetry in In lineshape a challenge



“bulk” sensitive

Hinkle, et al. APL 95 (2009) 151905

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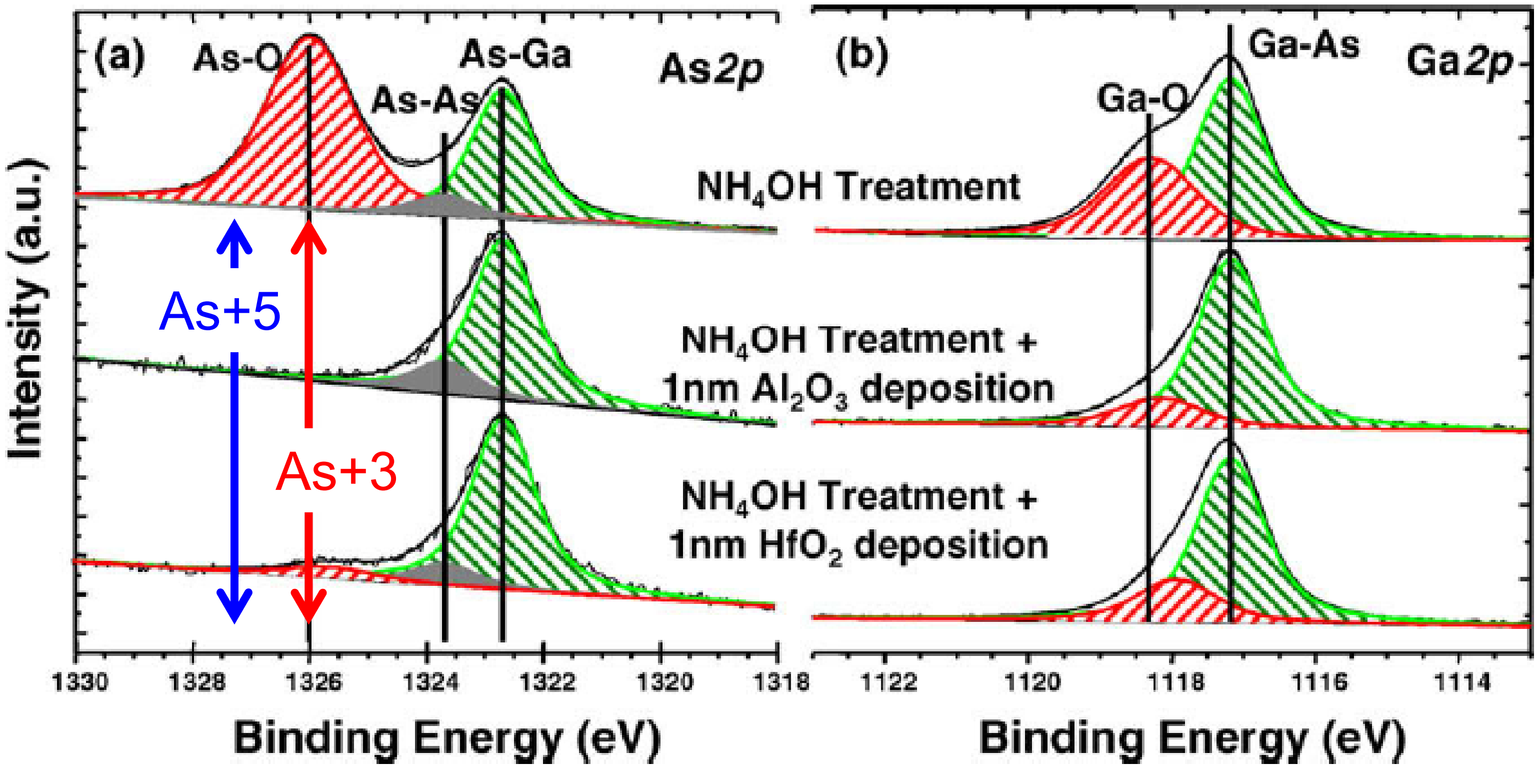
The “Cleanup Effect”: ALD process and interfacial chemistry on GaAs

Oxide reduction of NH_4OH treated GaAs surface following ALD deposition



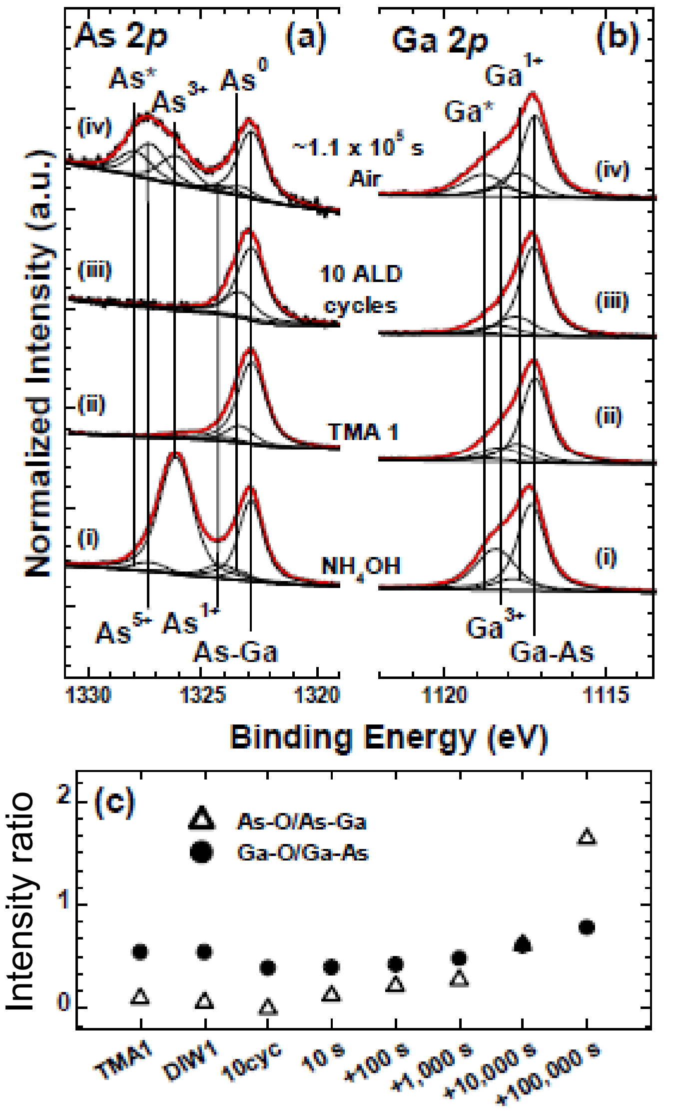
- ALD Process reduces As-oxides readily
- ALD process impacts Ga-oxides as well, but some Ga-oxide remains
- The ALD precursors remove *different* As oxidation states.
  - TMA removes the As^{3+} state while TEMAH removes the As^{5+} state.

See : Hinkle, et al., APL 92 (2008) 071901, Micro.Eng.86(2009) 1544

Apparent contradictions in prior interface studies – some examples

- Dalapati, et al. (IEEE TED 54 (2007) 1831)
  - concluded via ex situ XPS that both 1 nm Al_2O_3 and HfO_2 films had detectable arsenic oxides present at the oxide/semiconductor interface
- Suri, et al. (APL 96 (2010) 112905)
  - concluded via ex situ XPS no significant arsenic oxide reduction using TDMA-Hf at 200°C
- Hackley, et al. (APL 92 (2008) 162902)
  - Concluded that there is a thickness dependence to the oxide “clean-up” effect
- Shahrjerdi, et al. (APL 91 (2007) 193505)
  - Concluded via ex situ XPS no significant reduction of AsO_x upon deposition of HfO_2 on GaAs using TDMA-Hf

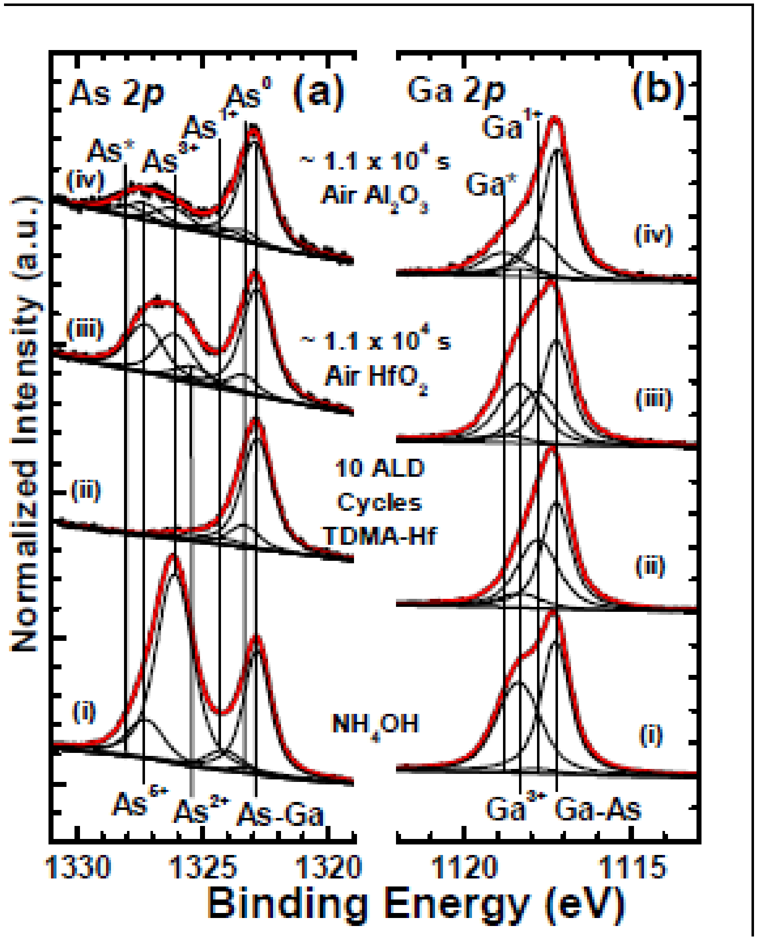
In-situ vs. Ex-situ Studies: TMA and GaAs



- NH$_4$OH-treated GaAs
- TMA exposure reduces oxides
- Exposure to air results in oxidation
  - GaAsO$_4$/hydroxide formation

McDonnell, et al., APL 100 (2012) 141606

In-situ vs. Ex-situ Studies: TDMA-Hf and GaAs



- NH_4OH-treated GaAs
- TDMA-Hf exposure reduces oxides
- Exposure to air results in oxidation
  - $GaAsO_4$/hydroxide formation
- Al_2O_3 interface oxidation less than that detected for HfO_2
- Suggests that caution is needed in concluding mechanisms from ex-situ studies of thin (<5nm) films

McDonnell, et al., APL 100 (2012) 141606

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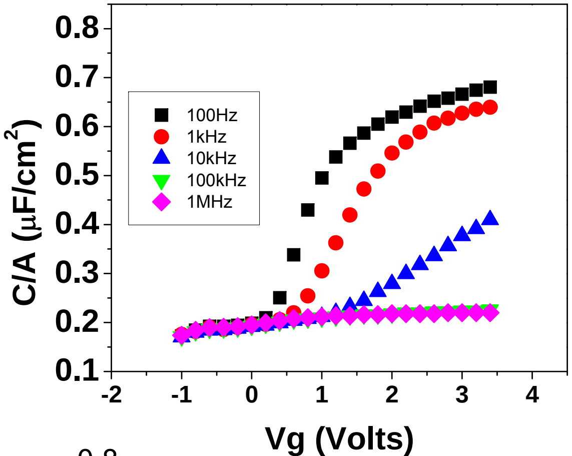
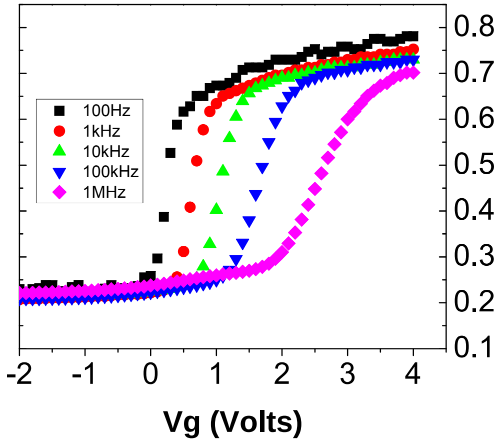
CV and high-k III-Arsenides

NH_4OH Clean/ Si interlayer/1.1 nm Si/10nm Al_2O_3
(oxide at interface)

Atomic Hydrogen/ Si interlayer/1.1 nm Si/10nm Al_2O_3
(No oxide at interface)

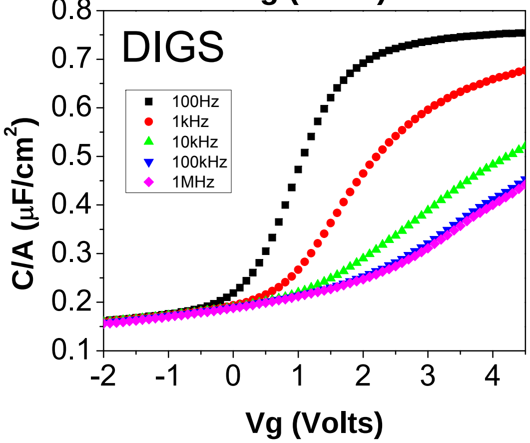
Data

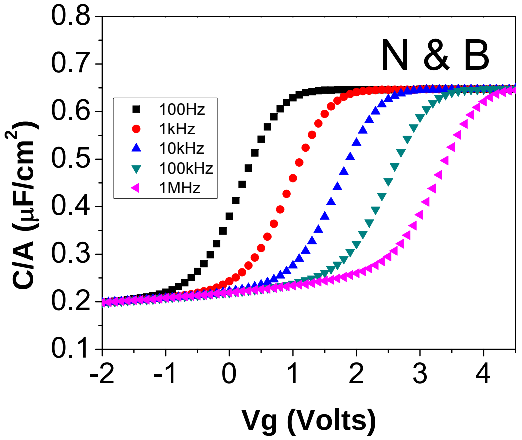




Models

$D_{it} = 5 \times 10^{13}$ cm^{-2} eV^{-1}





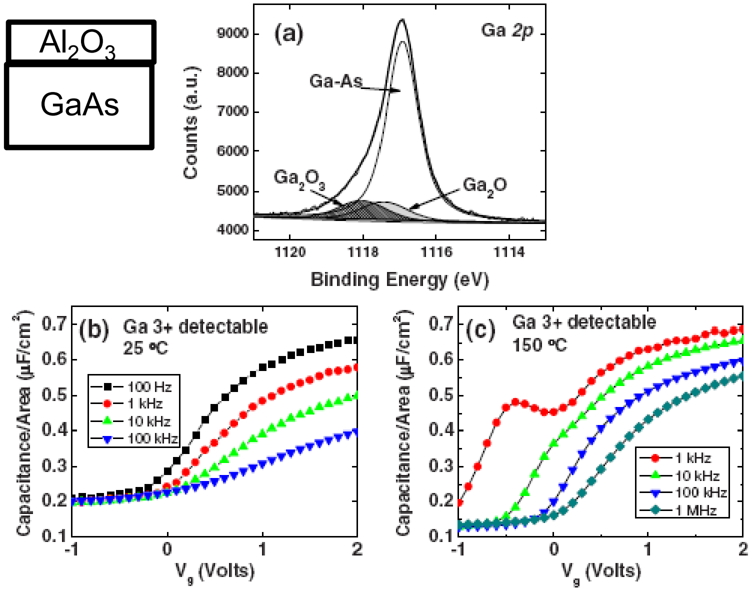
- Marked reduction in accumulation capacitance frequency dispersion.
- The starting surface with its lack of oxygen from atomic H cleaning appears to be the key.
- The primary difference between the N&B interface state model and the H&S model is a low bandgap interlayer (assumed to be disordered) permitting tunneling of carriers to defects.

ECS Transactions, 25 (4) 115-122 (2009); IEEE TED 57(2010) 2599; Curr. Op. Sol. St. Mat. Sci. 15 (2011) 188

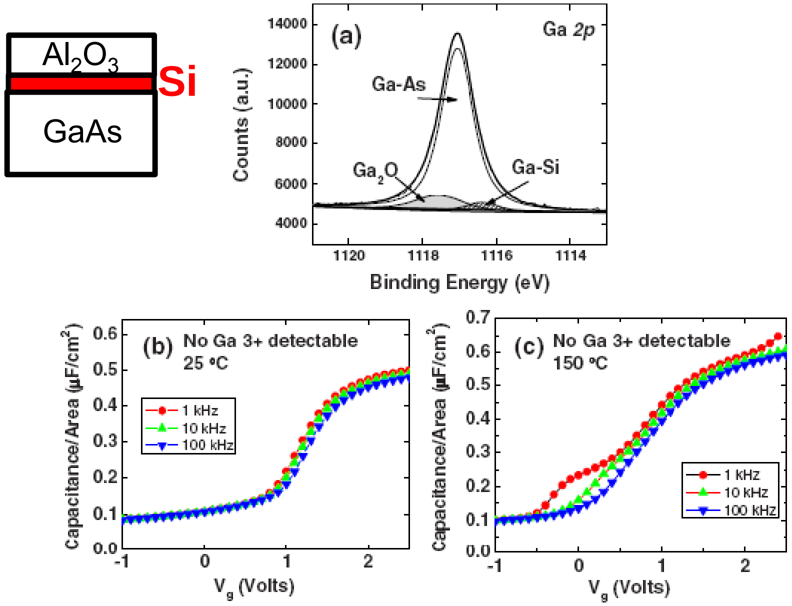
Effect of Si-IPL on device performance

- Prior work on high-k/III-Arsenides
  - o Al_2O_3/GaAs
  - o Al_2O_3/$In_xGa_{1-x}As$
  - o Al_2O_3/InAs
- Defect formation and oxidation
- Correlated capacitor and transistor performance with interfacial properties

With Ga 3+

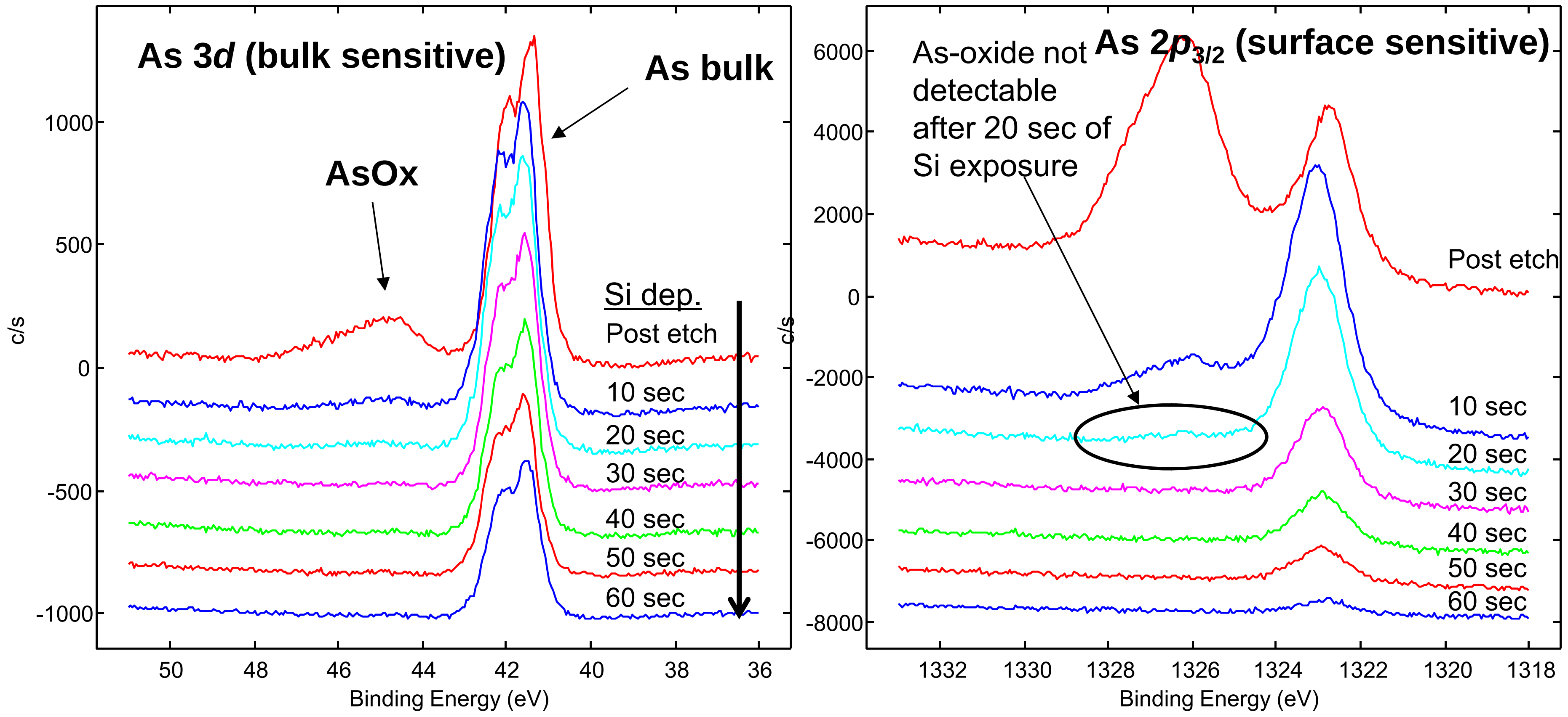


Without Ga 3+



Hinkle, et al., APL **94,** 162101 (2009)

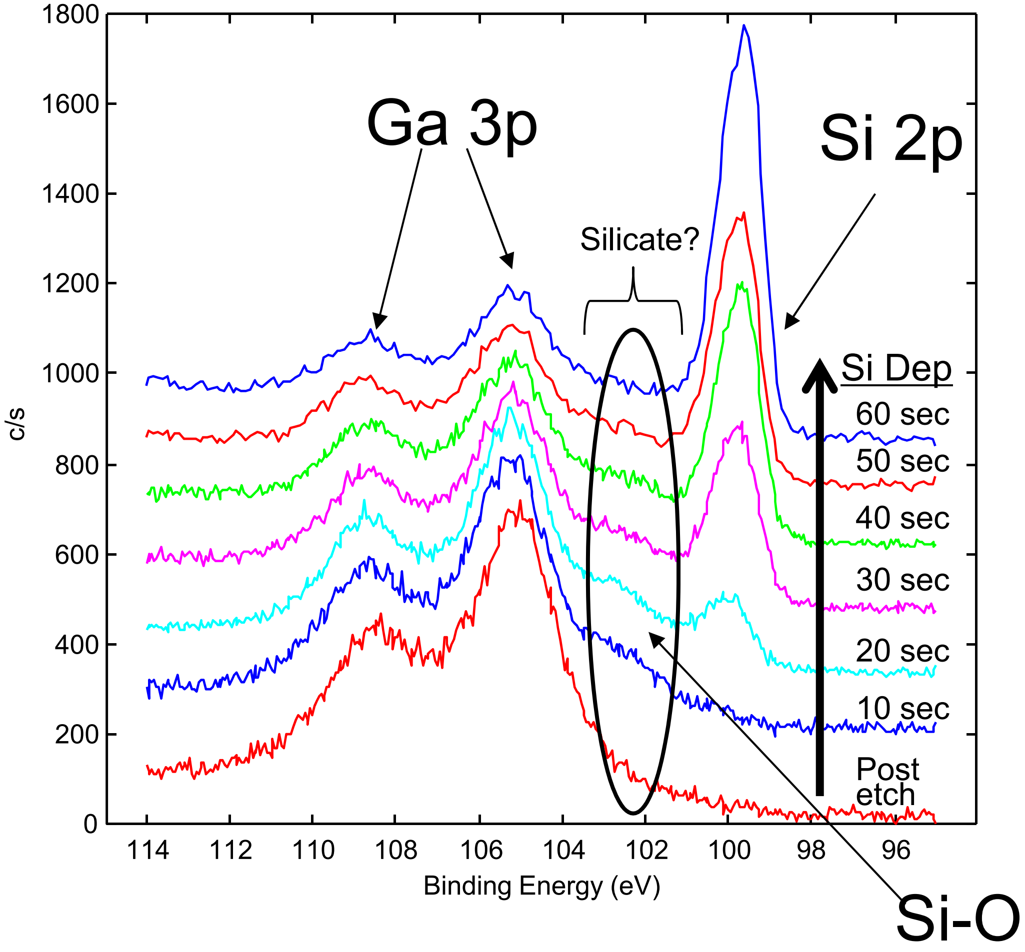
Removal of As-Oxides:
NH_4OH etch + anneals+ Si interlayer



- As-O bonding can be removed easily through a variety of techniques including ALD ligand exchange, a-Si deposition, and chemical and thermal treatments.

Microelect. Eng. 86 (7-9) 1544 (2009); ECS Trans. 16 (5) 255 (2008)

Surface oxide evolution with processing: NH_4OH etch + anneals+ Si interlayer

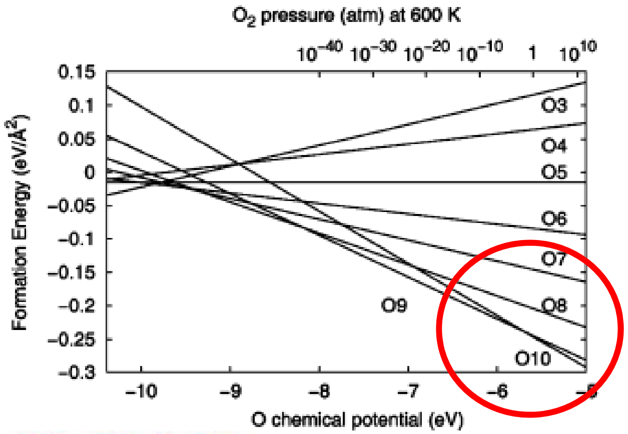


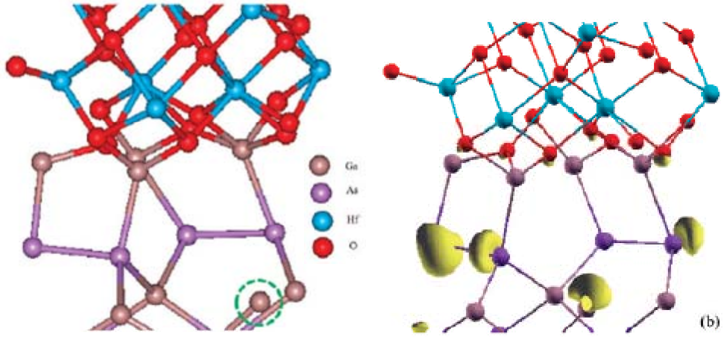
- Silicon is initially detected as Si-O (~10 s of Si flux exposure)
- The detection of Si-Si bonds after 20s coincides with the reduction of As-O below detection limits.
- This implies an initial bond conversion from As-O to Si-O from *in-situ* process
- Subsequent ALD likely to result in a thin silicate high-k layer with elemental Si fully consumed.
- Compare to *ex-situ* XPS results where As-O and As-Si-O formation is reported.*

- See: Zhang, et al., J. Appl. Phys. 101 (2007) 034103 and Oktyabrsky, et al., Mat. Sci. Eng. B 135 (2006) 272
- Hasegawa, et al. JJAP 27 (1988) L2265; JVST B 7 (1989) 870; Mat.Sci.Eng. B 165 (2009) 122; JVST B 27 (2009) 2028; Microelect. Eng. 86 (7-9) 1544 (2009); ECS Trans. 16 (5) 255 (2008)

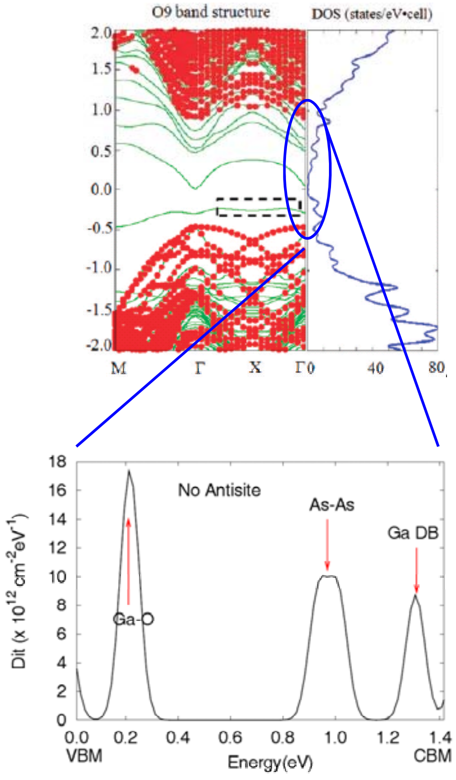
Al_2O_3/III-Arsenide Interfaces

- DFT Modeling of Effect of Oxidation: strain free HfO_2/GaAs
- O-rich is most stable
- Major defects in gap from oxidation: As-As dimer, Ga db, Ga+3





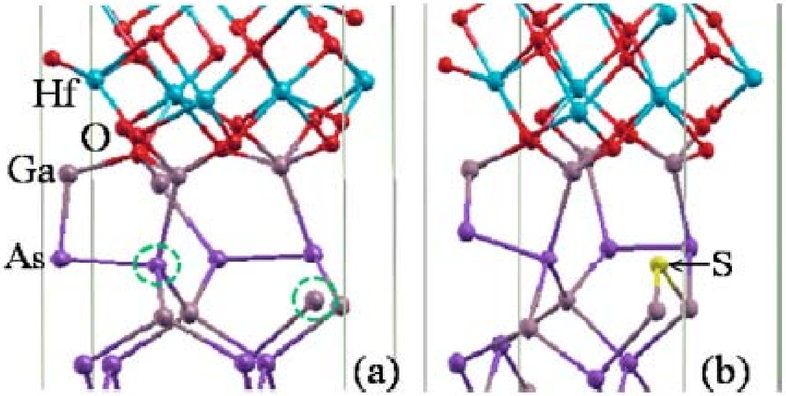
“O9”

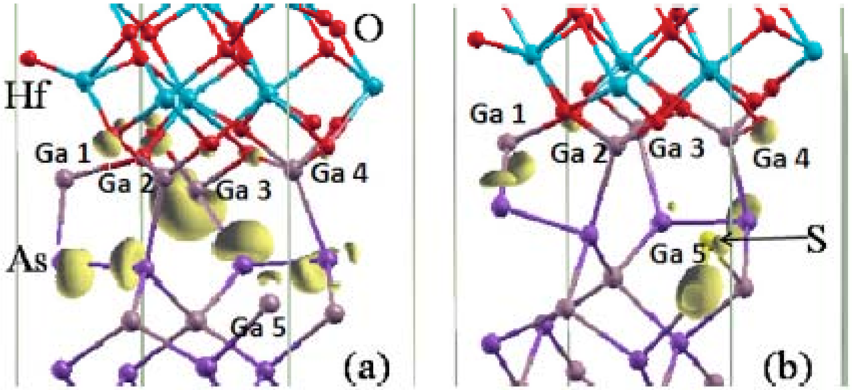


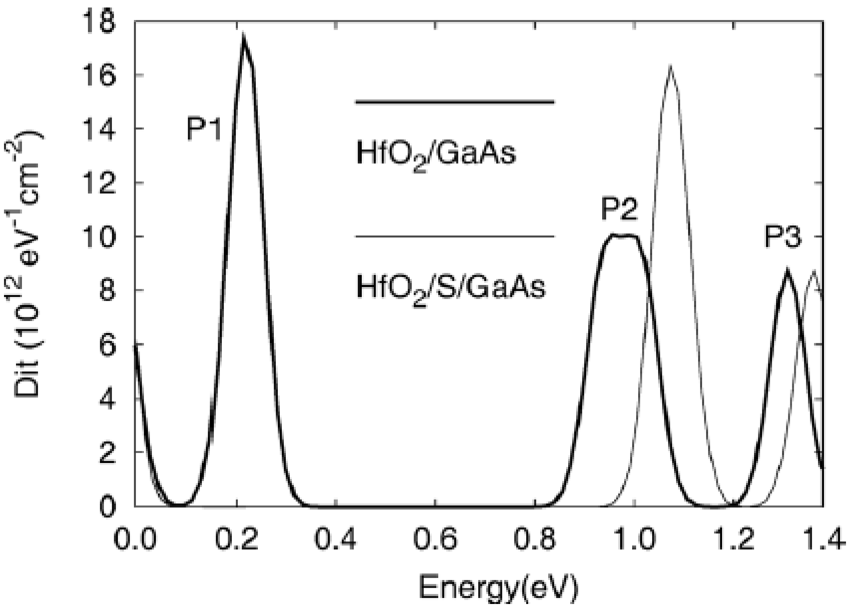
Ga^{+3} As-As Ga db

Wang, et al., J. Phys. Chem. C 114, 22610 (2010); Microelect. Eng. 88, 1061 (2011)

Interface passivation: Sulfur





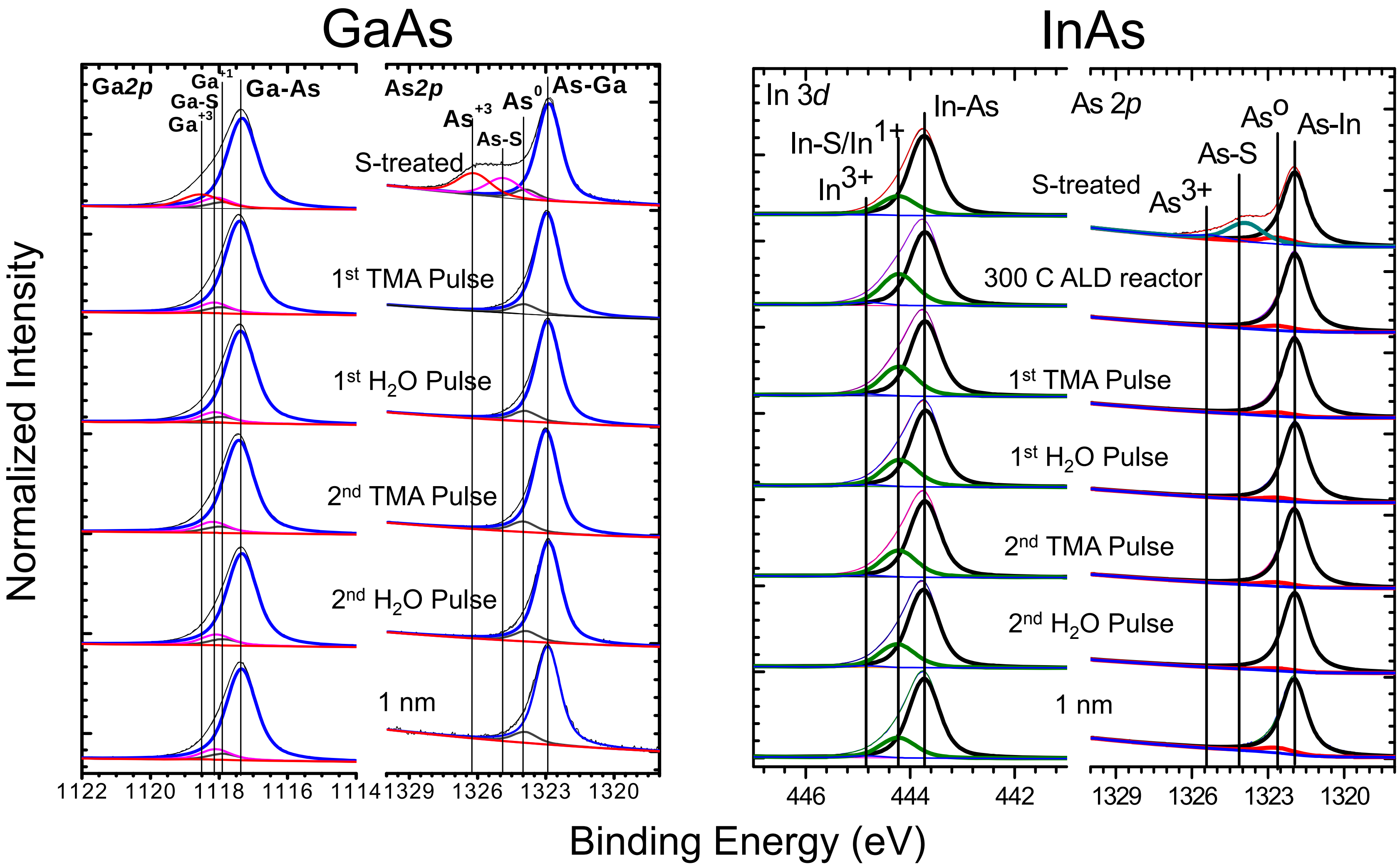


- S passivation helps mitigate defects from oxidation (Ga+3, As-As, Ga db)
- Defect states move toward the CB edge

Wang, et al., APL **98** (2011) 232113

S-passivated III-As Interfaces

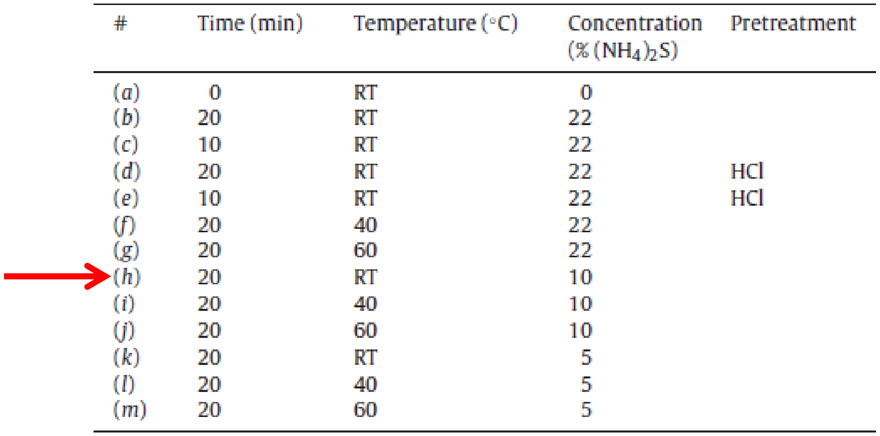
- Oxidation minimized, but not eliminated by wet chemical treatment
- As^0 (As-As) bonding persistent, though less for In-rich surface



APL **93** (2008) 252905; APL **96** (2010) 202905

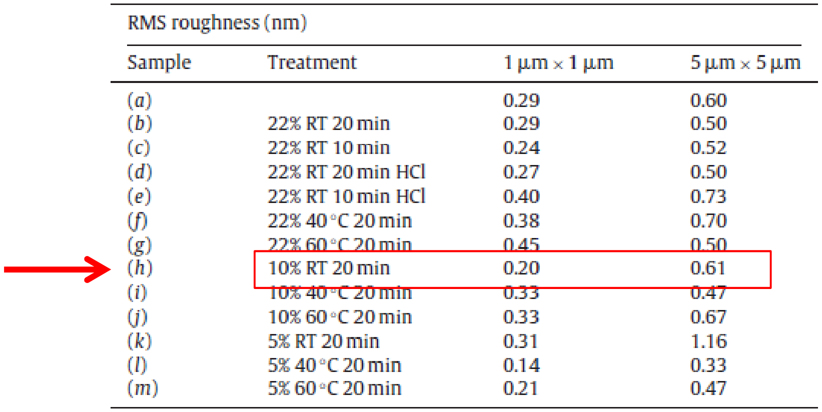
Optimization of S-Passivation: $In_{0.53}Ga_{0.47}As$

Table 2
$(NH_4)_2S$ processing parameters for InGaAs samples.



#	Time (min)	Temperature (°C)	Concentration (% $(NH_4)_2S$)	Pretreatment
(*a*)	0	RT	0	
(*b*)	20	RT	22	
(*c*)	10	RT	22	
(*d*)	20	RT	22	HCl
(*e*)	10	RT	22	HCl
(*f*)	20	40	22	
(*g*)	20	60	22	
(*h*)	20	RT	10	
(*i*)	20	40	10	
(*j*)	20	60	10	
(*k*)	20	RT	5	
(*l*)	20	40	5	
(*m*)	20	60	5	

Table 4
RMS roughness from AFM measurements of samples after $(NH_4)_2S$ and subsequent annealing.



		RMS roughness (nm)	
Sample	Treatment	1 µm × 1 µm	5 µm × 5 µm
(*a*)		0.29	0.60
(*b*)	22% RT 20 min	0.29	0.50
(*c*)	22% RT 10 min	0.24	0.52
(*d*)	22% RT 20 min HCl	0.27	0.50
(*e*)	22% RT 10 min HCl	0.40	0.73
(*f*)	22% 40 °C 20 min	0.38	0.70
(*g*)	22% 60 °C 20 min	0.45	0.50
(*h*)	10% RT 20 min	0.20	0.61
(*i*)	10% 40 °C 20 min	0.33	0.47
(*j*)	10% 60 °C 20 min	0.33	0.67
(*k*)	5% RT 20 min	0.31	1.16
(*l*)	5% 40 °C 20 min	0.14	0.33
(*m*)	5% 60 °C 20 min	0.21	0.47

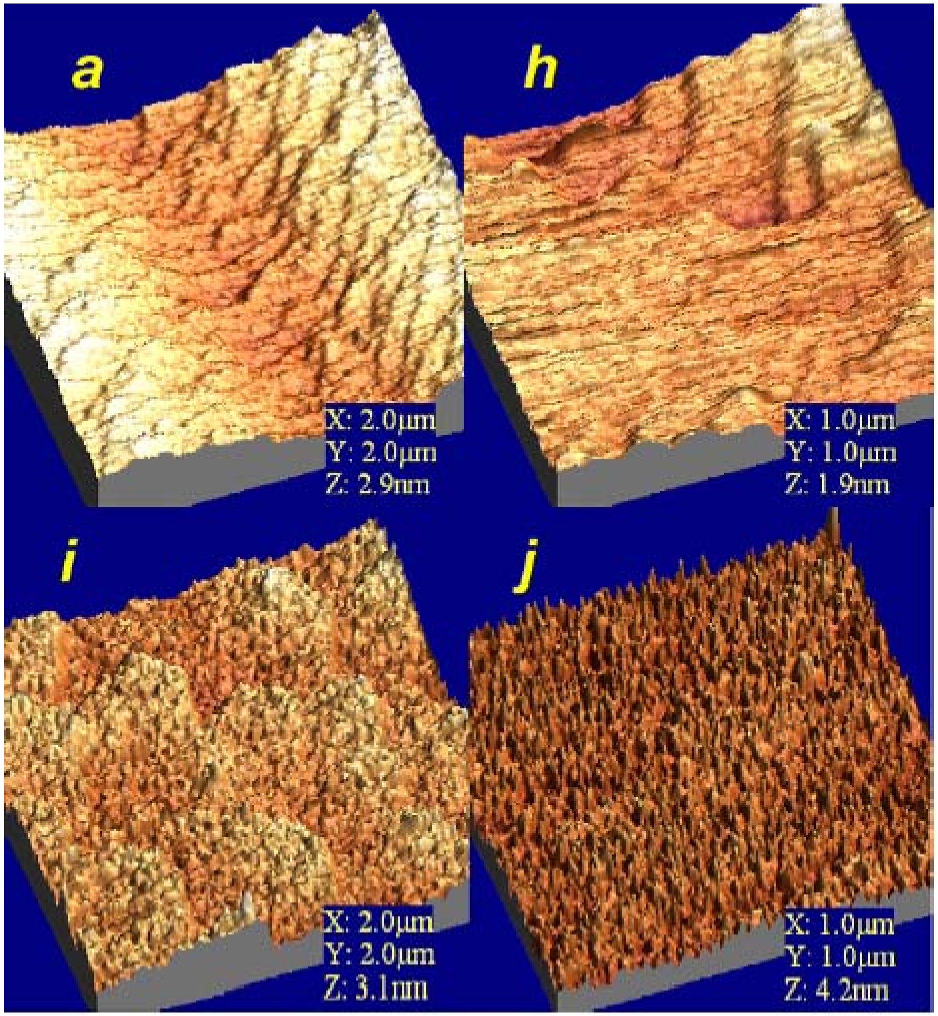
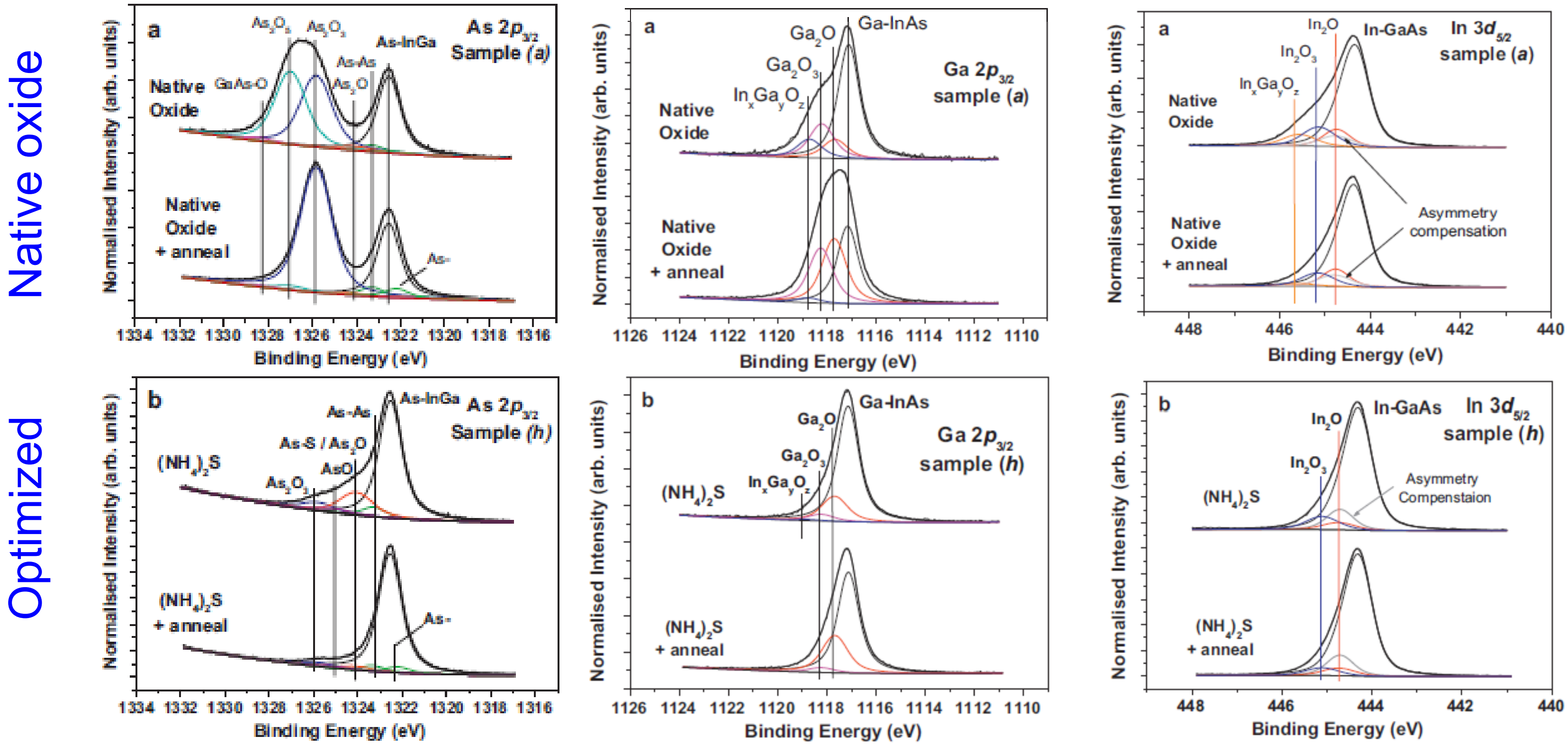


Fig. 8. AFM images from samples (*a*) and (*h*–*j*) with 1 µm × 1 µm and 2 µm × 2 µm scan areas after $(NH_4)_2S$ treatment and subsequent annealing at 300 °C.

Appl. Surf. Sci. 257 (2011) 4082; JAP 109 (2011) 024101

Optimization of S-Passivation: $In_{0.53}Ga_{0.47}As$

Anneal: 300°C in vacuum (ALD reactor)

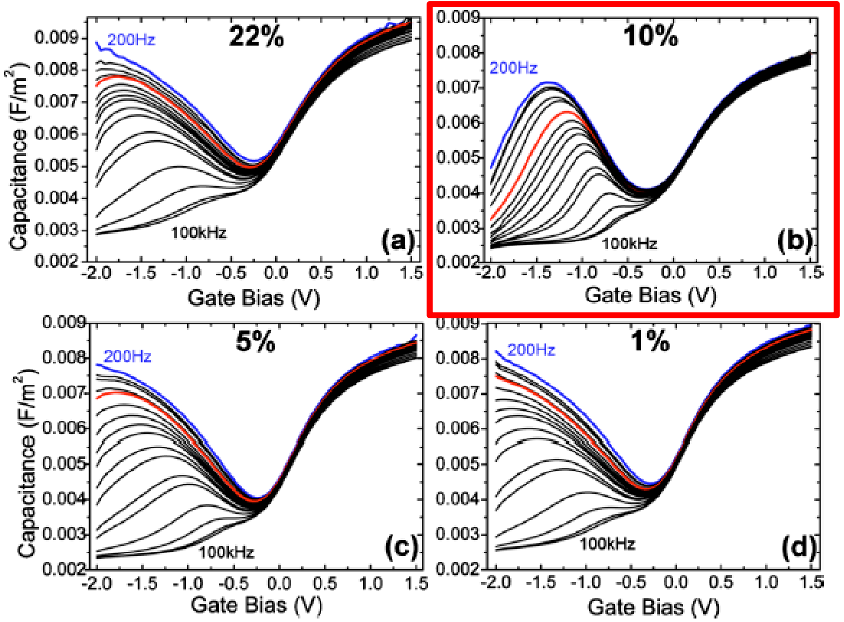


- Optimized wet S-passivation: 10% $(NH_4)_2S$, Room Temp., 20 min + DIW rinse
- Native oxides reduced and reoxidation inhibited
- Anneal results in further oxide reduction and minimized As-As formation
- Interfacial roughness minimized

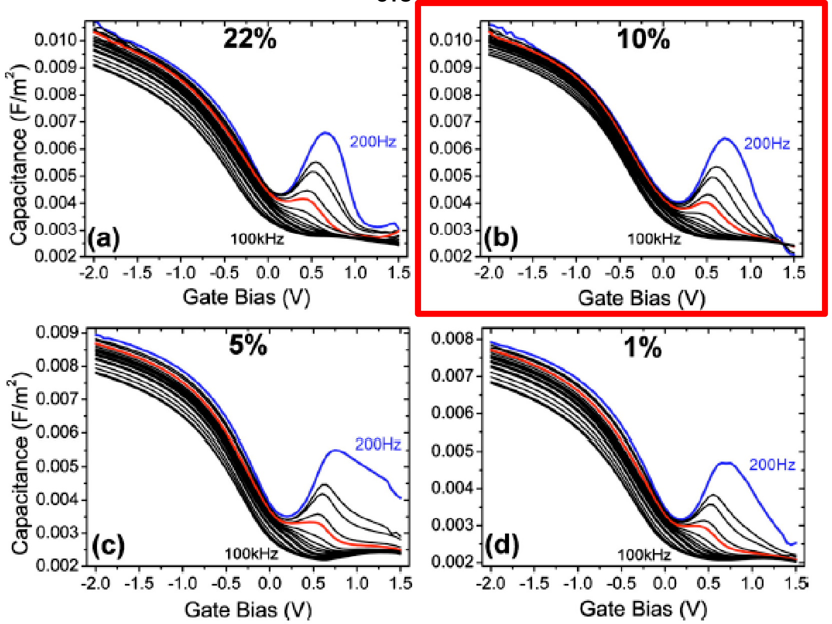
Appl. Surf. Sci. 257 (2011) 4082; JAP 109 (2011) 024101

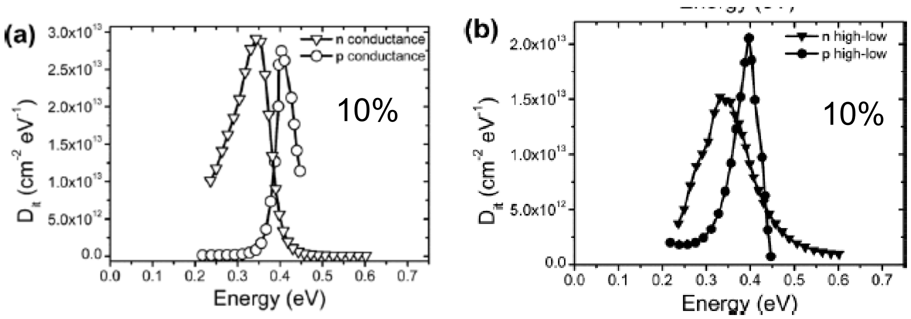
Optimization of S-Passivation: $In_{0.53}Ga_{0.47}As$

n-$In_{0.53}Ga_{0.47}As$



p-$In_{0.53}Ga_{0.47}As$





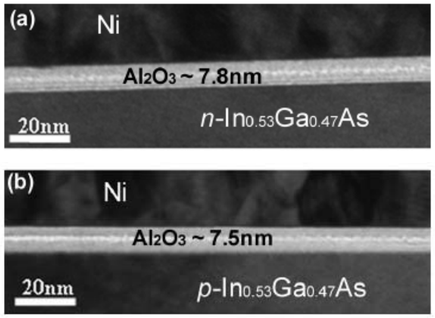


FIG. 1. Cross-sectional TEM micrographs of (a) 10%$(NH_4)_2S$ treated, Au/Ni/7.8 nm Al_2O_3/n-$In_{0.53}Ga_{0.47}As$/InP, and (b) 10%$(NH_4)_2S$ treated, Au/Ni/7.5nm Al_2O_3/p-$In_{0.53}Ga_{0.47}As$/InP device structures.

- Frequency dispersion minimized for 10% $(NH_4)_2S$ treatment
- Hysteresis also minimized
- Important to keep post-etch surface exposure to atmosphere minimized as well (<7 min)
- Mid-gap D_{it} remains significant, likely As-As related

Appl. Surf. Sci. 257 (2011) 4082; JAP 109 (2011) 024101

Summary: III-V

- Conclusions from ex-situ surface analysis of interfaces must be drawn very carefully
  - In-situ studies can serve as a baseline for interfacial chemistry
  - Enables sorting out extrinsic effects
- High-k on III-arsenides
  - Oxidation leads to defect states (As-As, Ga db) which can be *partially* mitigated
  - Si IPL effective in reducing defect states in interfacial region (e.g., silicate formation)
  - S passivation effective at minimizing reoxidation, and can remain through deposition process
  - In-rich arsenides preferred from defect perspective
- Interfacial region CAN be engineered with clusterable process

To Gr

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- Conclusions

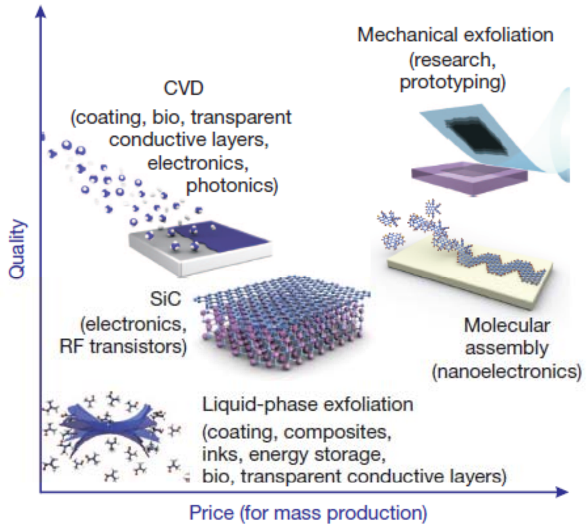
Graphene at a Crossroads

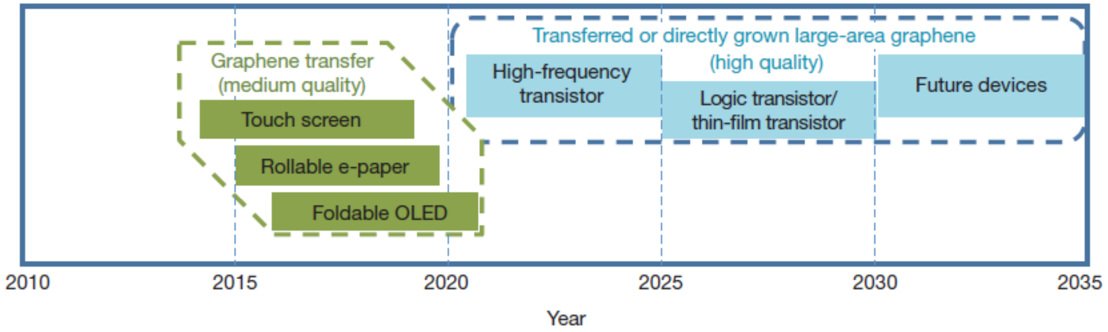
- Transitioning from science to technology
  - Exploiting interesting phenomenon
  - Routes toward integration into useful products
  - Mass production challenges
  - Establishing cost/performance space

See: Nature 490 (2012) 192

Graphene-based Electronics

- Large area synthesis of device quality graphene
- Low cost, reliable CVD (+ transfer) process
- Interaction of contacts
- Interaction of dielectrics
- Packaging (atmospheric exposure/sensitivity)





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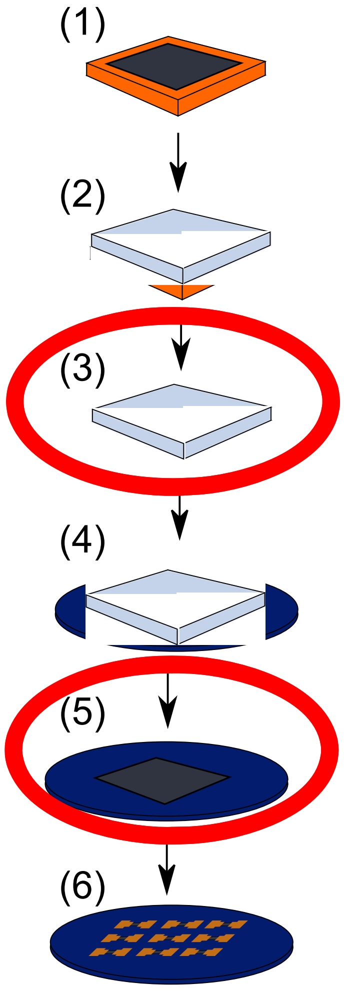
Graphene Transfer Process Flow

Pioneered By Ruoff's group*

1. Graphene growth on Cu substrate
2. Spin on PMMA dissolved in chlorobenzene.
3. Etch Cu substrate in 3:1 DIW:HNO_3 for 1 min followed by 3 hrs + 15 hrs in fresh ammonium persulfate baths
4. Draw PMMA/graphene membrane onto a SiO_2/Si wafer
5. Remove PMMA "handle" layer in acetone
6. Three-terminal graphene FET fabrication using photolithography

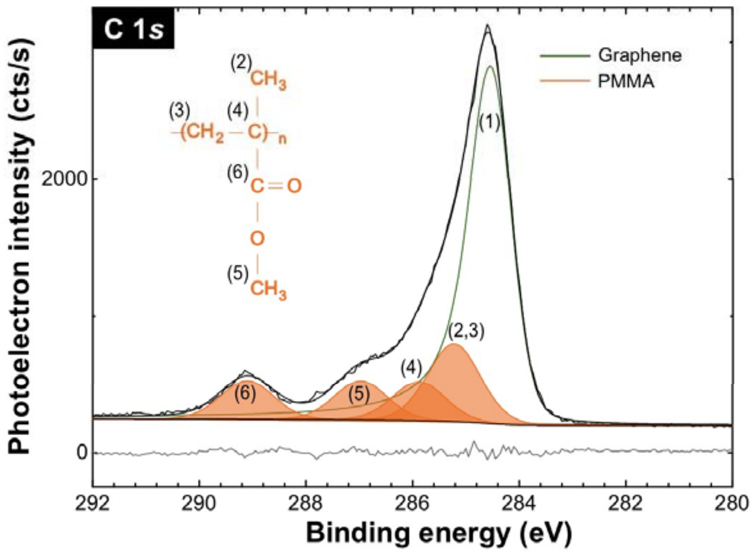


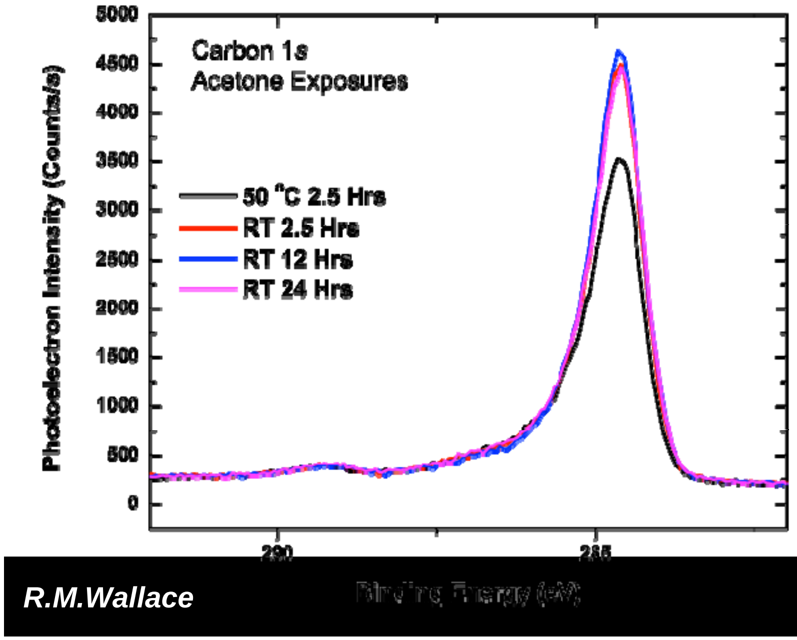
- Steps 3 (the removal of copper) and step 5 (the removal of PMMA) are key points in the transfer process optimization
- Result in reduced chemical residues and increase device performance.

* X. Li *et al.* Nano. Lett. 9(12) 4359 (2009)
** J. Chan et al. ACS Nano 6(4) 3224 (2012)

Step 5: PMMA Residue from Transfer Process

CVD Graphene





- PMMA ‘handle’ is typically removed with an acetone rinse*
- XPS shows that some PMMA residue is left**
- Longer acetone rinses in hot (~50 °C) acetone have also been reported***
- Longer acetone rinses including hot acetone are shown here to be ineffective at providing an increased reduction to the remnant C=O and C-O bonds concentrations.

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* B. Fallahazad *et al.* Phys Rev B **85** 201408(R) (2012)

** A. Pirkle *et al.* Appl. Phys. Lett. **99(12)** 122108 (2011)

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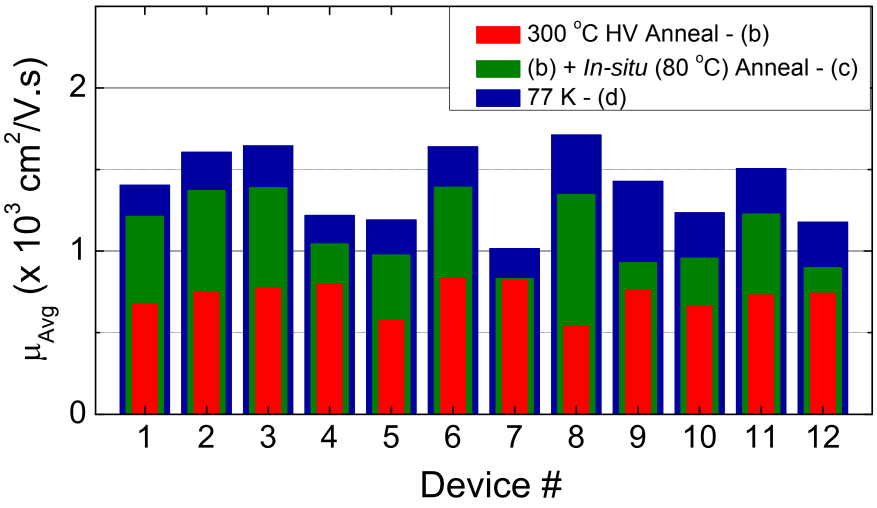
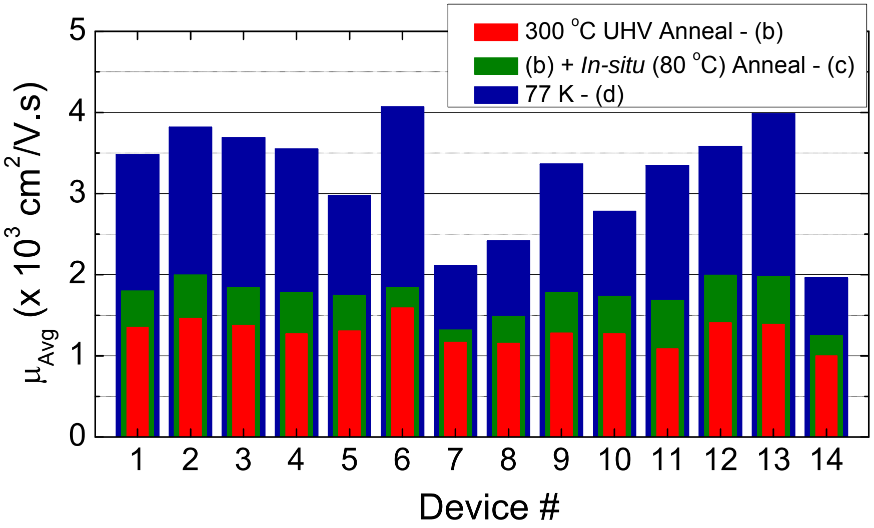
Residue Removal by Vacuum Annealing: UHV vs HV

HV 10^{-7} mbar



UHV 10^{-9} mbar

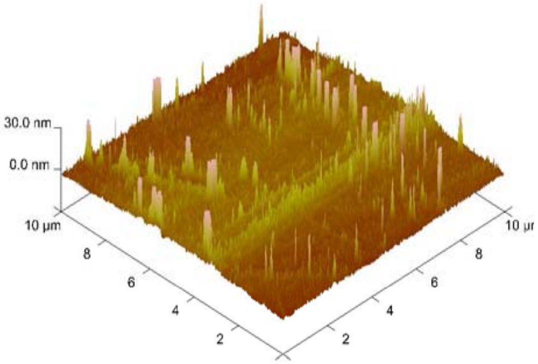


- The UHV anneal result in a factor of 2 increase in the mobility with respect to the HV anneal

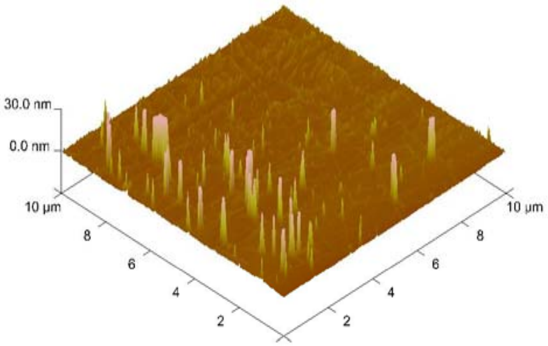
- UHV is required for annealing to yield significant mobility increase

High temperature Annealing

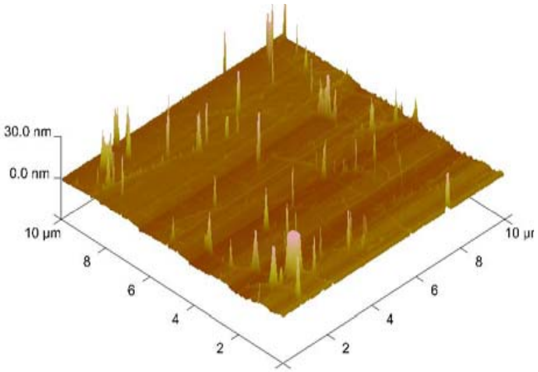
As transferred



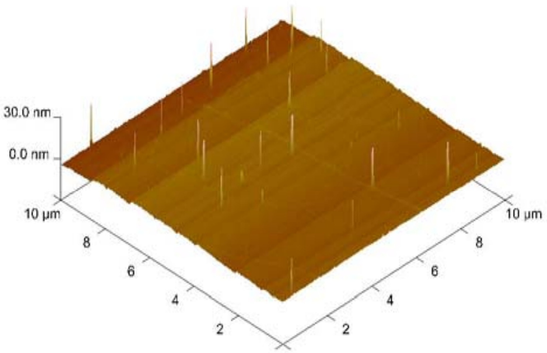
300 °C Anneal



300 °C + Atomic H

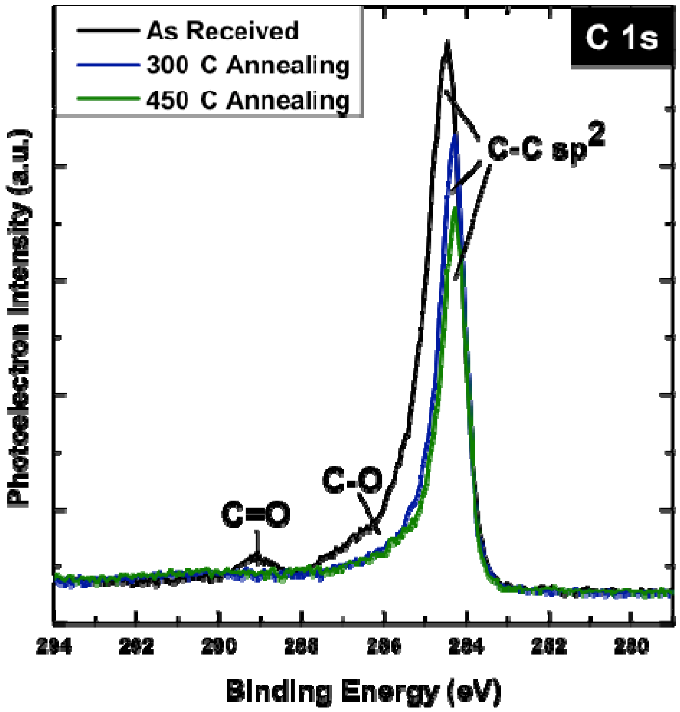


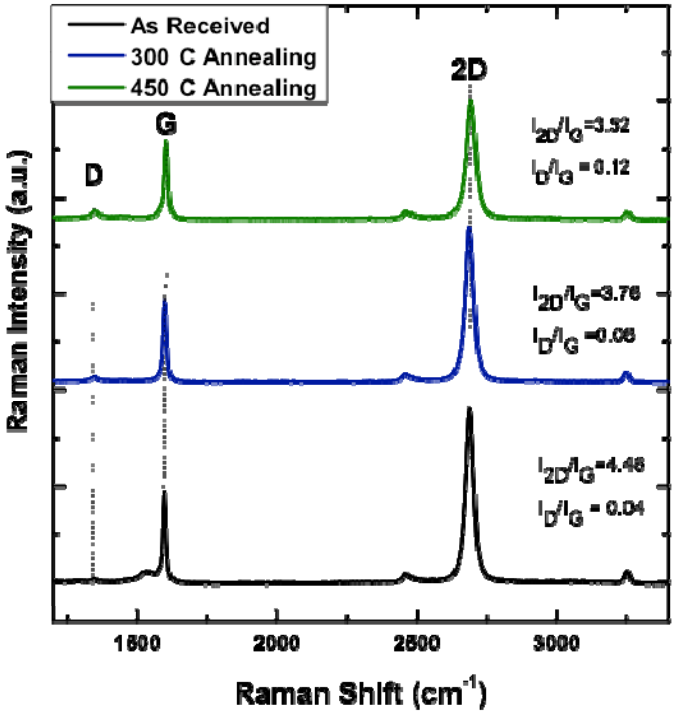
450 °C anneal



- AFM shows the reduction in surface roughness with UHV anneals
- 300 °C Atomic hydrogen shows a slight improvement over just 300 °C anneal
- 450 °C results in the smoothest surface

High temperature Annealing





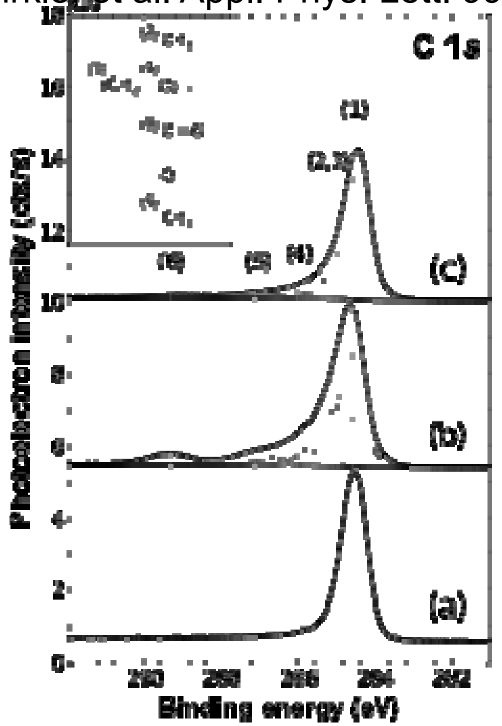
- Higher temperature anneals suggest increased PMMA residue reduction
- Increased I_{2D}/I_G ratio is consistent with increased P-type doping due to reduced PMMA
- Increased D peak highlights that annealing may be causing damage to the graphene.
- This is consistent with recent reports suggesting that thermal decomposition of PMMA may produce radicals that could react with the graphene*

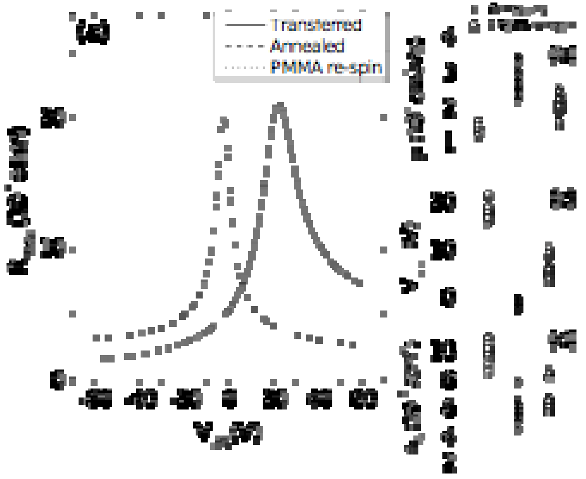
* Nano. Lett. **12** 4141 (2012)

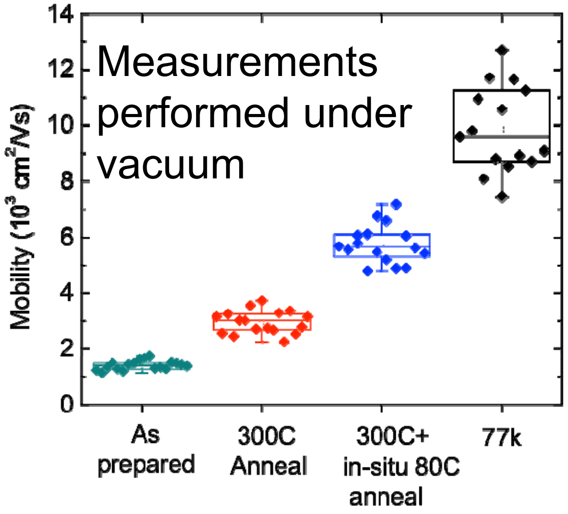
Optimizing the Transfer Process: Effect of Residues

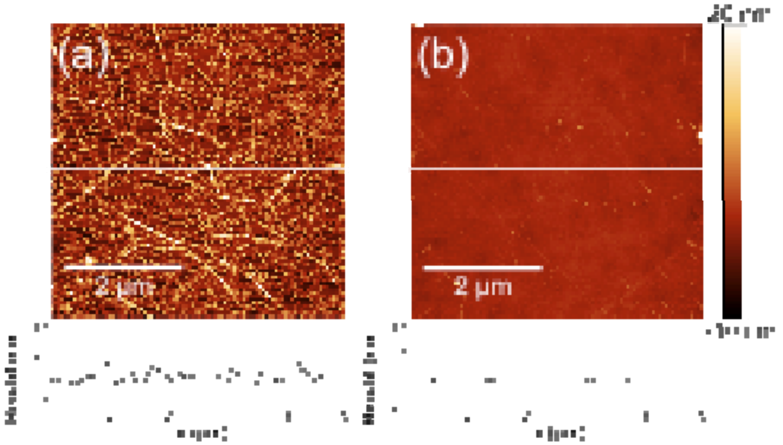
* Pirkle, et al. Appl. Phys. Lett. 99(12) 122108 (2011)

** Chan, et al., ACS Nano 6(4) 3224 (2012)









- Transfer residues such as PMMA have been identified*
- 300°C UHV anneal results in a significant reduction*
- PMMA re-spin confirms that PMMA reduces graphene mobility*
- Mobilities as high as 12,700 cm^2/Vs have been achieved on SiO$_2$**

* Appl. Phys. Lett. 99(12) 122108 (2011)
** ACS Nano 6(4) 3224 (2012)

Summary: Transfer Optimization

- Four potential PMMA removal methods beyond acetone rinsing having been highlighted.
  - Extended (Hot Acetone), UHV anneals, reducing environment anneals and reactive metal sacrificial layers

- With the exception of extended and hot acetone anneals all show further reduced PMMA residue with little or no degradation of the graphene based on Raman analysis.

- UHV ambient required for effective PMMA removal

- High temperature UHV anneals can induce damage

To end

Summary: Graphene

- Ozone treatment can result in ALD nucleation without detectable damage
- Surface contamination likely responsible for high-k nucleation
- Residence time on surface important
- High-k seed layer approach has limited scalability

Conclusions

- In-situ studies enable the understanding of …
  - Interfacial chemistry and resultant defects
  - Mechanisms of film nucleation and growth
  - The “baseline” to which ex-situ grown films/interfaces can be compared
  - Electrical device performance
- Future extensions are underway to…
  - Examine reactions at high pressures
  - Provide advance-studies prior to synchrotron work where beam time is a premium
  - Investigate processes in realistic environments

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