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INTERFACIAL ANALYSIS of *n*-ALKANETHIOL SAMs on GaAs(001) by ARXPS

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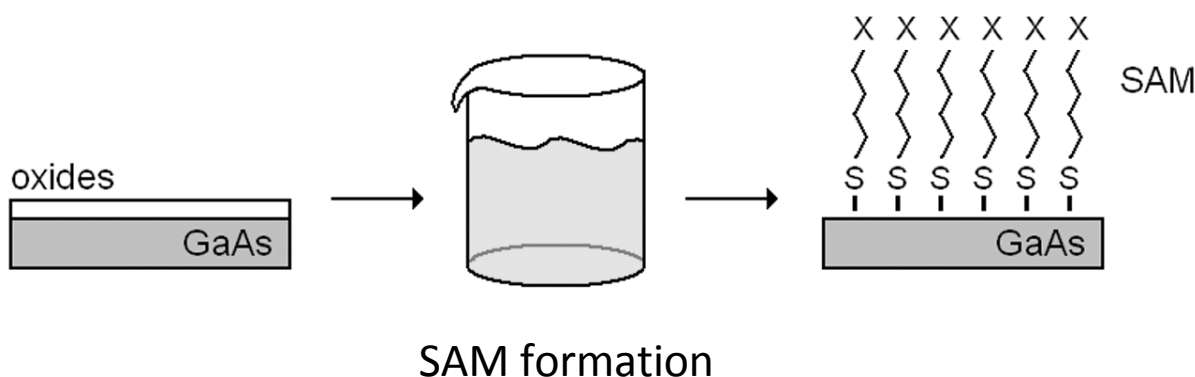
Presentation Overview:

- 1) Research Objectives (alkanethiol SAM-GaAs interface)
- 2) Fractional Overlayer Models (ARXPS)
- 3) Compositional Analysis
- 4) Structural Morphology

Research Objectives:

n-alkanethiol SAMs on GaAs(001)

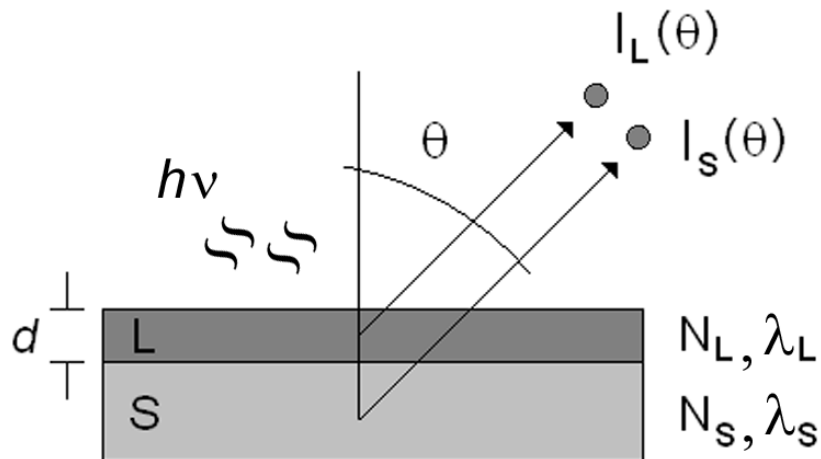
- chemical passivation (oxide)
- electronic passivation (surface barrier)
- functional molecular assemblies (sensors)



SAM = HS [CH₂]₁₅ CH₃
or X = functional groups
COOH, NH₂ ...

Research Objectives:

- SAM-GaAs interface well-studied using XPS
- need to reconcile peak fitting with structural models

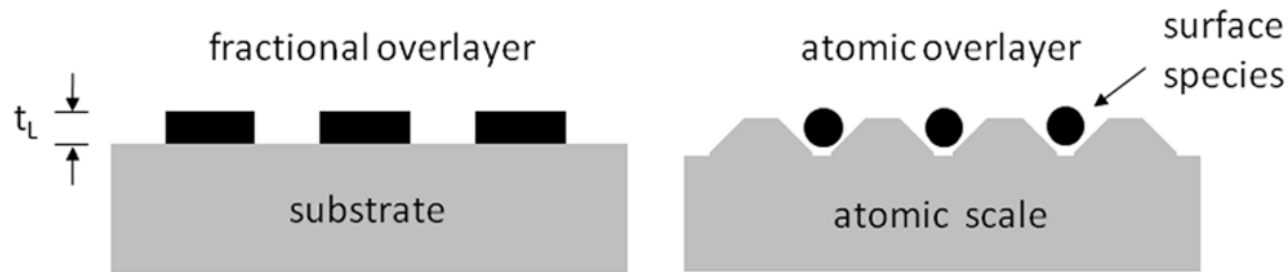


- compare ARXPS data with calculated photoelectron intensity ratios

Fractional Overlayer Models:

- $I(\theta)$ is attenuated in overlayer by inelastic scattering
- assume gaps in surface layer $\rightarrow$ define fractional area (f)

Paynter, R. W. *Surf. Interface Anal.* **1999**, 27, 103.

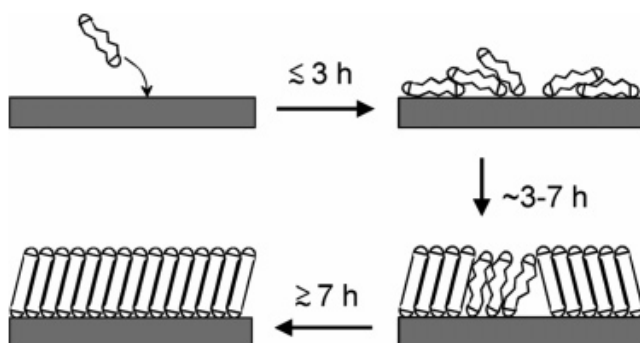


SAM uniformity

sub-monolayer

Fractional Overlayer Models:

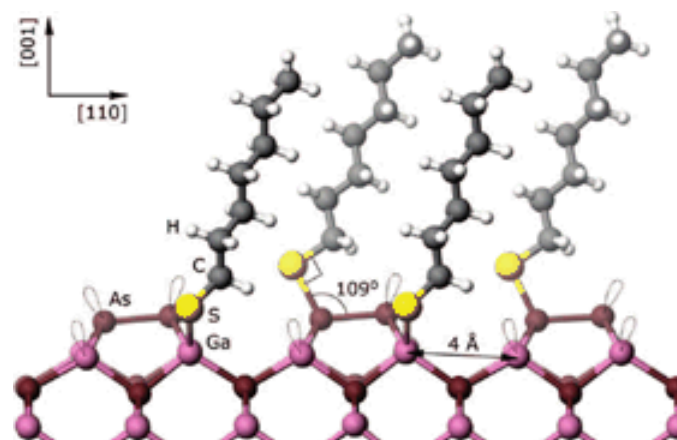
SAM uniformity



McGuiness et al. *Am. Chem. Soc.* **2006**, 128, 5231.

- domain boundaries
- conformational defects

sub-monolayer



Voznyy, O., Dubowski, J. J. *Langmuir* **2008**, 24, 13299.

- steric-limited coverage
- elemental As

Fractional Overlayer Models:

- 3D functional form (SAM)

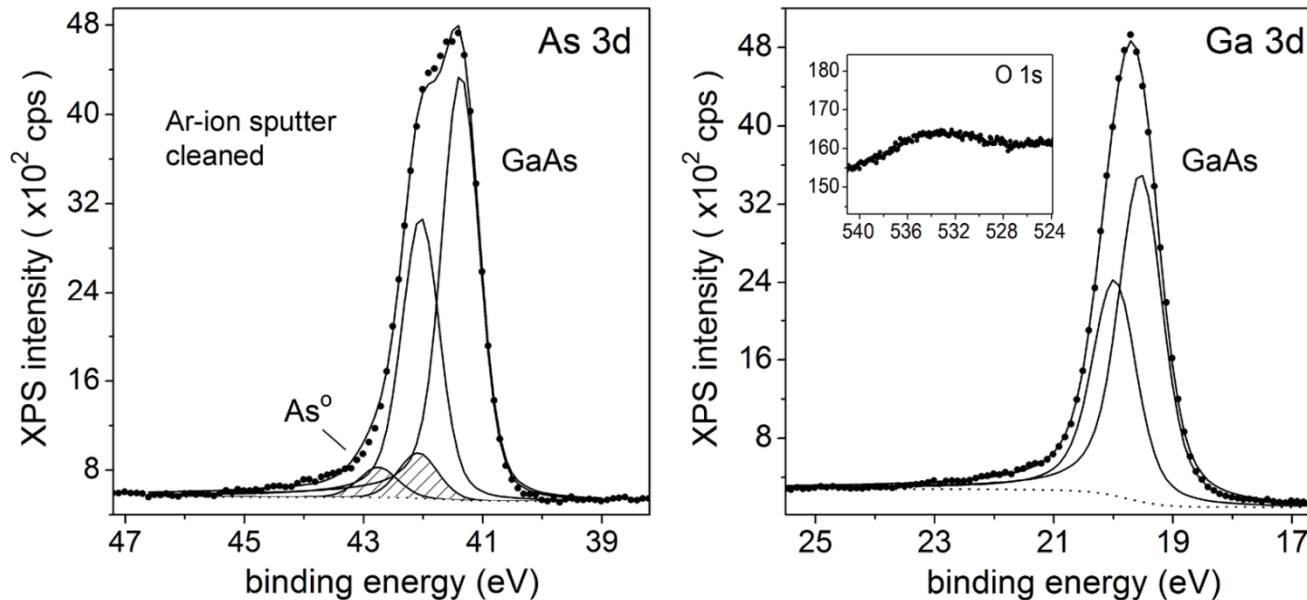
$$\frac{I_L(\theta)}{I_S(\theta)} = \frac{N_L \lambda_L}{N_S \lambda_S} \left[\frac{f_L [1 - \exp(-t_L / \lambda_L \cos \theta)]}{f_L \exp(-t_L / \lambda_S \cos \theta) + (1 - f_L)} \right]$$

- 2D functional form (sub-monolayer)

$$\frac{I_L(\theta)}{I_S(\theta)} = \frac{f_L \rho_{max}}{N_S \lambda_S \cos \theta} [1 - f_L + f_L \exp(-d_L / \lambda_S \cos \theta)]^{-1}$$

Compositional Analysis:

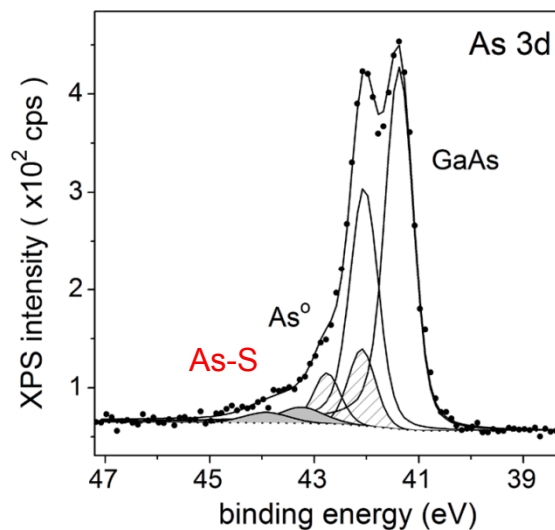
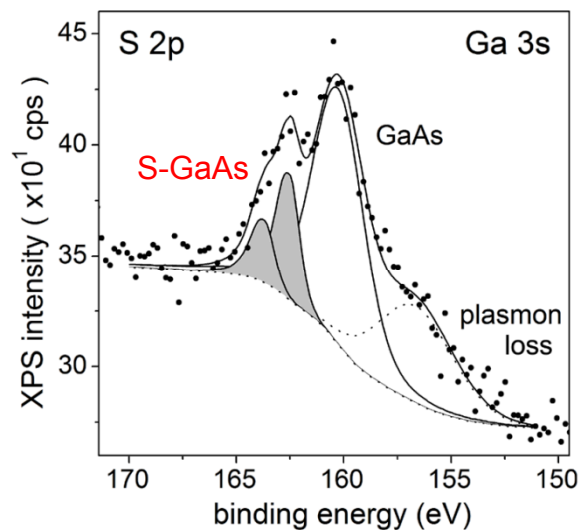
- Doniach-Sunjc model of photoemission (asymmetric tail)



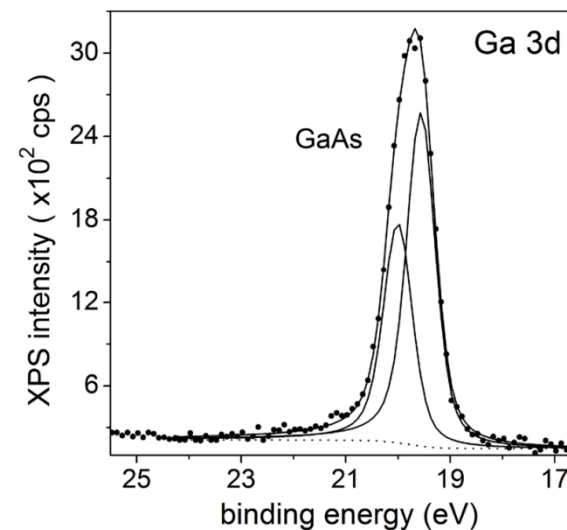
- parameters based on Ar-ion cleaned GaAs
- more accurate fitting of SAM-GaAs oxidation states

Compositional Analysis:

- surface species S-GaAs and As-S



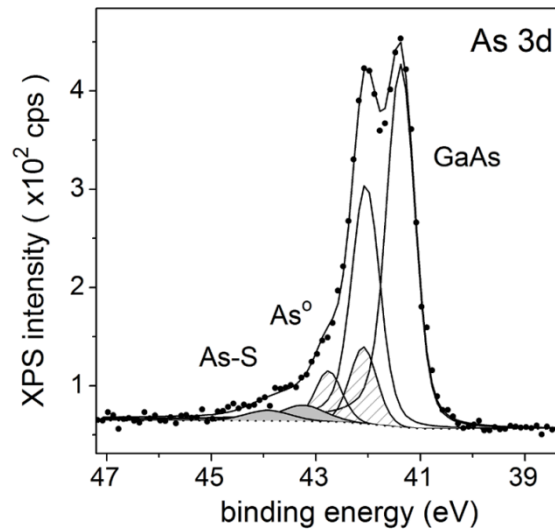
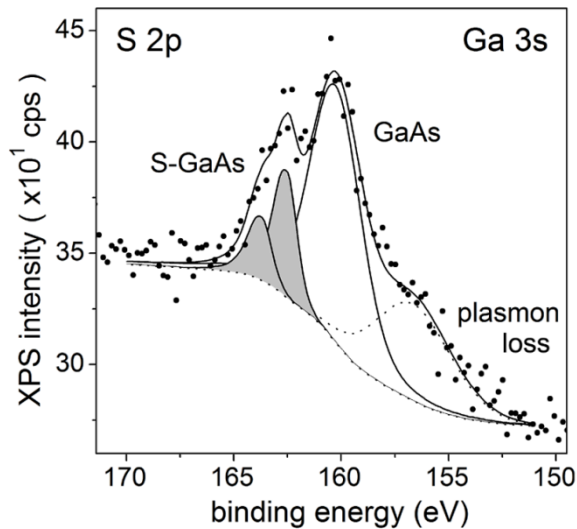
(no Ga-S observed)



($\theta = 60^\circ$)

Compositional Analysis:

→ 2D model with $f_L \rho_{max} = \rho_{SAM}$ and $f_L = \rho_{SAM} / \rho_{GaAs}$



calc & exp ratios ($\theta = 60^\circ$)

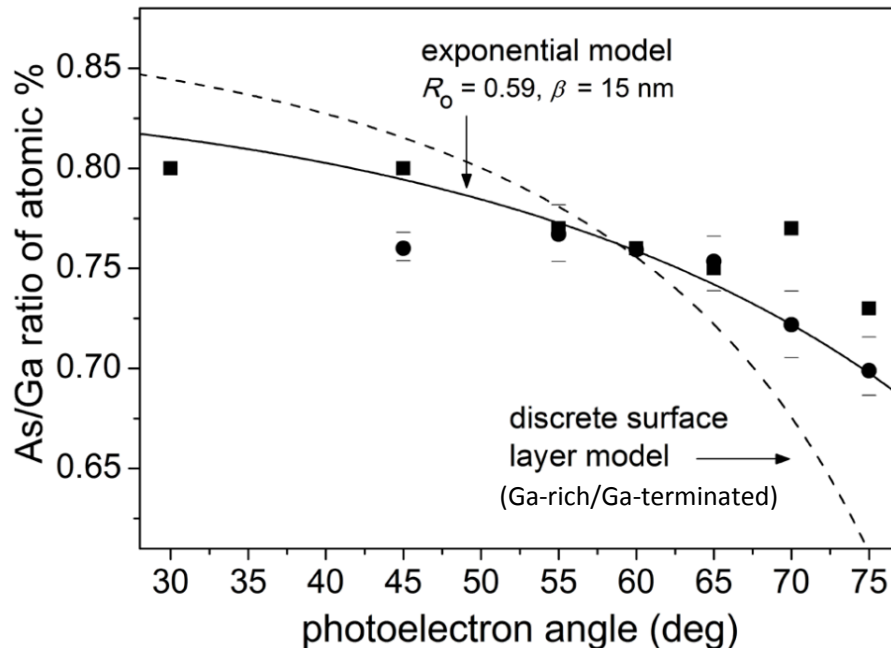
I_{surf} / I_{bulk}	Calc.	Data
$I_{S-GaAs} / I_{Ga(As)}$	0.18	0.21
$I_{As-S} / I_{As(Ga)}$	0.09	0.06



As-S/GaAs-S interface fraction of 1

Structural Morphology:

■ As/Ga ratio depth profile



$$I(\theta) = \frac{1}{\cos \theta} \int N(z) \exp(-z / \lambda \cos \theta) dz$$



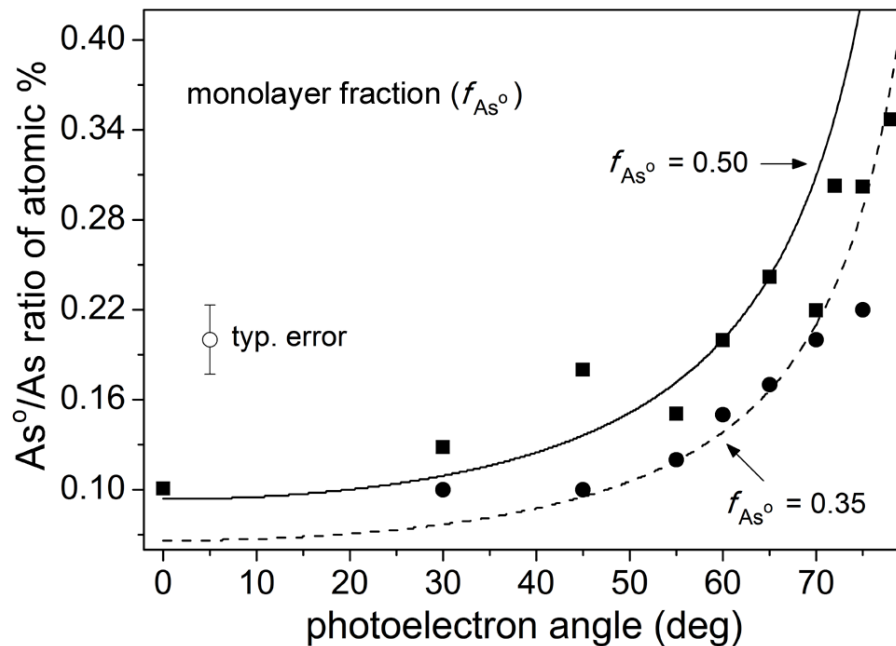
sensitive to precision-limited data !

→ qualitative result only

→ Ga-rich within XPS sampling depth

Structural Morphology:

- elemental As sub-monolayer fraction



→ estimated range $f = 35\text{-}50\%$

$$2.9\text{-}4.2 \times 10^{14} \text{ cm}^{-2}$$

→ compare to max SAM density

$$4.7 \times 10^{14} \text{ cm}^{-2}$$

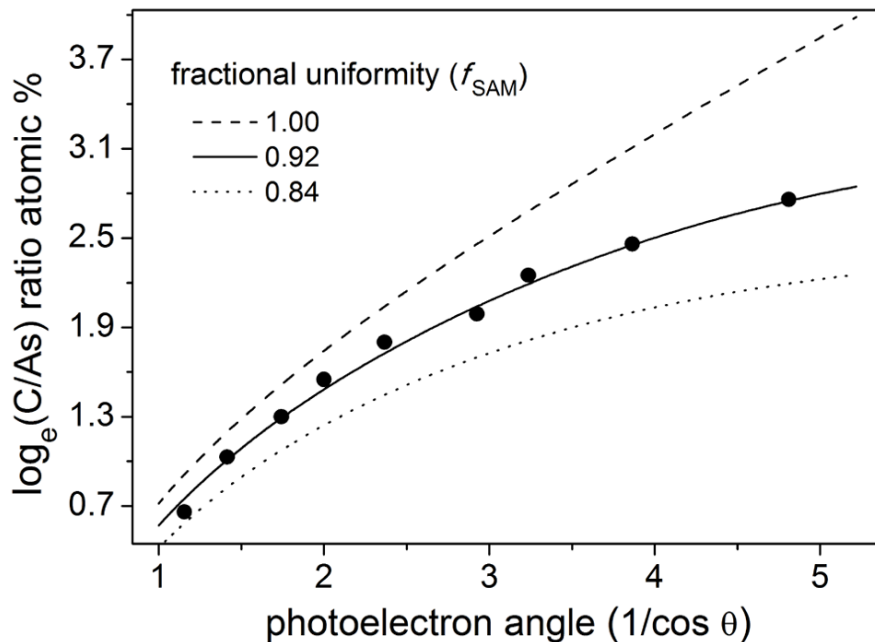
* recall SAM steric limit is 50%



As⁰ is surface interstitial

Structural Morphology:

- SAM fractional uniformity based on C / As photoelectron ratio



→ estimated value $f_{SAM} = 92\%$

* $\frac{N_C \lambda_C}{N_{As} \lambda_{As}}$ is also a fitting parameter



~ 8% > theoretical
(reduced N_{As} / G-rich surface)

Summary:

- ARXPS fractional models useful for SAM characterization
→ Doniach-Sunjic for accurate component fitting
- GaAs surface Ga-rich within XPS sampling depth
- As⁰ surface interstitial commensurate with SAM density
- SAM uniformity is limited by domains/defects



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