

# Surface dipole layer potential induced IR absorption enhancement in *n*-alkanethiol SAMs on GaAs(001)

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## SUPPORTING INFORMATION

- A) Angle Resolved XPS analysis of S 2p / Ga 3s ratio upon thermal disordering.
- B) CPD sampling series.
- C) Background referencing in the S 2p / Gas 3s region.
- D) CPD of *n*-alkanethiol SAMs on n<sup>+</sup>-type GaAs(001).
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### A) Angle Resolved XPS analysis of S 2p / Ga 3s ratio upon thermal disordering.

In this section, a characterization of the disordered SAM is made, specific to the claim that the surface concentration of thiolate remains nearly constant after 55°C thermal disordering. Despite the use of equivalent S 2p / Ga 3s ratios in Figure 5, which is qualitatively correct in terms of the underlying assumption, a more quantitative assessment is required in order to justify the use of different ToAs (60° and 75°). Upon thermal disordering, loss of the attenuation factor associated with a reduced path length through the SAM will increase the photoelectron intensity from the substrate, artificially decreasing the S 2p / Ga 3s ratio. This necessitates the use of an increased ToA in order to provide an equally surface sensitive measurement. As the calculation below demonstrates, the use of equivalent S 2p / Ga 3s ratios for these angles is justified where a 2-3× reduction in the carbon overlayer thickness is assumed. We qualify the analysis here as an estimate, but reiterate from the text that we expect that no significant desorption will occur for covalent bonds energies exceeding 40 kcal/mol at this temperature. Moreover, we acknowledge that any thickness reduction factor assumed is an idealization, particularly in view of the non-uniform surface that may result. Nonetheless, an effective 2-3× thickness reduction may be a reasonable value to expect.

In general, the normalized XPS photoelectron intensity is,

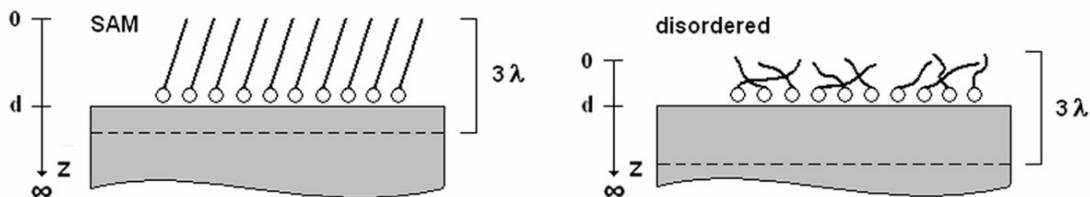
$$I \cos(\theta) = \int_a^b N(z) e^{-z/\lambda \cos(\theta)} dz \quad (1)$$

where  $N$  is the number density of the target material,  $\lambda$  is the IMFP at the kinetic energy measured, and  $\theta$  is the photoelectron ToA as defined in the text. The cosine term on the left accounts for the analysis area projected as a function of the ToA.

For a 2D layer, representing the surface concentration of thiolate, the photoelectron intensity can be written directly in terms of the surface density of sulphur ( $\chi_s$ ),<sup>1</sup>

$$I \cos(\theta) = \chi_s \quad (2)$$

Now consider the following diagram, with overlayer thickness  $d$  in either the ordered



SAM or disordered monolayer case. The term  $3\lambda$  represents the sampling depth of the measurement, which in the case of the disordered layer extends deeper into the GaAs material and necessitates the use of a higher ToA in order to compensate for the *apparent* increase in Ga 3s intensity.

Integrating in (1), dividing (1) in (2), and canceling common terms associated with attenuation through the carbon overlayer the photoelectron intensity ratio is,

$$\frac{S_{2p}}{Ga_{3s}} = \frac{\chi_s e^{d/\lambda_{GaAs} \cos(\theta)}}{N_{Ga} \lambda_{GaAs} \cos(\theta)} \quad (3)$$

Implicit is the cancellation of the cosine factor upon integration in the denominator. Note that the effect of Ga 3s attenuation through the S 2p atomic layer is small and ignored. To compare ratios at  $60^\circ$  and  $75^\circ$ , we need only consider the exponential and cosine terms in (3), as the other terms remain constant in the case where no surface desorption occurs. With an all-*trans* molecular length ( $d$ ) of about  $21 \text{ \AA}$  for  $n_{15}$ -SAMs at  $60^\circ$ , and taking a value of  $20 \text{ \AA}$  for  $\lambda_{GaAs}$  at  $1325 \text{ eV}$ ,<sup>2</sup> an equivalent ratio is obtained for the disordered monolayer with  $d = 7.5 \text{ \AA}$  at  $75^\circ$ , i.e., a reduction factor of about  $3\times$ . The equivalency of (3) between  $60^\circ$  and  $75^\circ$  is clear from the data in Table SI-i below.

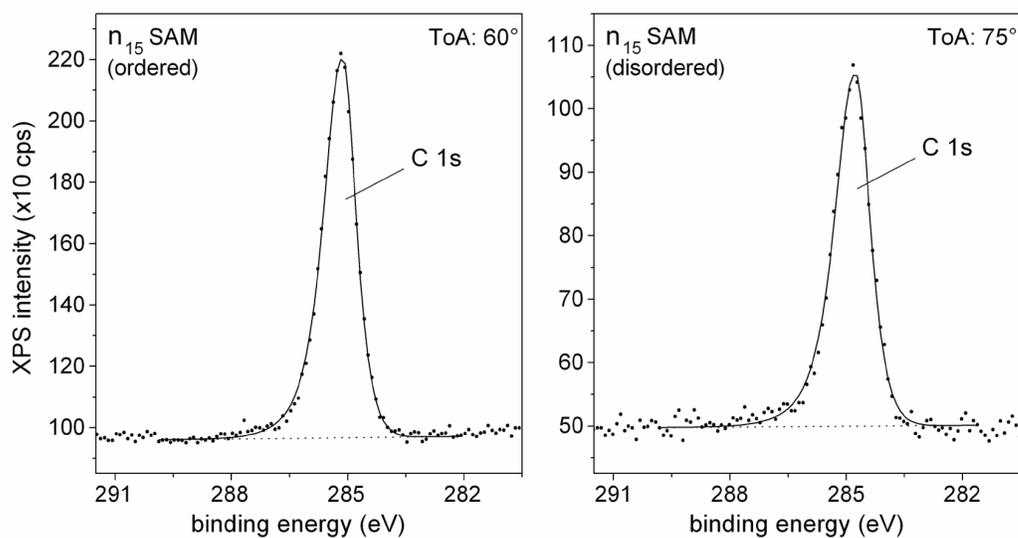
Now consider a limiting case where every other molecule in the nearest-neighbour direction is removed from the pseudo-hexagonal herringbone surface cell structure as defined for the SAM in McGuinness et al.<sup>3</sup> This will yield a loss factor of about 21% in terms of the surface density in (2). Using the same parameters as above, equivalency is obtained with  $d = 8.7 \text{ \AA}$ , or a reduction factor of  $2.4\times$ . We suggest that the actual material loss factor necessary to accommodate disordering may be this much or less, but would remain unresolved due to the uncertainty of peak fitting in the complex Ga 3s region. Similar quantifications can be made using the C 1s data shown in Table SI-i.

**TABLE SI-i.** Angle-Resolved XPS component data in the ordered ( $60^\circ$ ) and disordered ( $75^\circ$ ) SAM phase (see Fig. 5)

atomic orbital	binding energy <sup>a</sup> (eV)		intensity (cps)	
	$60^\circ$	$75^\circ$	$60^\circ$	$75^\circ$
C 1s	285.12	284.75	1426	710.9
S 2p <sup>b</sup>	162.53	162.23	89.6	43.6
Ga 3s	160.34	160.35	346.0	165.5

<sup>a</sup> referencing as described in the Experiment Details.

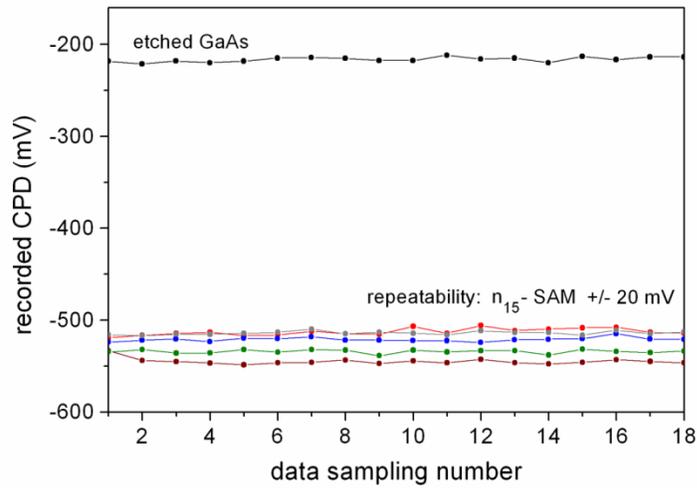
<sup>b</sup> reference the 5/2 spin-orbit branch of S 2p doublet with  $\frac{1}{2}$  splitting ratio and +1.18 eV separation to 3/2 branch.



**XPS C 1s.** Spectra before ( $60^\circ$ ) and after ( $75^\circ$ ) thermal disordering of  $n_{15}$ -SAM, complement to S 2p / Ga 3s data in Figure 5 and in Table SI-i.

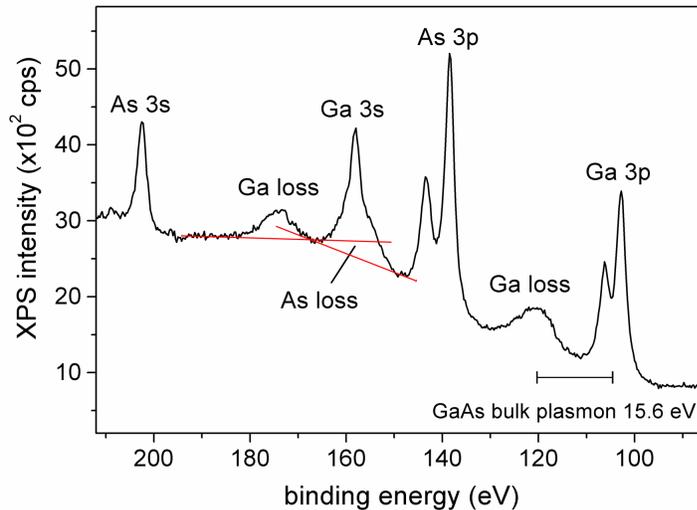
With respect to the above analysis, we should note the various uncertainties implicit in Angle-Resolved XPS results, particularly: non-uniform surfaces, very high ToAs, limited number of angles and peak fitting precision (especially for the disordered system). As such, the discussion above is not meant to achieve high accuracy. The data should not stand alone in the characterization of the SAMs, and should only be used to help verify the expectation of near constant thiolate concentration after thermal disordering.

**B) CPD sampling series.** Kelvin Probe CPD sampling data from an etched GaAs reference and the CPD repeatability of  $n_{15}$ -SAMs estimated at  $\pm 20$  mV.



**C) Background referencing in the S 2p / Gas 3s region.**

In this section, additional information is provided with respect to the referencing of the background of inelastic scattering in the S 2p / Ga 3s region. The figure below shows an expanded view of this region. Clearly, the Ga 3s region overlaps with an As plasmon loss peak. Moreover, as the red lines suggest, the region does not offer a suitable choice of background subtraction (linear or Shirley), as the background changes slope on either side of the region.



Error can be manifested in terms of inconsistent atomic percentages relative to the other Ga peaks, e.g., Ga 3d. One alternative is to calibrate the Ga 3s intensity against the Ga 3d line using an etched GaAs reference surface. Since this surface is unpassivated with thiol, it is always contains oxide despite best efforts to control the environment. However, suitable quantification in the Ga 3d region leads to a reasonable estimate of the corresponding Ga 3s peaks. The difference with respect to the spectrum envelope is filled with *artificially assigned* components associated with inelastic scattering in the bulk material. We suggest this approach produces fewer artefacts than a blind choice of a more common background function. However, we acknowledge these efforts provide only an estimate fitting of this complex region. Applied systematically, the method provides a reasonable approach to the evaluation of the S 2p peak. The Ga 3s + background specifications were imported to the analysis of the S 2p region with constraint, such that only their intensities were allowed to vary in order to match the attenuation factor of the SAM overlayer. The S 2p peaks were then fitted in the remaining spectral area. Below are figures representing the bare Ga 3s region (left), and the bare Ga 3d region (middle) used for the calibration approach. A table summarizing the component specifications is provided following. In addition, the Ga 3d spectra corresponding to a sample of  $n_{15}$ -SAM (HDT) is shown (right) demonstrating that no GaOx component is detectable after SAM formation.

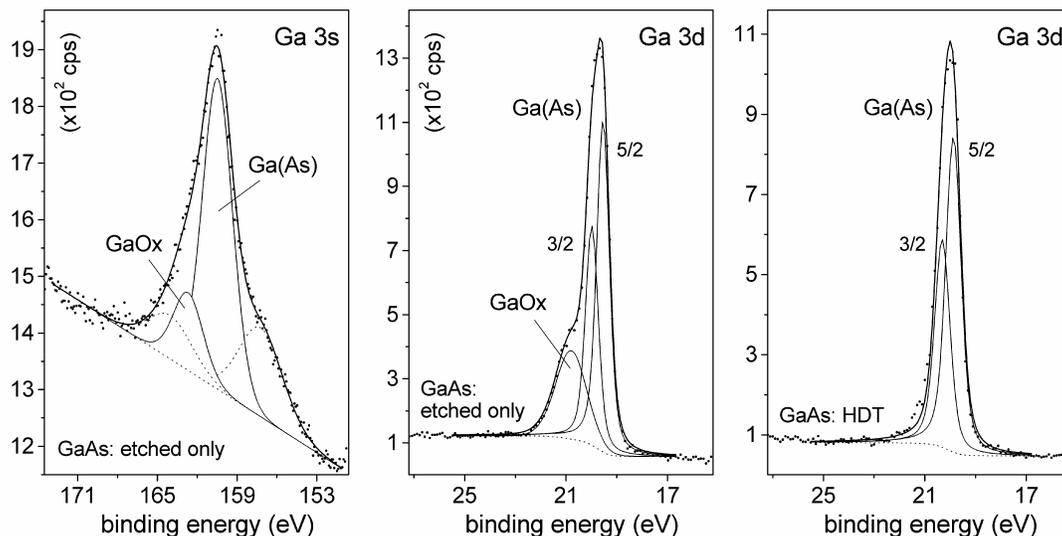


TABLE SI-ii. Component assignments, specifications and fractional intensities of XPS spectra recorded from etched only semi-insulating GaAs(001) and used for S 2p peak analysis.

Region <sup>a</sup>	Type	Position <sup>b</sup> (eV)	FWHM (eV)	Area (cps)	Total RSF <sup>b</sup>	Fraction (%) <sup>c</sup>
GaAs	background	164.0	3.9	325	-	-
Ga 3s	GaOx	162.7	2.7	395	0.91	9.7
Ga 3s	Ga(As)	160.5	2.7	1580	0.91	38.9
GaAs	background	157.2	3.9	663	-	-
Ga 3d	GaOx	20.8	1.4	430	0.77	12.5
Ga 3d (3/2)	Ga(As)	20.0	0.6	531	0.77	15.4
Ga 3d (5/2)	Ga(As)	19.5	0.6	805	0.77	23.4

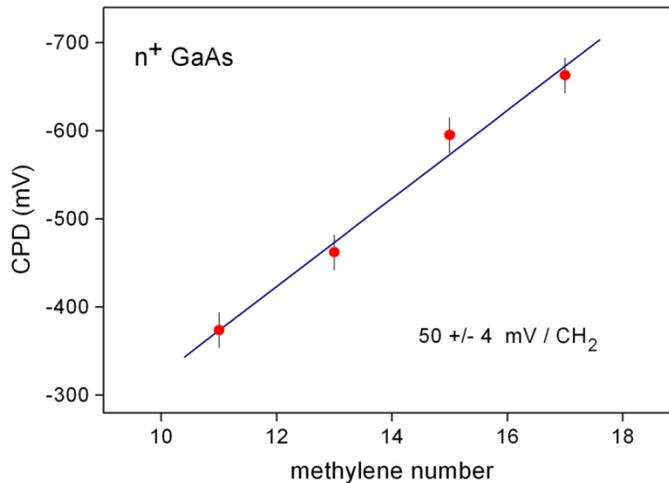
<sup>a</sup> Fractions refer to spin-orbit coupling branch ratios.

<sup>b</sup> Relative Sensitivity Factor: product of the photoionization cross-section, orbital asymmetry factor and instrument transmission function.

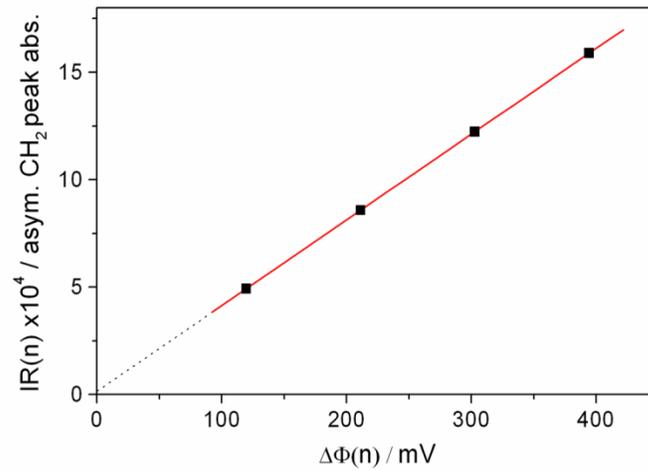
<sup>c</sup> Relative fraction, evaluated at photoelectron take-off 60° from normal.

Note the equal atomic percentages in red between Ga 3s and Ga 3d used in the calibration approach. The respective oxide peaks were estimated.

**D) CPD of *n*-alkanethiol SAMs on  $n^+$ -type GaAs(001).** CPD variation with methylene number (*n*) for SAMs on  $n^+$ -type GaAs ( $50 \pm 4$  mV/CH<sub>2</sub>) is equivalent with respect to the observations on semi-insulating material quoted in the in text ( $46 \pm 3$  mV/CH<sub>2</sub>).

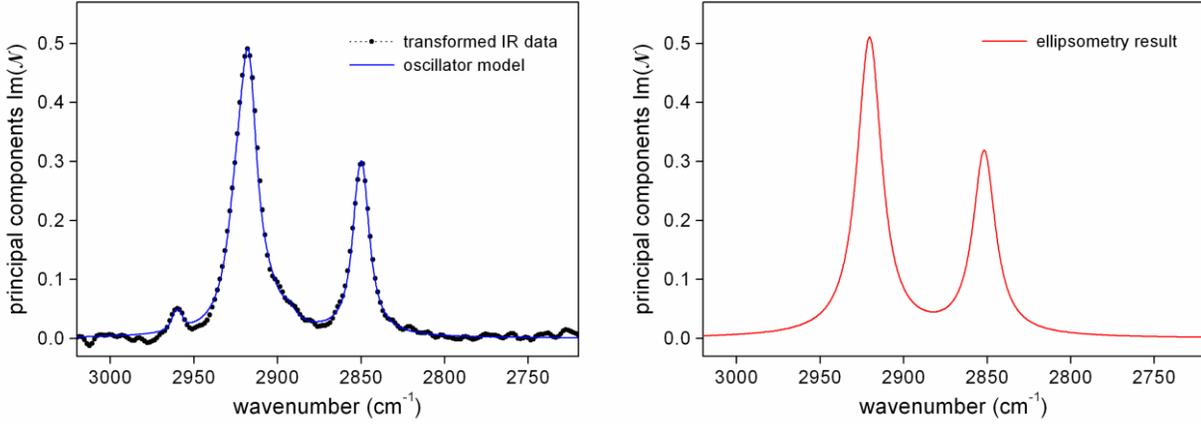


**E) Correlation of IR intensity with the 2D-DLP.** IR peak absorbance vs. the 2D dipole layer potential, based on their respective linear functions of the methylene number ( $n$ ) shown in Figures 2 and 6. The zero intercept illustrates their direct proportionality, as specified in (1) in the text. Note that in this case the IR amplitude has been scaled by 1/2 to account for the use of double-side polished wafer.



Assumed, but not reflected in the Figure, is the uncertainty on the 2D-DLP values estimated to be  $20 \pm \text{mV}$ , which results from uncertainty in the CPD baseline value in Figure 2. This would impart a systematic horizontal shift error in the linearization, but would not be considered significant to the conclusion of direct proportionality.

**F) IR spectrum model and comparison with ellipsometric result.**



Left: Measured IR spectrum of  $n_{15}$ -SAM (dotted), normalized to  $\alpha_{\text{SAM}}$  evaluated from Beer-Lambert analysis,<sup>4</sup> and transformed according to text Eqn. (4) into the principal extinction coefficients  $\kappa_{1,1} = \kappa_{2,2}$  and  $\kappa_{3,3} = 0$  specified in Eqn (5). Oscillator model approximation (blue) of the spectrum of  $\kappa$  evaluated using Eqn. (3), which is shown in Figure 7 along with its complementary real term of the refractive index ( $\eta$ ). Modal decomposition of the spectral envelope used for oscillator modeling followed similar assignments as tabularized in Marshall et al.<sup>4</sup> and from references therein.

Right: Calculated principal extinction coefficients  $\kappa_{1,1} = \kappa_{2,2}$  using the transformation in Eqn. (4) and the surface plane dielectric parameters given by Rosu et al.<sup>5</sup> as follows:

$$\epsilon'_{x,y}(\nu) = \sum_m \frac{M_m (\nu_m^2 - \nu^2)}{(\nu_m^2 - \nu^2)^2 + (\Omega_m \nu)^2} \quad \epsilon''_{x,y}(\nu) = \sum_m \frac{M_m \Omega_m \nu}{(\nu_m^2 - \nu^2)^2 + (\Omega_m \nu)^2}$$

$$M_1 = 67500, M_2 = 40500$$

$$\nu_1 = 2919, \nu_2 = 2851$$

$$\Omega_1 = 17, \Omega_2 = 16$$

The indices 1 and 2 refer to Lorentzian oscillators representing the generalized asymmetric and symmetric CH<sub>2</sub> stretching modes respectively. The oscillator strength is given by M in units cm<sup>-2</sup>, the wavenumber position is  $\nu$  in cm<sup>-1</sup> and the mode FWHM is  $\Omega$  in units cm<sup>-1</sup>.

## References

- 1 Carpenter, M. S.; Melloch, M. R.; Cowans, B. A.; Dardas, Z.; Delgass, W. N.  
*J. Vac. Sci. Technol. B* **1989**, 7, 845.
- 2 NIST Electron Inelastic-Mean-Free-Path Database: Version 1.1, © 2000.
- 3 Ref. [9].
- 4 Ref. [12].
- 5 Ref. [13].