

# *Supplemental Information for:* Molecular Self Assembly at Bare Semiconductor Surfaces: III. Chemical Properties of the Alkanethiol-GaAs (001) Interface

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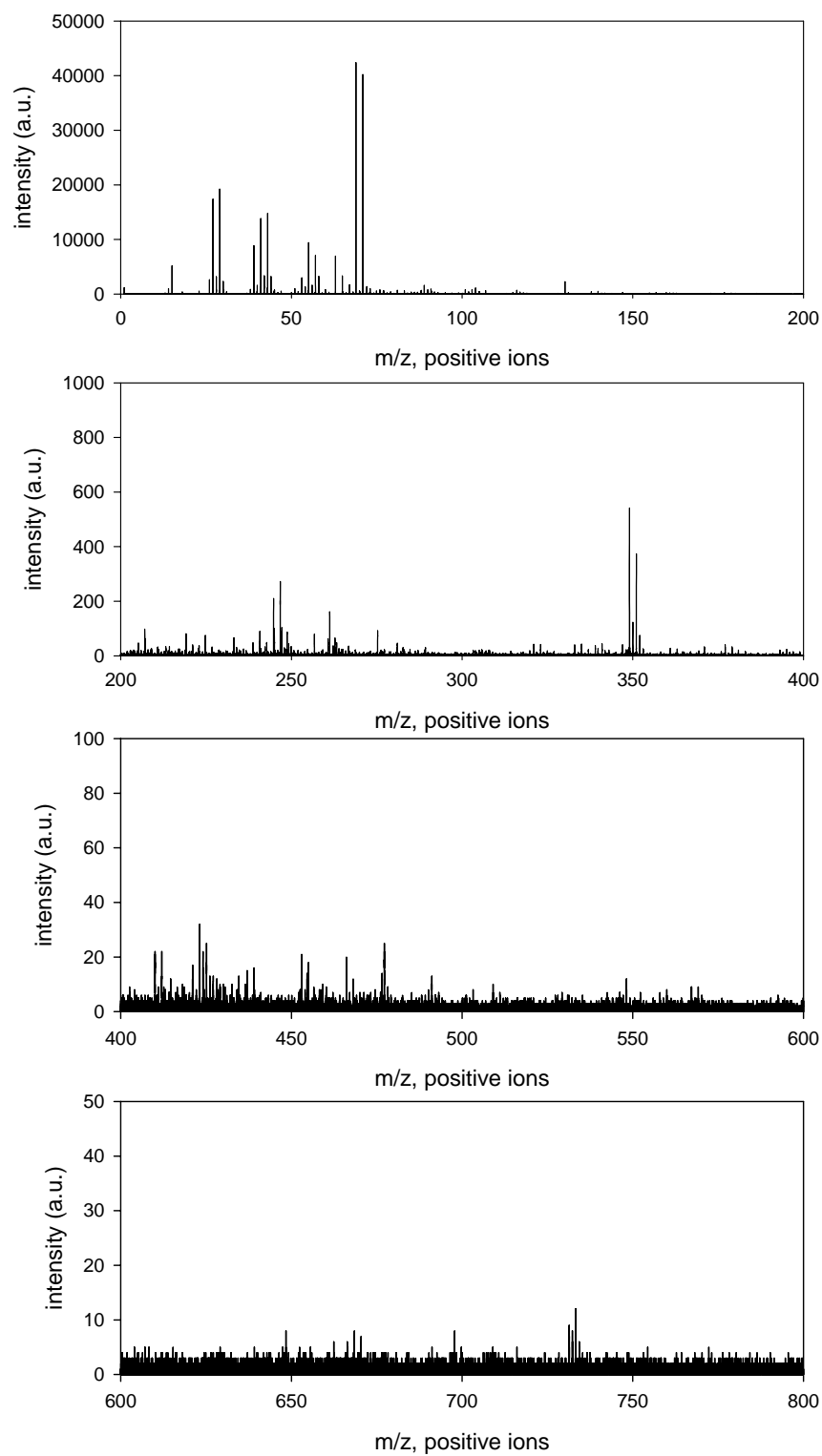
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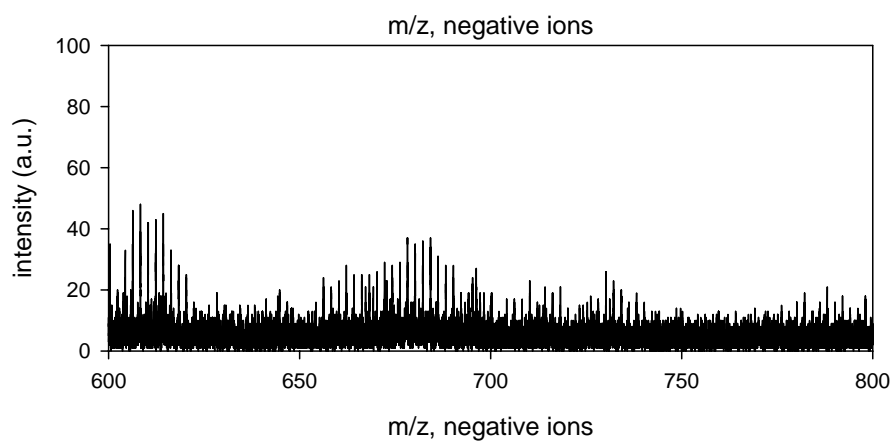
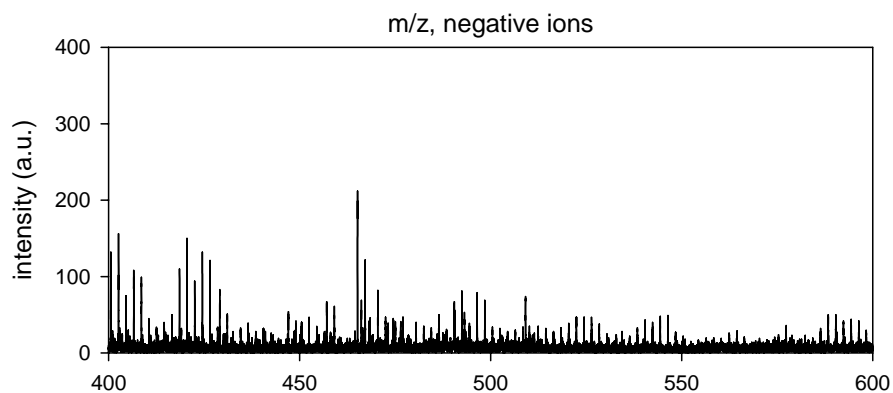
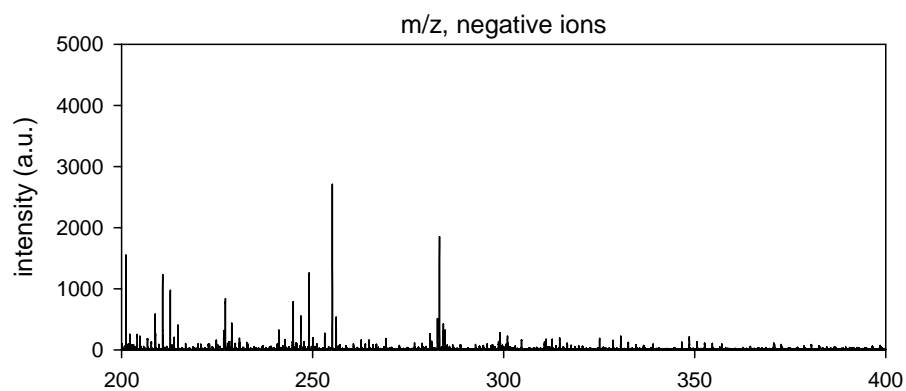
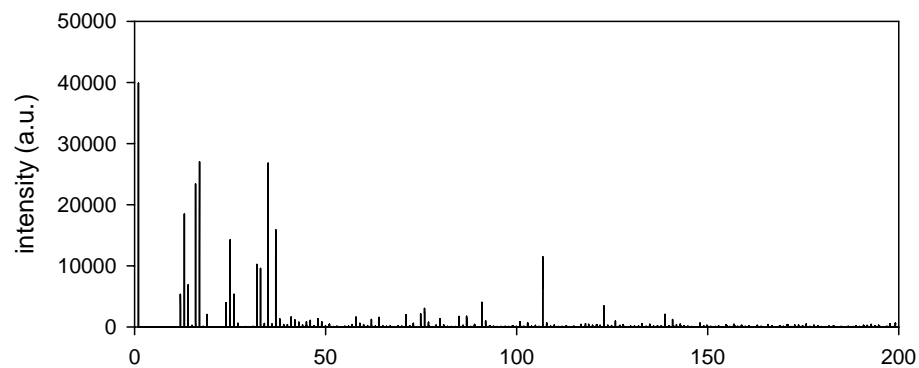
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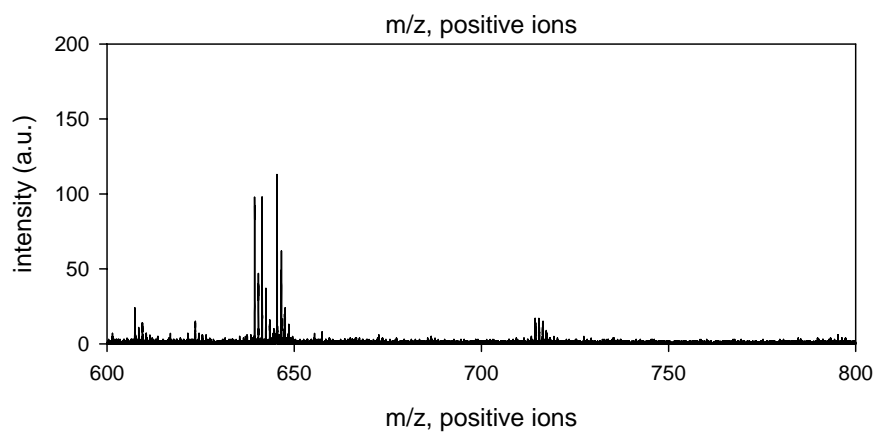
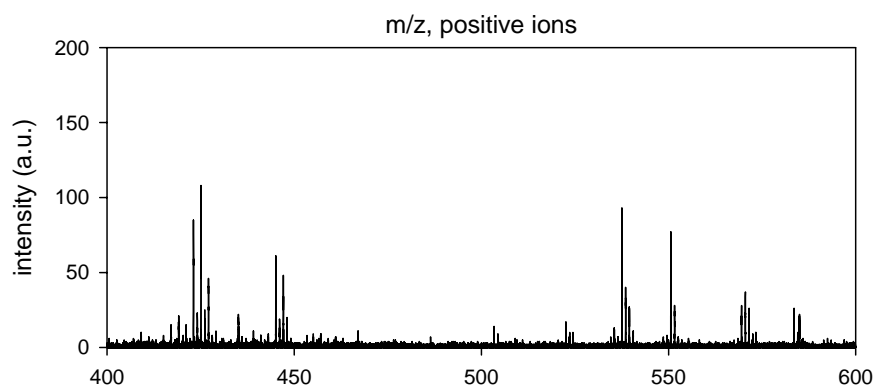
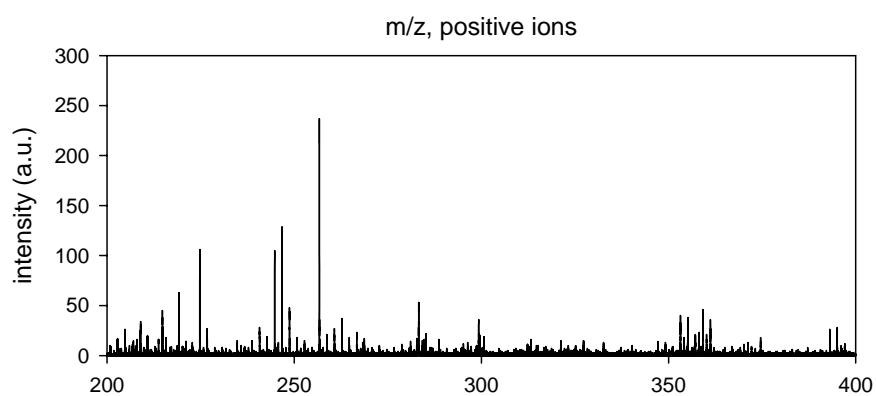
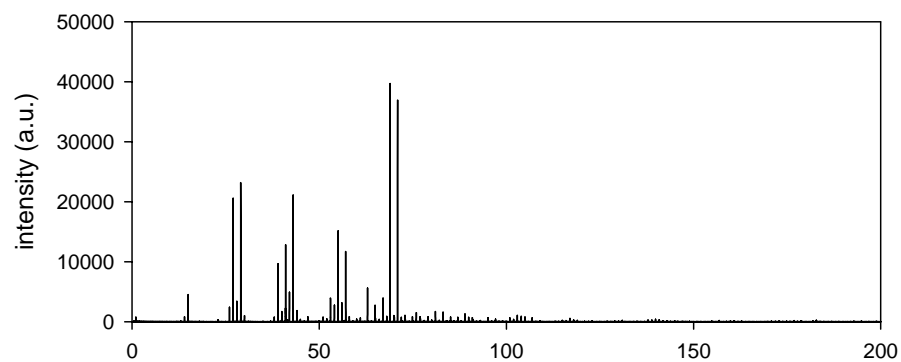
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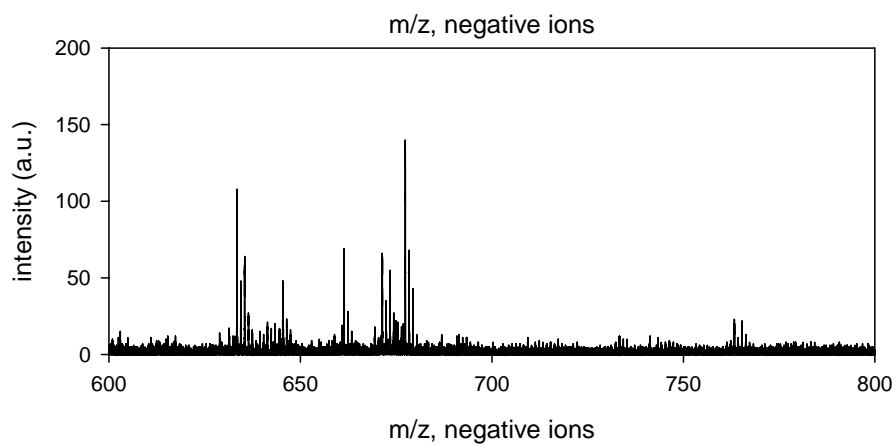
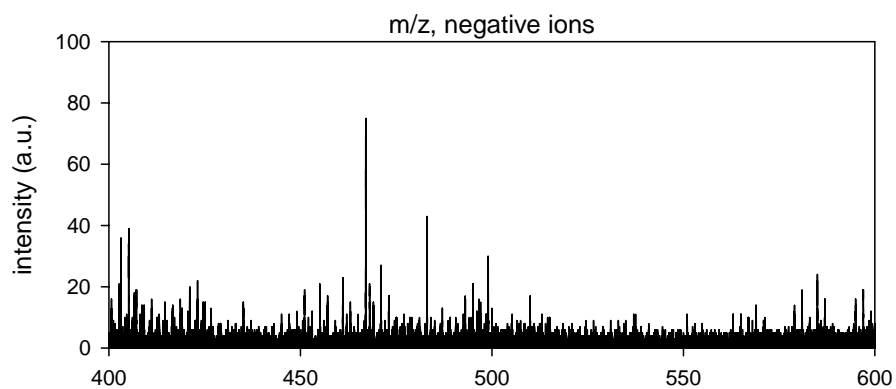
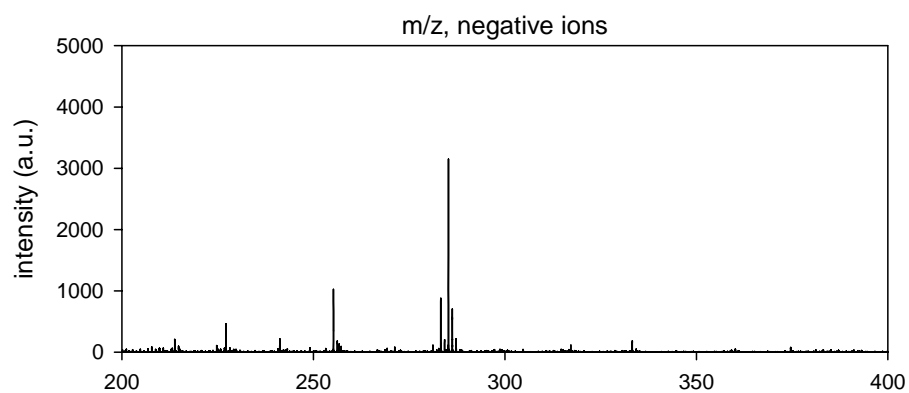
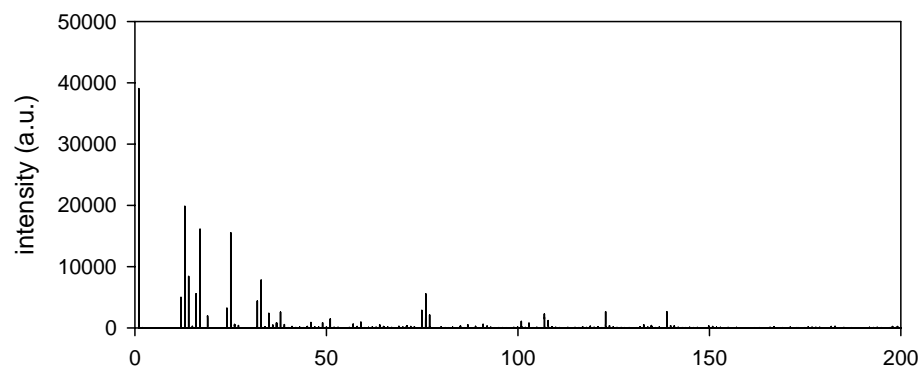
## 1. TOF-SIMs

### Positive Ion Mass Spectra of DDT: $m/z = 0 - 800$

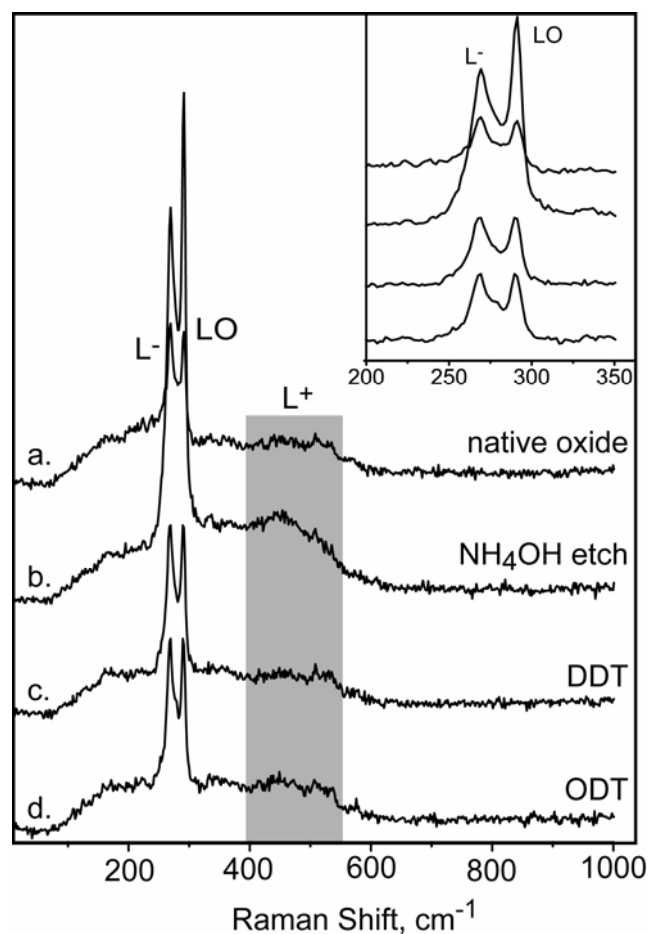


**Negative Ion Mass Spectra of DDT:  $m/z = 0 - 800$** 

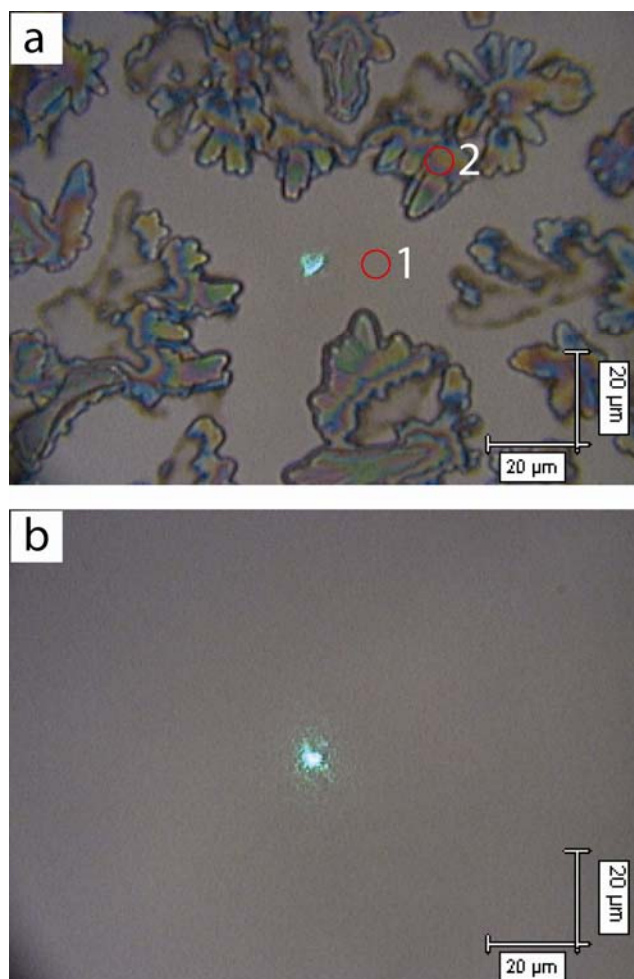
**Positive Ion Mass Spectra of ODT:  $m/z = 0 - 800$** 

**Negative Ion Mass Spectra of ODT:  $m/z = 0 - 800$** 

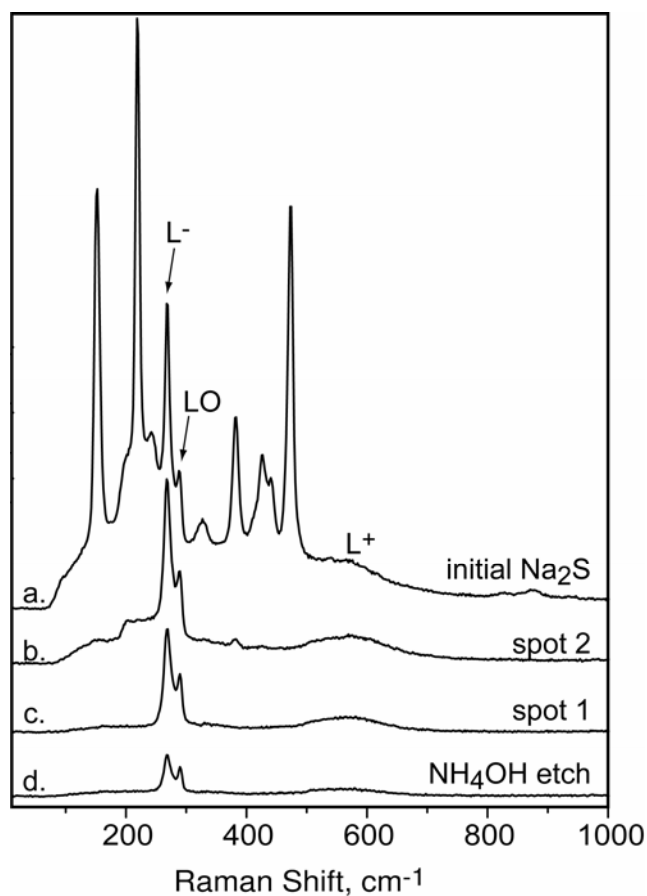
## 2. Raman Scattering



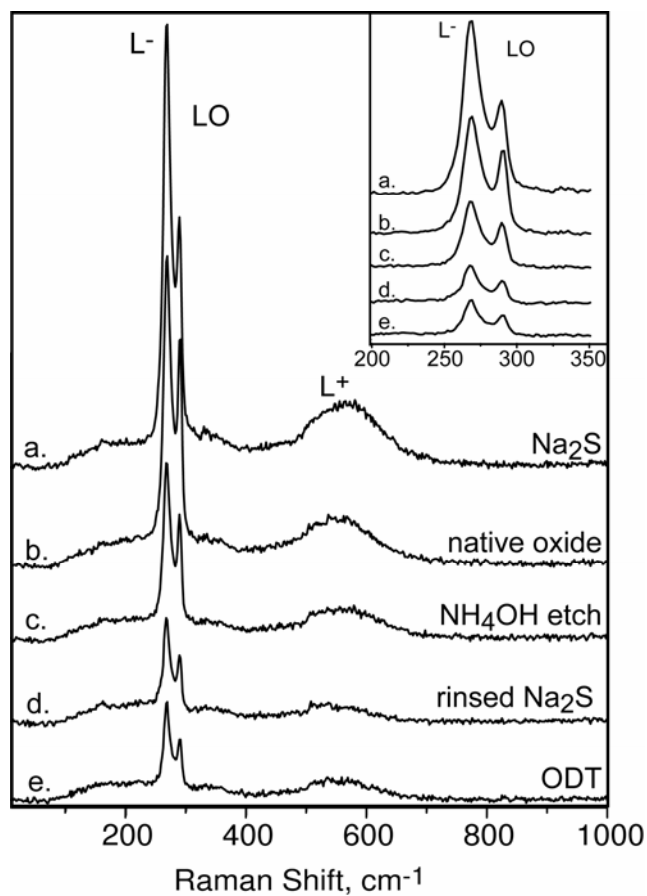
**Figure 1.** The Raman Spectra of a GaAs (100) wafer n+ doped at  $\sim 1.1 \times 10^{18} \text{cm}^{-3}$  shown for (a) the native oxide, (b) the  $\text{NH}_4\text{OH}$  etched surface, (c) the wafer functionalized with an **ODT** monolayer, and (d) the wafer functionalized with a **DDT** monolayer. Although overall intensities of the peaks changed under each treatment of the starting native oxide covered wafer, the ratio of the  $I_{LO}/I_{L^-}$  modes. Inset: Detailed spectra of the  $L^-$  and  $LO$  phonon modes.



**Figure 2.** Image captures from the Raman microscope of the GaAs surface functionalized with  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ . The position of  $\text{Ar}^+$  ion laser is seen as the green spot located in the center of both images. (a) Top. Surface inhomogeneities were observed on a surface freshly coated with 1M aqueous solution of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ . The two spots marked in the image were identified to have different Raman spectra. Spot 1 corresponds with scans in **Figure 3c** and **Figure 4a**. Spot 2 corresponds with **Figure 3b**. (b) Bottom. The surface inhomogeneities were removed upon rinsing with  $\text{H}_2\text{O}$  and ethanol. The resulting spectrum from this cleaned surface is shown in **Figure 4d**. This is also the typical visual appearance for an **ODT SAM** surface.



**Figure 3.** A comparison of the Raman spectra of a GaAs (100) wafer n+ doped at  $\sim 2.7 \times 10^{18} \text{ cm}^{-3}$  shown for (a) immediately, within 1-5 minutes after functionalization with  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ . The additional peaks seen in this spectrum gradually diminished after this time. (b) spot 2 – this spectrum is taken from one of the inhomogeneous regions observed after  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  functionalization and noted in **Figure 2**. (c) spot 1 – this spectrum is taken from one of the homogenous regions observed after  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  functionalization and noted in **Figure 2**. (d) the freshly etched  $\text{NH}_4\text{OH}$  surface. See text for details.



**Figure 4.** A comparison of the Raman spectra of a GaAs (001) wafer n+ doped at  $\sim 2.7 \times 10^{18} \text{ cm}^{-3}$  shown for (a) Spot 1 in **Figure 2** of a  $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$  functionalized wafer in comparison with the (b) native oxide, (c) the freshly etched  $\text{NH}_4\text{OH}$  surface, (d) the  $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$  functionalized wafer after rinsing with  $\text{H}_2\text{O}$  and ethanol, and (e) the **ODT** functionalized surface. See text for details.

**Table 1.** The changes in LO and L- phonon mode intensities as a function of surface treatment of the  $N_e$   
 $= 2.7 \times 10^{18} \text{ cm}^{-3}$   $n+$  GaAs (001)

$N_e, \text{ cm}^{-3}$	$I_{\text{LO}}/I_{\text{L}}$						
	native oxide	NH <sub>4</sub> OH etched	<b>ODT</b>	initial Na <sub>2</sub> S·9H <sub>2</sub> O <sup>a</sup>	Spot 1 <sup>b</sup>	Spot 2 <sup>c</sup>	rinsed Na <sub>2</sub> S·9H <sub>2</sub> O <sup>d</sup>
$2.7 \times 10^{18}$	0.76±0.00	0.74±0.02	0.74±0.03	0.16±0.02	0.61±0.06	0.57±0.02	0.75±0.03

<sup>a</sup>The  $I_{\text{LO}}/I_{\text{L}}$  ratio taken in the first 5 minutes after spin coating the GaAs wafer with Na<sub>2</sub>S·9H<sub>2</sub>O. <sup>b</sup>Spot 1 is noted in **Figure 2**. <sup>c</sup>Spot 2 is noted in **Figure 2**. <sup>d</sup>The  $I_{\text{LO}}/I_{\text{L}}$  taken from the spectra after rinsing with ethanol. See text for details.