

X-ray photoelectron spectroscopy study of self-assembled monolayers of alkanethiols on (001) GaAs

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Self-assembled monolayers of several alkanethiol molecules, with varying chain length and terminal groups, were investigated using x-ray photoelectron spectroscopy (XPS). The chain lengths varied from 10 to 15 methylene units, and the terminal group was either hydrophilic carboxylic acid and hydroxyl or hydrophobic methyl. The alkanethiol molecules were deposited on GaAs surfaces from liquid solutions. The impact of atmospheric exposure was examined by investigating one set of samples stored under atmospheric conditions and a second set that was stored in a nitrogen atmosphere prior to analysis. Carbon, oxygen, gallium, and arsenic core level XPS spectra were obtained on all surfaces. The intensity of the gallium and arsenic core levels indicates a considerable difference in the Ga/As ratio dependent on the terminal group of the alkanethiol. Additionally, the carbon and oxygen spectra indicate varying chemical bonding on the surface with the alkanethiol's having a carboxylic acid terminal group showing a more complex carbon and oxygen bonding. © 2006 American Vacuum Society. [DOI: 10.1116/1.2218850]

I. INTRODUCTION

Stabilization of the GaAs (001) surface has been an area of research due to the defect structure present. In most cases these studies were concerned with the stabilization of the surface for the modification of the Schottky barrier and improved performance of semiconductor devices. Through these investigations, a common thread has been the use of sulfur, in the form of a sulfuric acid etching followed by treatment in solution with sodium sulfide,¹⁻⁴ ammonium sulfide,³⁻⁸ organic alkanethiols,⁹⁻¹³ or through electrochemical deposition.¹⁴ All these studies have indicated a degree of stabilization but several authors have shown continued degradation of the surface after exposure to oxygen³ and air.⁷

In this article, we have implemented an x-ray photoelectron spectroscopy (XPS) technique to monitor the influence of alkanethiols deposited on (001) GaAs on the surface chemical stability of this material. We have established that self-assembled monolayers (SAMs) of hexadecanethiol (HDT: HS(CH₂)₁₅CH₃) on (001) GaAs provided the most efficient passivation among all the investigated alkanethiols.

II. EXPERIMENT

Deposition of various alkanethiols was carried out on *p*-type (001) GaAs wafers that were Zn doped with a concentration of 2×10^{17} at./cm³. Prior to the deposition, the wafers were cleaned in an ultrasonic bath sequentially with OptiClear, acetone, and isopropanol for 5 min each. Subsequently, they were etched for 1 min with concentrated HCl. After drying in nitrogen flow the wafer was immersed in a 5 mM alkanethiol solution in ethanol and 5% aqueous am-

monia for a period of 18 h at a temperature of 55 °C. The alkanethiols used in this study were 1-hexadecanethiol (HDT, HS(CH₂)₁₅CH₃), 1-undecanethiol (UDT, HS(CH₂)₁₀CH₃), 16-mercaptohexadecanoic acid (MHDA,

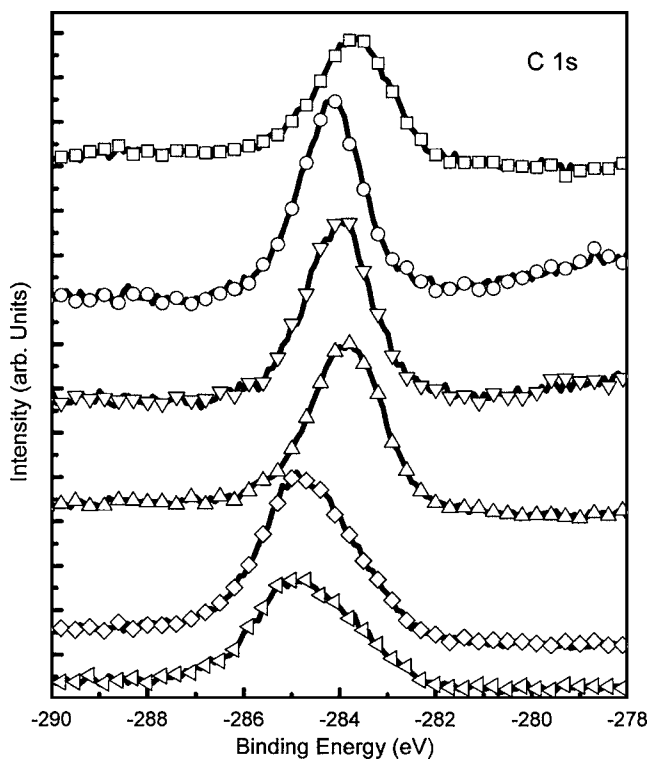


FIG. 1. XPS spectra of C 1s core level for all samples. Spectra have been offset vertically. The spectra are from samples treated with □-HCl etch, ○-HDT, ▽-UDT, △-MHDA, ◇-MUDA, and ◁-MUDO.

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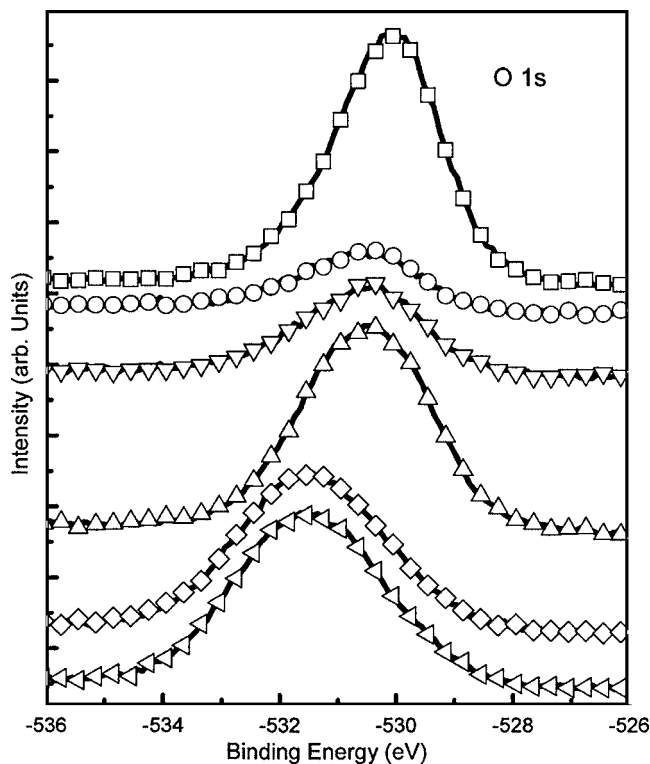


Fig. 2. XPS spectra of O 1s core level for all samples. Spectra have been offset vertically. The spectra are from samples treated with \square -HCl etch, \circ -HDT, ∇ -UDT, \triangle -MHDA, \diamond -MUDA, and \blacktriangleleft -MUDO.

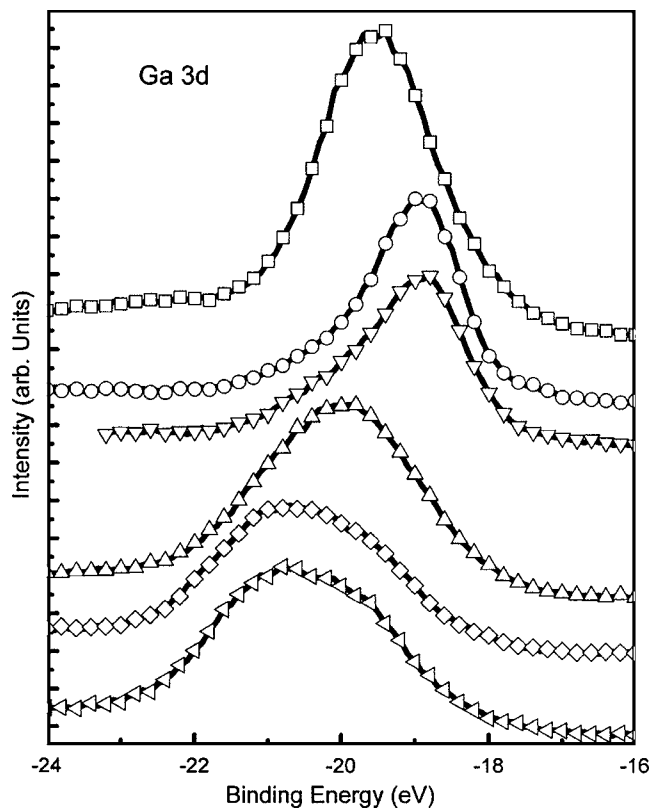


Fig. 3. XPS spectra of Ga 3d core level for all samples. Spectra have been offset vertically. The spectra are from samples treated with \square -HCl etch, \circ -HDT, ∇ -UDT, \triangle -MHDA, \diamond -MUDA, and \blacktriangleleft -MUDO.

HS(CH₂)₁₅CO₂H), 11-mercaptoundecanoic acid (MUDA, HS(CH₂)₁₀CO₂H), and 11-mercapto-1-undecanol (MUDO, HS(CH₂)₁₁OH). The HDT and UDT alkanethiols were terminated with the hydrophobic CH₃ group, while the MHDA, MUDA, and MUDO were terminated with the hydrophilic groups CO₂H and OH, respectively. The alkanethiols were purchased from Aldrich and used as received. After deposition of the alkanethiols, one set of samples was stored in an atmospheric environment, while a second set was kept in a nitrogen atmosphere. All photoelectron spectra were obtained with a Kratos Axis HS spectrometer equipped with both Mg K α and Al K α x-ray sources. Additionally, the system was equipped with a charge neutralizer to reduce the effect of sample charging. The base pressure of the spectrometer was 5×10^{-10} torr with an operating pressure of 1×10^{-9} torr. The energy resolution of the system with the Al K α source is 1.1 eV as measured from the full width at half maximum (FWHM) of Ag 3d core level spectrum.

III. RESULTS

All data presented in this study were obtained with Al K α radiation. Spectra were obtained from the O 1s, C 1s, As 2p and 3d, Ga 2p, Ga 3p, and Ga 3d core levels. The spectra obtained with the Mg K α x-ray source could not be used due to a strong overlap of the Ga LMM Auger peak with the S 2p and Ga 3s core levels.

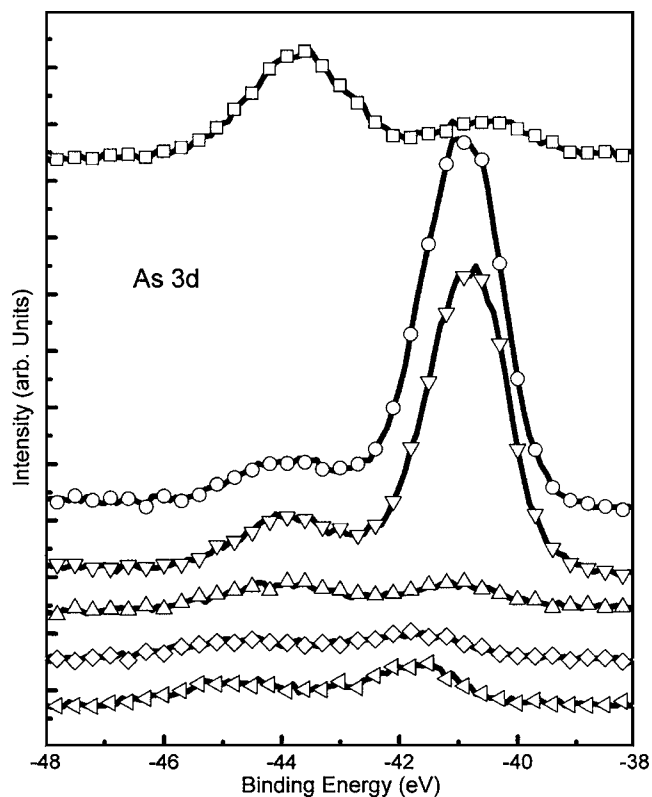


Fig. 4. XPS spectra of As 3d core level for all samples. Spectra have been offset vertically. The spectra are from samples treated with \square -HCl etch, \circ -HDT, ∇ -UDT, \triangle -MHDA, \diamond -MUDA, and \blacktriangleleft -MUDO.

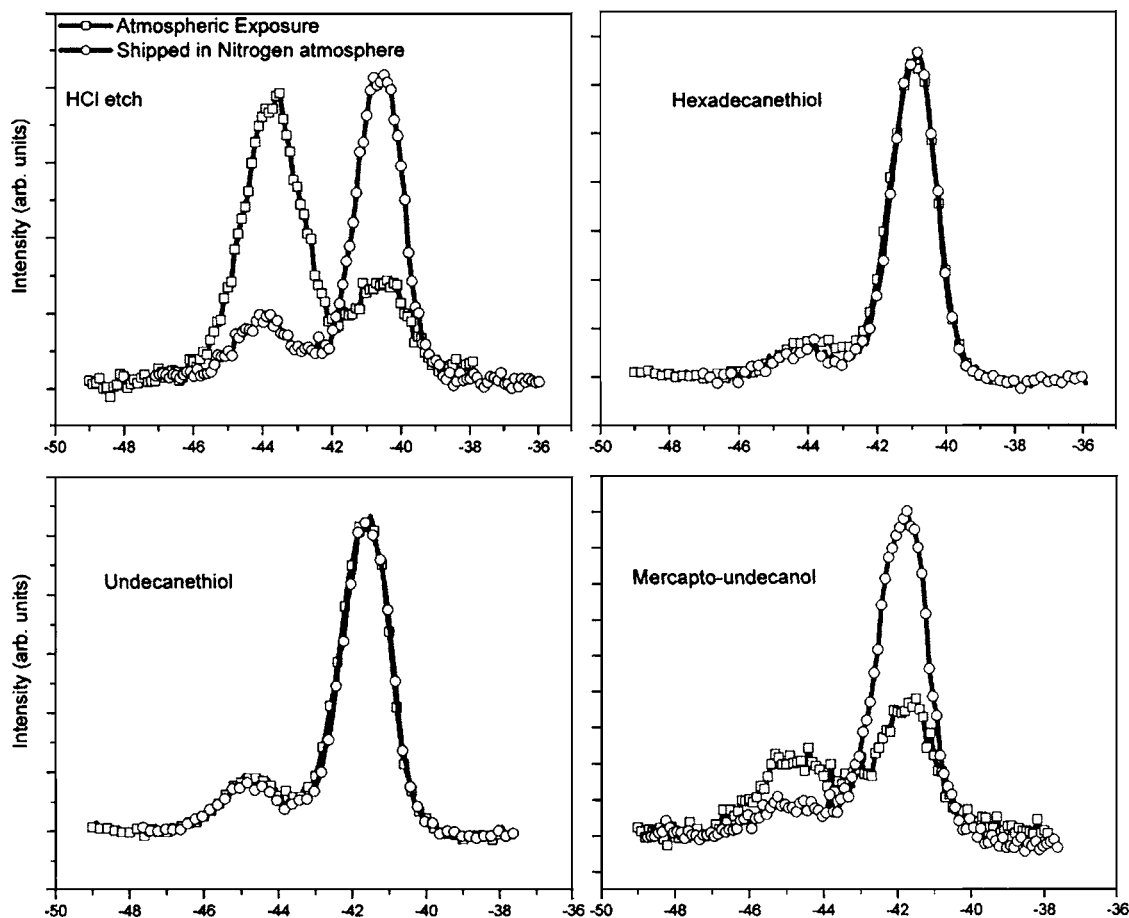


Fig. 5. XPS spectra of As 3d core level demonstrating the influence of atmospheric exposure for as etched surface and surfaces treated with HDT, UDT, and MUDO.

A. Carbon 1s

The carbon 1s core level spectra for all samples stored in an atmospheric environment are shown in Fig. 1. The spectra have been arbitrarily offset. The GaAs surface etched with HCl shows the major C 1s contribution at 283.8 eV that is due to adventitious carbon from atmospheric exposure. The surfaces that have been treated with HDT and UDT also show a single C 1s core level shifted slightly to higher binding energy and consistent with the presence of C–C bonds associated with the backbone of the alkanethiol. In contrast, the three samples treated with alkanethiols having hydrophilic end groups (MHDA, MUDA, and MUDO) show broader C 1s core levels with peak energies of 283.8, 284.9, and 284.9 eV for MHDA, MUDA, and MUDO, respectively. The broadening is due to the presence of C–O bonds on the surface due to surface contamination from atmospheric exposure. The finite resolution of 1.1 eV attributes to not resolving the various C states as well as the fact that a complex chemistry occurred on these samples from atmospheric exposure. It is not clear what C states are on the surface and with what concentration since these states are a mixture of the alkanethiol group as well as the hydrocarbon, CO, and CO₂ exposure. In addition to the changes in binding energy, the relative intensities show the minimum C on the etched

sample and the sample treated with MUDO. It is interesting to note that the highest C intensities appear on the two samples exposed to the hydrophobic alkanethiol chains (HDT and UDT).

B. Oxygen 1s

The oxygen core levels shown in Fig. 2 show a range in binding energies from –530.1 to –531.4 eV. The deepest binding energy is associated with the carboxylic acid group of the MHDA and MUDA alkanethiols. The relative oxygen intensity is the lowest for the two hydrophobic alkanethiols, HDT and UDT, indicating that SAMs of these two alkanethiol chains inhibit oxidation of the GaAs surface. If the only oxide formed on these surfaces were Ga oxide, the oxygen should appear at a fixed binding energy. The fact that the oxygen shows a range of binding energies indicates a complex oxygen chemistry.

C. Gallium

Although several gallium core level spectra were obtained, only the Ga 3d spectra are shown here in Fig. 3. The spectrum from the HCl etched surface shows a broad core level composed of two species: Ga associated with GaAs and

oxidized gallium. The two samples treated with alkanethiols having hydrophobic terminal groups show an asymmetric peak with a binding energy of -18.9 eV. The asymmetry is due to a small gallium oxide component on the surface of these samples, consistent with the minimal oxygen $1s$ intensity. The three GaAs samples treated with alkanethiols having hydrophilic terminal groups show a shift in the Ga $3d$ core to deeper binding energy and with at least two states present, neither of which is associated with GaAs.

D. Arsenic

The arsenic $3d$ spectra are shown in Fig. 4. Notice the dramatic decrease in the As intensity for the samples treated with the alkanethiols having hydrophilic terminal groups. The reduced arsenic intensity coupled with the large gallium intensity indicates a well-oxidized gallium surface that is rich in gallium. The samples with SAMs of HDT and UDT show an intense core level with a binding energy at -40.9 eV corresponding to arsenic bound to gallium in GaAs. The deeper binding energy feature corresponds to oxidized arsenic.

Figure 5 is a comparison of the arsenic $3d$ core level spectra for samples treated with different alkanethiols and shipped under exposure to the atmosphere and in a nitrogen environment. Figure 5(a) shows the comparison of a GaAs surface which has been etched in HCl. Notice the change in intensities of the As $3d$ core level associated with GaAs and that associated with oxidized arsenic. The nitrogen environment reduces the oxidation of the as etched surface. In addition, the Ga:As ratio is much closer to 1:1 for this sample as determined from the total measured core level intensity of the As and Ga $3d$. Figures 5(b) and 5(c) (the upper right corner and lower left corner) show GaAs surfaces treated with HDT and UDT, respectively, after HCl etch. The amount of oxide is not influenced by the exposure to atmosphere during shipment. The presence of the SAM associated with these two alkanethiols stabilizes the GaAs surface and protects it from extreme oxidation. Figure 5(d) (the lower right graph) shows a comparison of the GaAs surface treated with MUDO. The nitrogen environment has protected the surface of this sample and reduces the effect of oxidation. A much larger component of arsenic bound to gallium is observed in this sample.

IV. SUMMARY

The data presented here show the effective stabilization of the GaAs (001) surface through the use of 1-hexadecanethiol

and 1-undecanethiol, which have hydrophobic terminal groups. It is not clear, from the XPS results, whether the chain length has an impact on the stabilization, although the photoluminescence (PL) from similar samples shows a greater PL from samples treated with long chains.¹⁵ The three alkanethiols with hydrophilic terminal groups not only do not passivate the surface or protect it from oxidation but appear to produce surfaces that have a minimum arsenic within the surface region. Additional data should be obtained to determine whether the arsenic is removed from the surface or if the hydrophilic alkanethiol in connection with atmospheric exposure produces a surface energy in which the gallium preferentially diffuses to the surface leaving an arsenic rich layer below the surface.

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