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Adsorption and thermal stability of alkanethiol films on GaAs(110): A comparative study by TOF-DRS and TOF-SIMS

Luis M. Rodríguez [a], Lucila J. Cristina [a], Leonardo Salazar Alarcón [a], Bárbara Blum [b], Roberto C. Salvarezza [b], Luan Xi [c], Woon Ming Lau [c], Esteban A. Sánchez [a], J. Esteban Gayone [a], Oscar Grizzi [a,*]

[a] Centro Atómico Bariloche, CNEA, I. Balseiro, UNC & CONICET, Bustillo 9500, R8402AGP Bariloche, Argentina
[b] INIFTA, Depto. de Química, UNLP & CONICET, CC. 16-Suc. 4, BI904DPI La Plata, Argentina
[c] Surface Science Western, University of Western Ontario, London, Ontario, Canada N6A 5B7

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ABSTRACT

We present an ion beam study of the adsorption and the thermal stability of short alkanethiol molecules adsorbed on GaAs(110). Direct recoiling spectroscopy shows that the adsorption of ethanethiol and hexanethiol proceeds directly towards a dense standing up phase without passing through a stable phase of lying down molecules as is the case for Au(111). Measurements along specific azimuths suggest that both Ga and As rows are covered by the organic molecules. Short adsorption times from the vapor phase result in films having two desorption peaks near 300 and 500 K. On the other hand, leaving the sample in a thiol atmosphere for several hours produces more stable films, similar to those produced by immersion in the corresponding thiol-ethanol solution. TOF-SIMS results confirm the C–S scission mechanism during the thermal desorption.

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1. Introduction

The growth of thiol based films on compound semiconductors is a growing field motivated by their applications in optoelectronics [1]. In general, the high complexity of the surfaces of thin organic films makes characterization of their chemical, electronic and thermal properties a difficult task. The high sensitivity of these films to being damaged by the irradiation of the incident beam probes complicates the field even further. In this context, high sensitive techniques based on ion probes can provide information that is complementary (and sometimes unique) to that provided by electron spectroscopies and microscopies. In this work we study the adsorption and the thermal stability of alkanethiols (Cn: HSC_nH_{2n+1}) films grown on GaAs(110) by TOF-DRS[1] [2]. We compare the results to those from similar measurements performed on the better known Au(111) substrate. The thermal desorption is studied by TOF-DRS and by TOF-SIMS[2] [3]. A common advantage of these techniques is the low irradiation dose required to obtain the spectra, which normally results in negligible damage to the film. This work is the continuation of a previous one carried out for hexanethiol (C6) on GaAs(110) [4]. In that work we showed that C6 molecules can chemisorb on GaAs(110) from the vapor phase, completely covering the surface. The shape of the H and C direct recoil (DR) peaks was very similar to that corresponding to the same molecule adsorbed on Au in the dense (selfassembled) layer, suggesting that in the case of GaAs the C6 molecules go directly to a similar dense packaging without passing trough the lying down (striped) phase that is characteristic of Au [5,6]. In contrast to Au, annealing the film produced a double-peaked desorption curve, showing a first desorption process slightly above room temperature, and a second one near 500 K.

Some questions that remained opened in that work are addressed here: TOF-DRS can only detect atomic elements, therefore no information about the molecular composition at the surface, and their dependence with temperature could be obtained. TOF-DRS detects the elements present at the top most layer; S, being closer to the interface could not be detected neither during the adsorption process nor during the first steps of desorption. TOF-SIMS has a higher sensitivity than TOF-DRS, a higher mass range and more molecular sub-products can be detected in the sputtering process, which allows us to discuss some of these topics in more detail. On the other hand, TOF-DRS can detect both neutral and ionic particles, making measurements independent of the local variations of the surface electronic structure. Here, we illustrate the complementary character of both techniques, and provide a comparison for films grown on Au and on GaAs, from both the vapor phase and from solution. For the case of GaAs we show that by cleaving a (100) wafer directly in the ethanol solution containing the thiol molecules a clean and passivated Cn/GaAs(110) surface can be obtained without going through complicated (in air)

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* Corresponding author.
E-mail address: grizzi@cab.cnea.gov.ar (O. Grizzi).

[1] Direct Recoiling Spectroscopy with Time of Flight analysis.

[2] Secondary Ion Mass Spectrometry with Time of Flight analysis.

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cleaning procedures. Other topics such as the effect of surface roughness on the adsorption kinetics and the changes in the thermal stability of the film observed after leaving the GaAs surface in a thiol atmosphere for several hours are discussed.

2. Experimental details

The experimental work was carried out in two laboratories: the Surface Science Laboratory of Centro Atómico Bariloche (CAB), Argentina, and the Surface Science Western (SSW) of the University of Western Ontario, Canada. The TOF-DRS measurements were performed at CAB and the TOF-SIMS at SSW. In the first case, the set up consists on a 1–100 keV ion accelerator connected to an UHV chamber with facilities for forward and backward ion scattering with TOF analysis. The ions are mass selected by a switching magnet, collimated through several apertures to 0.1 deg, and finally pulsed to ∼50 nsec, 30 kHz. The scattered and recoiled ions plus neutrals are detected by a channeltron electron multiplier after traversing a 109 cm collimated drift tube at a fixed scattering angle ($\delta = 45^\circ$). Different GaAs(110) surfaces were prepared, depending on the purpose of the measurement. One of the samples consisted on a disk of 8 mm diameter, 2 mm thick, p type, cleaned by many cycles of grazing sputtering with 20 keV Ar^+ ions and annealing to 720 K. During sputtering the polar incidence angle θ is set to within 2–3 degree (with respect to the surface plane) and the azimuthal angle φ rotated continuously within a 70 degree range (see the inset of Fig. 2b for the angle definition). This method is useful to smooth out the surface and generates a flat and well ordered GaAs(110) sample [7]. The clean GaAs(110) samples were then exposed *in situ* to the vapors of alkanethiols at pressures in the range of 1×10^{-9}–1×10^{-4} Torr. The pure thiols (Aldrich, 98% purity) were contained in a glass tube connected to a leak valve with stainless steel (SS) tubes. A 6 mm diameter SS tube ran from the leak valve to 3 cm from the sample. Prior to exposure, the thiols were further purified by freeze–pump-thaw cycles. The thiol pressures were not corrected for the ion gauge sensitivity and do not take into account any enhancement due to the adsorption geometry, therefore, the reported dose values are not absolute values and should only be used to compare different adsorption curves since all of them have been done under the same conditions. The base pressure during the measurements remained below 1×10^{-9} Torr. To check the effect of surface roughness, adsorption measurements were also carried out on rougher samples, i.e., on samples sputtered at slightly higher polar incident angles (around 5–6 deg, with all polar angles referred to surface plane). The cleaning–smoothing method is effective and allows studying of the first adsorption stages in well reproducible samples, but requires preparation times that can extend for a week or more. For some adsorptions where full coverage was desired without going through intermediate adsorption steps we used fresh and new GaAs(110) samples prepared by cycles of low energy (600 eV), high angle (45 deg) sputtering, combined with annealing. No significant differences were detected in the thermal desorption measurements between the two preparation methods. For comparison, some TOF-DRS measurements were taken on an Au(111) single crystal obtained from MATEK. In this case the sample was a 6 mm disk cleaned by sputtering and annealing and the exposures were carried on *in situ*, under vacuum, as described above for the GaAs(110) single crystals.

TOF-SIMS measurements were performed on both GaAs and Au samples with a reflectron-type TOF-SIMS instrument (ION-TOF TOF-SIMS IV) operating at an incident angle of 45°. In order to minimize damage the primary analysis beam was a pulsed 8 keV Ar^+ [8]. The temperature dependent experiment is carried out by mounting the sample on a heating stage which is resistively heated *in situ* at a temperature ramp of about 5.5° C/min. A time profile of the species of interest in negative mode is recorded at every step. In this case, the thiol layers on the Au samples were prepared from solution on substrates of Au evaporated on mica, purchased from the Molecular Imaging Corporation. To remove the contamination and improve the surface ordering we treated the Au surfaces by hydrogen flame annealing. After annealing, the atomic terraces of the Au (111) substrates typically evolve into a triangular shape with straight steps. Each terrace has the well-known $\sqrt{3} \times 23$ herringbone structure as observed by Scanning Tunneling Microscope. The Au(111) substrates are then immersed in 5 mM C6 ethanolic solution for 3 days and rinsed with plenty of ethanol to remove weakly adsorbed molecules before introducing to the TOF-SIMS analysis chamber immediately. In the case of GaAs, we cleaved a slice of fresh GaAs(001) substrate in 5 mM C6 ethanolic solution, so that a clean (110) surface is exposed to the thiols and the formation of native oxide is avoided. The GaAs was left in the solution for 4 days and gently rinsed by ethanol and introduced to the TOF-SIMS chamber immediately to study the cross sectioned surface. Investigation of the other half of the cross sectioned surface by XPS revealed that the Fermi level position is ∼0.1 eV, indicating that the sample is close to having a flat band condition. This shows that the surface passivation is effective and there is a lack of band gap states induced by the thiol adsorption.

3. Results and discussion

3.1. Adsorption followed by TOF-DRS

The GaAs(110) surface is an open surface presenting a strong relaxation in which the top As atoms move up by ∼0.2 Å and the Ga ones move ∼0.5 Å down from the ideal bulk termination. The surface relaxation is accompanied by rehybridization of the dangling-bonds, with a charge transfer from the top Ga atoms to the top As atoms [9]. The fact that the interatomic distances are large and that the Ga and As masses are similar and makes the GaAs(110) surface particularly interesting for TOF-DRS studies [10]. A typical spectrum for the clean surface acquired with 4.2 keV Ar^+ ions along the [001] direction and at 20° polar incidence is shown in Fig. 1a. At this relatively large incident angle there are no shadowing effects for top layer atoms. The dominant peak corresponds to Ar scattering from both Ga and As surface atoms. The technique allows detection of both Ga and As recoils, which at 45° of scattering angle appear to the right side of the Ar peak. No peaks are observed due to contaminants (H, C, O) at the left side of the Ar peak.

Due to the surface relaxation the Ga recoils are observed along few azimuthal directions, in most directions they are shadowed by the As atoms that are lying in a plane that is slightly above (∼0.7 Å) the Ga plane. The [001] direction is particularly useful because both As and Ga rows are equally exposed to the beam (inset of Fig. 1 a). When the As direct recoil (DR) intensity is recorded as a function of the azimuthal angle, keeping the polar incidence fixed at some low angle (9° in this case) there are strong changes that reflect the surface atomic structure (Fig. 1 b).

Upon exposure of the clean surface to the vapors of the thiol strong changes appear in the spectra. First, two new structures due to H and C DRs are observed at the left side of the Ar peak. The latter becomes attenuated, broadened and shifted towards lower TOFs due to Ar multiple scattering on both the atoms of the adsorbed molecule and the substrate atoms (Fig. 1a). S atoms are not detected due to shadowing from the above hydrocarbon chains. The example spectra shown in Fig. 1a center and bottom correspond to two different thiols: C2 and C6, respectively. The center one is recorded before saturation while the bottom one

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