Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface Science 600 (2006) 2305–2316

SURFACE SCIENCE

www.elsevier.com/locate/susc

Adsorption of short-chain alkanethiols on Ag(1 1 1) studied by direct recoiling spectroscopy

L.M. Rodríguez [a], J.E. Gayone [a,*], E.A. Sánchez [a], H. Ascolani [a], O. Grizzi [a], M. Sánchez [b], B. Blum [c], G. Benitez [c], R.C. Salvarezza [c]

[a] *Centro Atómico Bariloche, CNEA, Instituto Balseiro, UNC, CONICET, Bustillo 9500, 8400 S.C. de Bariloche, Río Negro, Argentina*
[b] *Planta Piloto de Ing. Química, Camino La Carringada km 7, Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina*
[c] *INIFTA, Departamento de Química, Universidad Nacional de La Plata y CONICET, C.C. 16, Suc. 4, B1904DPI La Plata, Buenos Aires, Argentina*

Received 27 December 2005; accepted for publication 21 March 2006
Available online 18 April 2006

Abstract

We use direct recoiling spectroscopy with time-of-flight analysis to study the adsorption of propanethiol on Ag(1 1 1) cleaned and polished in vacuum by cycles of grazing ion bombardment and annealing. We discuss the advantages and drawbacks of the technique to follow the growth of the organic film. In particular, the low damage imparted by the technique allows to follow in detail the evolution of the H, C and substrate recoiling peaks for a wide range of exposures ranging from 10^{-1} to 2×10^4 L. The shape of the TOF spectra and the evolution of the recoiling intensities are consistent with a *growth process in three stages*: an initial fast one related to the density of defects at the surface, a second one where the surface is covered with a thin layer of organic molecules, presumably associated with lying-down molecules, and a final stage corresponding to a thicker layer that can be associated with a standing-up orientation of the molecules in the film. Annealing of the organic film to 250 °C produces complete depletion of C and H, leaving a small amount of S. The final S coverage after annealing depends on the initial roughness, being higher for rougher surfaces. We also observe an increase in the surface roughness after desorption of the thiol layer. Re-adsorption on this post annealed surface presents a marked enhancement of the initial sticking.

Keywords: Ion scattering spectroscopy; Adsorption kinetics; Self-assembly; Sticking; Surface roughness; Silver; Alkanethiols; Solid–gas interfaces

---

1. Introduction

The study of sulphur-based organic molecule adsorption at surfaces, with traditional surface science techniques in UHV, has received considerable attention during the past 15 years, partly because of the foreseen applications [1,2], and also because its basic comprehension represents a challenge for a number of reasons: (1) the usually large number of atoms involved with each molecule, (2) the extremely delicate balance of forces (between substrate atoms and head-groups, and amongst the ad-molecules) that govern the transient and final equilibrium structures, (3) the large number of paths that the organic molecules can undergo upon impinging on the surface such as precursor states, physical and chemical adsorption, dissociation, self-assembly, (4) possible rearrangement of the substrate atoms and changes in topography [3,4] and (5) further modifications of the organic films arising from the high sensitivity of organic molecules to electron and ion irradiation, either from the source or from secondary processes [5–9].

For the past 20 years, and following the pioneering work of Nuzzo and Allara [10], a large amount of experimental and theoretical work has been devoted to the study

---

[*] Corresponding author.
E-mail address: gayone@cab.cnea.gov.ar (J.E. Gayone).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.03.024

of *n*-alkanethiols (HSC_nH_{2n+1}, hereafter C_n) on metals, particularly on Au, Ag and Cu, stemming from their stability and ease of preparation. Many studies have addressed their saturation coverage equilibrium structures, i.e., the denser and more stable phases obtained either by immersion of the samples in alkanethiol-containing solutions, or by exposing the cleaned surfaces to the vapours of pure alkanethiols in vacuum [1,2,11–18]. The kinetics of adsorption of the different phases formed on Au during exposure in vacuum has been delineated [4,11,19,20] by applying a combination of STM, thermal desorption, atom scattering, diffraction techniques, and electron spectroscopies. On Ag, the number of works describing the alkanethiol adsorption kinetics [21–24] is far less than on Au, and a full picture, starting from very low coverages, lags far behind. The case of adsorption of short-chain molecules on Au and Ag from the vapour phase has received particular attention very recently. For this case, part of the interest is based on the fact that electrical conductivity through the films increases with the shortening of the alkyl chain. Another interesting aspect is that, even on Au, the self-assembly process of short alkanethiols can be incomplete [25]. Experiments at low temperatures [26,27] show that short-chain molecules do not dissociate their H–S bonding, except for adsorption at defects, and desorb well below room temperature. Theoretical results support these findings of non-dissociative adsorption on atop sites [27]. We have shown recently [28] that for sufficiently high exposures it is possible to form a propanethiol layer on a clean and smooth Ag(111) surface from the vapour phase at room temperature, and that more than one phase is detected before reaching the saturation-coverage phase. In the present work we extend these results and discuss the pros and cons of direct recoil (DR) spectroscopy with time of flight analysis (TOF–DRS) [29,30] to study the adsorption kinetics of alkanethiols on Ag(111) surfaces. To our knowledge, this technique has been applied previously to just a few cases [28,31,32], while ion scattering spectroscopy (ISS), where only the ions are detected, has been used more often [33–35]. Here, we follow the H, C, and substrate DR intensities as a function of alkanethiol exposure. We discuss the products remaining at the surface after annealing these films at 250 °C, the effect of surface roughness on the adsorption kinetics, and the changes observed for exposures performed immediately after an adsorption/desorption cycle, without cleaning in between.

2. Experimental details

The TOF–DRS measurements were performed in a UHV chamber connected to an ion accelerator working from 1 to 100 keV [36]. The base pressure of the chamber was $2–3 \times 10^{-10}$ Torr when the ion beam line was open. The ions were generated in a radio frequency source, accelerated, and then mass selected and collimated to 0.1° of angular divergence. Most of the spectra were acquired by time of flight (TOF) methods with 4.2 keV Ar^+ pulsed ion beams (frequency 30 kHz, time resolution better than 50 ns); some spectra were acquired with Ne^+ and Kr^+ projectiles. The detection of both ion and neutral forward recoils was performed at a scattering angle $\delta = 45°$ with a channeltron located after a flight path of 96 cm. A deflector plate and grids located in front of the channeltron allows ion-fraction measurements [37]. Typical current densities in the continuous beam were 1 nA/mm^2, which were then reduced by three orders of magnitude during pulsing. The number of spectra required to follow a full adsorption process was between 10 and 30, amounting to a maximum total bombarding dose in the range of 10^{12} incident ions per cm^2. The damage generated by this total dose is typically not detectable [32].

The sample was an 8 mm in diameter and 1 mm thick Ag(111) single crystal (brand new from MaTecK GmbH, 99.99% purity, initial surface roughness < 0.03 μm, orientation accuracy < 0.5°). The sample was mounted on a manipulator allowing continuous variation of the projectile incident and azimuthal angles, and cooling and heating of the sample. The sample temperature was monitored by a chromel–alumel thermocouple mechanically attached to the sample surface, and controlled to within 1 °C. Cleaning and polishing of the sample were carried on by cycles of grazing sputtering and annealing [38], consisting on 20 keV Ar^+ bombardment at 2° or 3° from the surface plane (for 30–40 min, with current densities around 30 nA/mm^2 and continuous rotation of the sample azimuthal angle), followed by annealing at 500 °C for several minutes. This procedure was very effective to smooth out the initial surface roughness and the roughness generated at each thiol adsorption/desorption cycle. For comparison purposes, some measurements were performed on another Ag(111) single crystal that showed a higher initial roughness. This crystal was mechanically polished with alumina grit down to 0.05 μm, followed by a mechanical–chemical polish with aqueous $0.14\%H_2O_2 + 0.02\%NH_3$. Final cleaning of this crystal was performed in vacuum by sputtering and annealing.

Most of the shown spectra correspond to samples prepared by dosing with propanethiol (99% purity, Aldrich Chemical Company) of the surface sputter-cleaned and polished in UHV. The thiols were contained in a glass reservoir fixed to the vacuum chamber through a leak valve, and before each exposure the thiols were purified through freezing–pump–thaw cycles. The reported pressures are corrected by the gauge sensitivity, which for propanethiol should be around 3.7 [11]. For comparison purposes, some films were prepared with C6 and C12, either by exposure in vacuum to the pure thiols, or by immersion of the Ag(111) samples in 2 mM ethanolic solutions, with typical immersion times varied between 5 h and 20 h. Some AES spectra were acquired in separate chambers with a 3 keV electron beam, with some spectra taken in the pulse counting mode to minimize beam damage, and some in the derivative mode at different sample regions.