Surface Science 604 (2010) 165–170

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

A scanning tunnelling microscopy investigation of gold island formation from an octanethiol self-assembled monolayer on Au(1 1 1)

Richard Taylor, Nicholas Torr, Zhao Huang, Fangsen Li, Quanmin Guo *

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

ARTICLE INFO

Article history:
Received 17 September 2009
Accepted for publication 30 October 2009
Available online 13 November 2009

Keywords:
Self-assembled monolayer
Scanning tunnelling microscopy
Gold
Nucleation and growth
SAMs
STM
Self-assembly
Surface diffusion

ABSTRACT

The release of gold atoms from an octanethiol monolayer on Au(1 1 1) and the subsequent formation of single-layer-high gold islands have been investigated using a scanning tunnelling microscope (STM) in air. When the bias voltage between the STM tip and the sample is above the threshold for water electrolysis, reactive desorption of the thiol molecules takes place leading to the release of gold adatoms. The number of released atoms has been evaluated as a function of exposure to the tip current under both positive and negative bias voltages. Tip-induced ripening of the gold islands, and more interestingly, tip-induced disintegration of small islands are observed.

1. Introduction

Self-assembled monolayers (SAMs), products of self-driven formation of regularly orientated molecules on solid surfaces, have been the subject of numerous studies [1,2] due to their potential applications in molecular electronics, nanopatterning, surface modification and corrosion inhibition [3,4]. The alkanethiol SAMs on Au(1 1 1), in particular, has been the focus of many studies as a model self-assembled system for more than two decades [3–7], and there has been renewed interest during the last few years due to the discovery of adatoms of gold within the SAM [8,9]. Whilst it is now generally agreed that the incorporation of Au adatoms, retrieved from the Au bulk, are involved in the binding of the thiol molecule to the Au(1 1 1) surface, the exact structure of the Au–S bond is still not resolved. Gold dithiloate bonding schemes have been proposed [8] based on density functional theory (DFT) calculations, and normal incidence X-ray standing wave analysis (NIXSW) has yielded evidence for a monothiolate bonding scheme leading to a proposed 0.33 ML coverage of gold-thiolate [9], in close agreement with more recent measurements [10].

It is known that when performing STM in ambient conditions a water film exists between the scanning tip and the surface [11]. The subsequent products of water electrolysis under a suitable bias are able to break the Au–S bond of an adsorbed gold-thiolate, causing the detachment of the adsorbed molecule and the simultaneous release of the gold adatom [10] according to the following scheme:

$$H_2O \rightarrow OH^- + H^+ \qquad (1)$$

$$H^+ + H_2O \rightarrow (H_3O)^+ \qquad (2)$$

If the sample is positively biased, OH^- will drift to the SAM/Au interface, where the following reaction can take place:

$$OH^- - e \rightarrow 1/2O_2 + H \qquad (3)$$

$$H + AuSR \rightarrow Au + HSR \qquad (4)$$

If the sample is negatively biased, the following reaction can proceed:

$$(H_3O)^+ + e + AuSR \rightarrow H_2O + Au + HSR \qquad (5)$$

The gold atoms released in step (4) or (5) are expected to combine in a standard nucleation and growth process, such as that demonstrated when the SAM is bombarded by atomic hydrogen [12]. Whilst the gold islands can be located quite easily with the STM, the destination of HSR from the above reactions is not that clear. Due to the existence of the water film, HSR molecules can be trapped in between the water film and the substrate. Experimental evidence will be presented to highlight the role of re-adsorption of HSR to the fate of the gold islands.

The removal of the thiol molecules from the Au(1 1 1) substrate using the method based on STM induced electrolysis is a

---

* Corresponding author. Tel.: +44 121 414 4657; fax: +44 121 414 7327.
E-mail address: Q.Guo@bham.ac.uk (Q. Guo).

0039-6028/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2009.10.034

complicated process. This is because the removed molecules may stay at the SAM/water interface and may even re-adsorb. Since re-adsorption is more than likely to consume gold atoms from the gold islands created by desorption, this makes accurate quantification of the number of released gold atoms from the SAM rather difficult. Our recent study [10] and that of Kandel et al. [12] have identified gold atoms released during the removal of the adsorbed SAM. By measuring the total amount of gold released, it was hoped to provide the much-needed direct experimental evidence to evaluate the correctness of recent structural models. Our initial findings [10] are largely consistent with the monothiolate model [9] although the amount of gold found in our experiment is still someway below the expected value of 0.33 ML. Several reasons, including the incorporation of gold atoms into step edges, were proposed [10] to be responsible for an under estimation of the amount of gold released from the SAM. So far, the mechanism of gold atom release from SAM desorption is very well understood, but accurate quantitative analysis of the relation between the molecular coverage and the number of gold atoms released is still prohibited due to various uncertainties in the experiments. Here we report findings from a systematic study, which follows our earlier investigation [10], about the gold island formation and evolution under various conditions. The new findings give a deeper insight into the stability of the gold islands and suggest the possible role of molecular re-adsorption.

2. Experimental

Gold of 99.99% purity was evaporated in a BOC Edwards Auto 306 system (BOC Edwards, UK) under a 1×10^{-6} mbar vacuum directly onto a freshly cleaved mica substrate held at 630 K as measured by a thermocouple. The thickness of the deposited film was determined to be 300 nm as read from a quartz crystal microbalance. The sample was then removed form the evaporator and submerged in a 1 mM octanethiol–ethanol solution in which the octanethiol (purity 98.5%) was purchased from Sigma–Aldrich without further purification, and left for 24 h at room temperature to ensure the formation of a complete octanethiol monolayer. Upon removal of the sample from the solution, it was rinsed with pure ethanol (purity 99.9%) to remove excess physisorbed molecules and then dried using nitrogen gas. The sample was then annealed in vacuum for 30 min at 350 K to remove etch pits and ensure large atomically flat terraces.

The SAM/Au surface was imaged using a benchtop DI Nanoscope 3000 STM (Veeco, Santa Barbara, CA) with a mechanically cut Pt/Ir tip. Imaging was conducted using constant current mode with a tunnelling current $I = 40$ pA and bias voltage $V = -0.8$ V as they are known as the "safe imaging parameters" which do not alter the SAM monolayer [10]. To induce the desorption of the octanethiol SAM in a step wise manner a bias of +1.5 V and 40 pA was applied to an area of 10 nm × 10 nm, located in the centre of each terrace, for a total of 5 s. It was found that such parameters induce localised desorption within a ~100 nm × 100 nm region surrounding the initial 10 nm × 10 nm area. The released Au adatoms subsequently nucleate and grow into islands of various sizes. In the case of surface modification with negative bias voltages, −2.0 V was applied at 40 pA current.

To examine the influence of the scanning Pt/Ir tip on island formation and growth, an atomically flat 200 nm × 200 nm area was selected and desorption of the octanethiol monolayer was

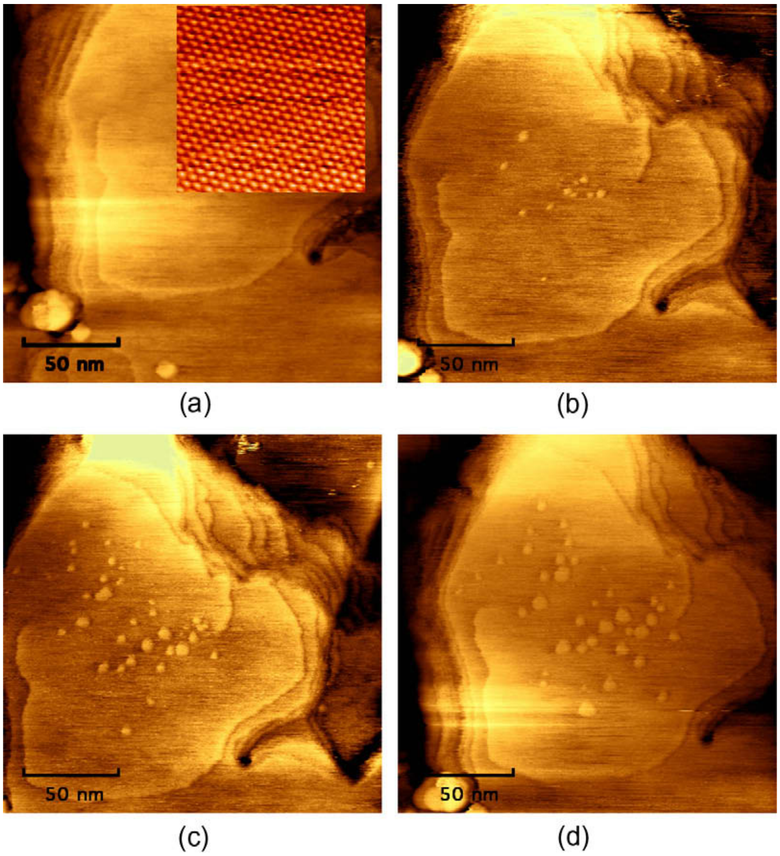

Fig. 1. STM images showing the creation of single layer gold islands due to partial desorption of the thiol molecules: (a) the initial surface; inset shows a molecularly resolved image (10 nm × 10 nm) of the $\sqrt{3} \times \sqrt{3}R30^{\circ}$ structure of the SAM; (b) the same region of the sample after the central part was modified by a 5-s exposure to +1.5 V; (c) and (d) images taken after further exposures to +1.5 V for 5 s and 15 (3 × 5 s) s, respectively. All images were taken with −0.8 V and 40 pA.