

Noble metal surface degradation induced by organothiols

Wester de Poel^a, Anouk Gasseling^a, Peter Mulder^a, Antoon P.G. Steeghs^b, Johannes A.A.W. Elemans^a, Willem J.P. van Enckevort^a, Alan E. Rowan^a, Elias Vlieg^{a,*}

^a Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, Nijmegen 6525AJ, The Netherlands

^b ASV Venlo, Laurentiusstraat 90, 5921GM Venlo, The Netherlands

ARTICLE INFO

Keywords:

Surface degradation
Noble metal
Organothiols

ABSTRACT

Copper, silver and gold layers evaporated on the muscovite mica (001) surface were exposed to a series of molecules containing an organothiol and/or a carboxylic acid chemical functional group to investigate the potential of these compounds to modify the surfaces. The surfaces were investigated using optical microscopy, atomic force microscopy, scanning electron microscopy, energy dispersive analysis of X-rays, and X-ray diffraction. Organothiols containing a carboxylic acid group were found to change the surface morphology drastically over a period of days, while molecules containing only one of these functional groups were usually not able to do so. The mechanism is most likely a reaction between the organothiol and the metal surface, forming a thermodynamically stable new compound. This finding could be of importance in the many applications where organothiols are used to functionalize noble metal surfaces.

1. Introduction

Organothiol self-assembled monolayers (SAMs) on solid gold substrates have been of great scientific interest since their discovery by Nuzzo and Allara in 1983 [1]. Since then, it has been shown that silver and copper surfaces are equally suitable for the formation of SAMs of organothiols [2,3]. Molecules containing a carboxylic acid functional group have also been reported to form stable monolayers onto the copper (110) surface [4,5]. A problem with the organothiol-noble metal combination is the reported ability of organothiols to etch the noble metals [6–8]. But to the best of our knowledge it has not yet been investigated to what extent organothiols are able to corrode different noble metals and which chemical groups are important in this process.

In this research we systematically investigate the stability of noble metal surfaces functionalized with different organothiols. The noble metal surfaces are exposed to a drop of pure organothiol and subsequently washed with dichloromethane. The treated surfaces were monitored for the duration of one month using a combination of techniques, i.e. atomic force microscopy, scanning electron microscopy, and optical microscopy. The surfaces were also analysed with X-ray powder diffraction (PXRD) and energy dispersive analysis of X-rays (EDS) to investigate the surface constituents. The importance of the chemical terminal group of the organothiol (i.e. carboxylic acid or methyl) and the chain length is also investigated. Three different

lengths were selected for the alkyl chain: three, six, and eleven carbon atoms long. The reason for selecting molecules with different chain lengths is the reported chain length dependence on the ability of the molecules to protect the metal surfaces from (electro)chemical degradation [9]. The chemical functionality added to these hydrocarbon chains are a thiol group, a carboxylic acid group, or the combination of the two. The molecules that were used are shown in Fig. 1.

2. Materials and method

2.1. Surface preparation

Copper and silver were evaporated onto freshly cleaved muscovite mica using an e-beam evaporator at a rate of 1 Å/s to obtain a 200 nm thick metal surface. Gold was evaporated in the same way to obtain a thickness of 50 nm. Silver was grown at 230 °C, while the other surfaces were grown at room temperature. A noble metal surface texture with the crystallographic [111] direction perpendicular to the muscovite mica (001) surface was obtained in all cases. The surfaces consisting of the same noble metal that were used for organothiol treatment were all grown in the same run, and then cut into smaller fragments. The metal surfaces were treated with the different molecules on the same day as the metal surface was prepared.

A pure drop of the relevant liquid molecule (approximately 20 µL) was deposited onto the noble metal surface and left there for 10 s. In

* Corresponding author.

E-mail address: E.vlieg@science.ru.nl (E. Vlieg).

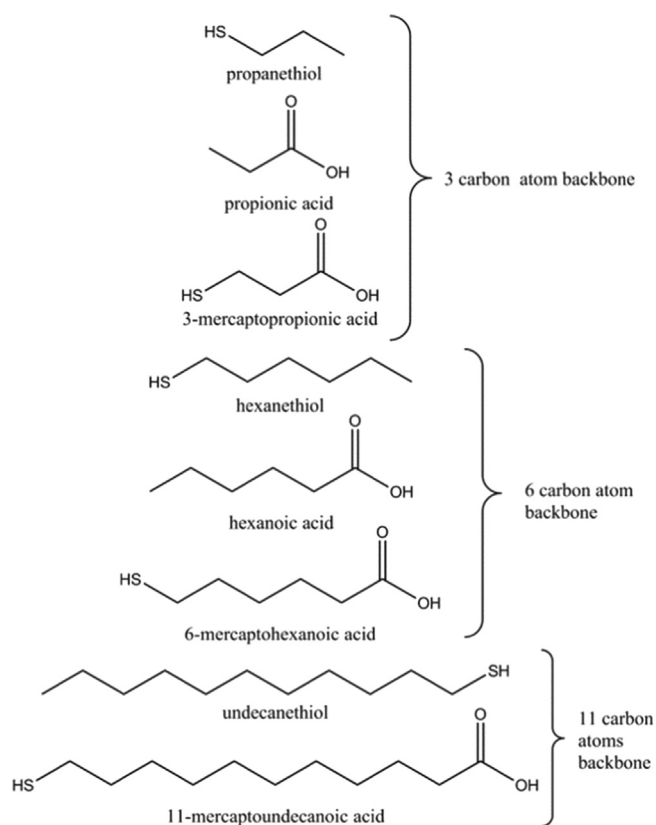


Fig. 1. Chemical structures of the investigated molecules.

the case of 11-mercaptohexanoic acid, which is a solid at room temperature, a 10^{-2} M solution was prepared in dichloromethane (CHROMASOLV for HPLC $\geq 99.8\%$ pure, obtained from Sigma Aldrich), and a drop from this solution was deposited on the surface, and left there for 10 s. The excess material was washed away with dichloromethane, by immersing the sample in approximately 15 mL of solvent, washing for 60 s, and repeating this procedure twice in fresh solvent. Samples were stored under ambient conditions.

2.2. Surface observations

The resulting surfaces were investigated with optical reflection differential interference contrast microscopy. Atomic force microscopy (AFM) (Dimension 3100, Veeco) was performed in contact mode with CSG10 tips from NT-MDT. Images were flattened using Veeco soft-

ware. Scanning electron microscopy (SEM) was done on a Phenom SEM, model nr. 800–03103-02, images were captured at an acceleration voltage of 5 kV (square images). EDS was performed on a SEM Philips XL-20, combined with a Noran system SIX. Images were captured at an acceleration voltage of 25 kV (rectangular images), and EDS spectra were recorded at 5 kV. Powder X-ray diffraction experiments were carried out on a Bruker D8 diffractometer using Cu-K α radiation. All experiments were performed in triplicate.

2.3. Materials

Muscovite mica (quality grade ASTM-V1) was obtained from S & J Trading Inc. (Glen Oaks, NY, USA). 1-Propanethiol (99% purity), 3-mercapto-1-propionic acid (99% purity), 1-propionic acid (99% purity), 1-hexanethiol (95% purity), 6-mercapto-1-hexanoic acid (90% purity), 1-hexanoic acid (99% purity), 1-undecanethiol (98% purity), and 11-mercapto-1-undecanoic acid (95% purity) were obtained from Sigma Aldrich and were used without further purification.

3. Results and discussion

3.1. Surface morphology

Fig. 2 shows AFM images of the different as-grown metal surfaces. The copper and gold surfaces are relatively flat showing numerous nanocrystals at the smallest scale (Fig. 2B-C); both were grown at room temperature. The silver surface (Fig. 2A) is only partially covered, which is known to occur for noble metal surfaces grown on muscovite mica at higher temperatures [10,11]. These surfaces were subsequently treated with a pure drop of the different compounds depicted in Fig. 1, or a solution drop containing 11-mercapto-1-undecanoic acid in dichloromethane (conc. 10^{-2} M) followed by washing in dichloromethane, and were subsequently investigated with optical microscopy and AFM to study their effect on the surface morphology.

Fig. 3A-C depict optical microscopy images of an evaporated silver layer kept at ambient conditions for three weeks. Fig. 3D-F show the same time evolution for a silver surface treated with 6-mercapto-1-hexanoic acid. As can be seen from these images the untreated silver surface remains stable, while the treated surface shows marked changes in morphology, with clusters of non-transparent material and larger transparent patches emerging, indicating surface modification. The surface modification has finished its course after two weeks, and remains stable afterwards. The process of surface modification was also followed with the help of AFM (Fig. 4), which shows the surface modification at a smaller length scale. The lateral and height scales are kept constant for this time series, to better compare the images and follow the nucleus formation and growth of the features. The height of

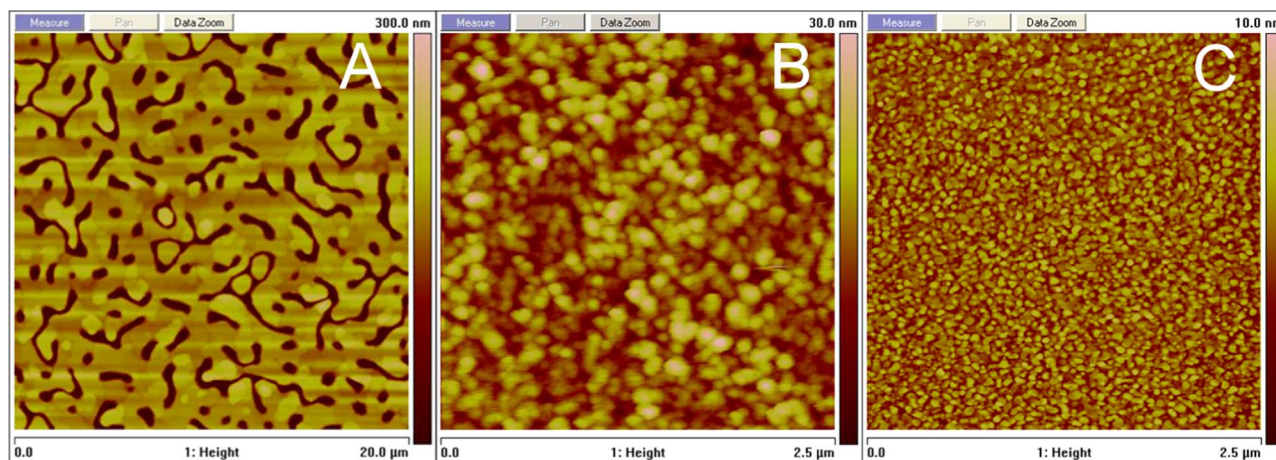


Fig. 2. AFM height images of silver (A), copper (B), and gold (C) deposited on muscovite mica. Note the different scales for the different images.

Download English Version:

<https://daneshyari.com/en/article/5421181>

Download Persian Version:

<https://daneshyari.com/article/5421181>

[Daneshyari.com](https://daneshyari.com)