Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 595 (2005) 56–63
SURFACE SCIENCE
www.elsevier.com/locate/susc

Removal of self-assembled monolayers of alkanethiolates on gold by plasma cleaning

Kevin Raiber [a], Andreas Terfort [a,*], Carsten Benndorf [b], Norman Krings [c], Hans-Henning Strehblow [c]

[a] *Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany*
[b] *Institut für Physikalische Chemie, Universität Hamburg, Grindelallee 117, 20146 Hamburg, Germany*
[c] *Institut für Physikalische Chemie und Elektrochemie 2, Heinrich-Heine-Universität, Universitätsstraße 1, 40225 Düsseldorf, Germany*

Received 23 December 2004; accepted for publication 28 July 2005
Available online 18 August 2005

Abstract

Plasmas of hydrogen or oxygen were used to remove self-assembled monolayers (SAMs) of alkanethiolates from gold surfaces. X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), ellipsometry, and contact angle measurements were used to compare the efficiency of the different plasmas and to explore their respective influence on the surface topology. Both plasmas were able to remove the SAM from the gold surface within less than 60 s. While the hydrogen plasma produces a de facto sulfur-free surface, oxygen plasma cleaning leads to an Au_2O_3 surface contaminated with oxidized sulfur species (probably sulfonates and sulfate). Nevertheless, the plasmas alter the roughness of the gold surfaces only marginally, as demonstrated by STM.

Keywords: Self-assembled monolayers (SAMs); Thiols; Gold; Plasma processing; X-ray photoelectron spectroscopy; Ellipsometry; Contact angle; Micro-contact printing (μCP)

1. Introduction

Self-assembled monolayers (SAMs), in particular those of thiols on gold, are used for micro-fabrication frequently. The possibility to structure these monolayers laterally by a number of lithographic techniques, such as photo- or electron beam lithography [1,2], provides a useful tool

* Corresponding author. Tel./fax: +49 40 42838 6102.
E-mail addresses: raiber@xray.chemie.uni-hamburg.de (K. Raiber), aterfort@xray.chemie.uni-hamburg.de (A. Terfort).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.07.038

particularly in the lower micrometer regime. A very prominent example for these techniques is micro-contact printing [3,4], for which a microstructured stamp inked with an alkanethiol is brought into contact with a gold or silver surface generating the laterally structured monolayer. Such a laterally structured alkanethiol SAM can act as a resist in a following etching step, where the unprotected metal is selectively removed resulting in a gold or silver film with the same lateral structure as the SAM (for this purpose only simple, hydrophobic SAMs of *n*-alkanethiols or perfluoro-*n*-alkanethiols can be used due to their low solubility in the etching solution as well as their low defect density). The metallic microstructures produced by this process are often used e.g. as elements of sensors, electrodes, or as arrays of any kind in combinatorial chemistry [5,6]. While some of these applications rely on bare gold surfaces, others use specifically functionalized SAMs (e.g. with bioreceptors), which cannot be used as resists for the micro-contact printing process. Since the alkanethiol SAM which acted as a resist is still present after the etching process, it becomes necessary to remove it efficiently before the subsequent steps. Known methods for SAM removal are etching with piranha solution (concentrated H_2SO_4/30%H_2O_2, 3:1) [7], electrochemical potential cycling [7], UV photooxidation [8–13], ozonolysis [14,15], thermal desorption [16–18], and plasma cleaning [19–23]. Of these, the first two are wet chemical processes which bear the danger of contamination by the reagents used and thus are very unfavorable for most applications. In addition, it has been shown that the piranha treatment induces recrystallization of the gold layer [24] and may even cause lift-off of the gold layer by etching away the frequently used adhesion layers. Even the UV oxidation and the ozone cleaning, while itself being gas phase processes, require an additional wet cleaning step, e. g. rinsing with ethanol, to remove the oxidation products from the surface [12,13,25]. The same might be true for the argon plasma method but has not been investigated sufficiently yet. Alternatively oxygen or hydrogen plasma can be used [26]. In contrast to the inert argon these are chemically reactive gases which react with the monolayer to form gaseous products during the cleaning process. These fragments should be volatile enough to be swept away by the continuous gas flow, so no further cleaning process, such as rinsing, is necessary. This makes plasma cleaning an attractive method for surface treatment. While recently a series of publications dealt with the interaction of different plasmas with monolayers from an academic point of view [27–30], a general method for convenient removal of monolayers has not been developed yet.

In this paper we explore the results of plasma treatment of SAM coated gold surfaces either with hydrogen or oxygen plasma by using XPS, STM, ellipsometry, and contact angle measurements for surface characterization. To simulate the conditions of the most frequently used patterning method—micro-contact printing—the SAMs used in this study were mostly deposited by using a planar PDMS-stamp without any structures.

2. Experimental section

2.1. Substrate preparation

Microscopy slides were used as substrates after the following cleaning procedure: first dust was removed by sonication in water (1 min). Then the slides were cleaned in piranha solution for 15 min (H_2SO_4/H_2O_2, 30%; 3:1; Caution! Piranha solution is a corrosive and strongly oxidizing agent.), rinsed with deionized water and dried in a stream of nitrogen. Forty nanometers of gold were deposited in ultra-high vacuum by an e-beam evaporator at a rate of approx. 1 nm/s with an underlying layer of 1.5 nm of chromium as an adhesion promoter.

For ellipsometry, 200 nm of gold with chromium as adhesion promoter were deposited onto (100) silicon wafers (used as delivered, Wacker Siltronic AG).

2.2. Stamp preparation

A planar stamp (without any pattern) was prepared by molding from a silicon wafer. PDMS (Sylgard 184®, Dow Corning) was mixed with the respective curing agent (10:1), poured over