The extraordinary stability imparted to silver monolayers by chloride

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ABSTRACT

While single crystal surfaces facilitate the majority of surface studies, only a handful of these materials are stable under ambient conditions and at extreme temperatures. Therefore, there is a continued interest in the development of robust and ordered surfaces that can be studied under realistic conditions. Electrochemical scanning tunneling microscopy (EC-STM) revealed that in a chloride-free electrolyte, Ag forms an ordered monolayer on Au(1 1 1) with a structure that could be atomically resolved. However, upon removal from the cell, these chloride-free Ag monolayers were subject to degradation by air and high temperatures. Interestingly, if the Ag layer was formed in the presence of chloride, the resulting $AgCl_x$ layer was stable both in air and at high temperatures. X-ray photoelectron spectroscopy was used to characterize the system and ambient-, low temperature-, and EC-STM revealed that even after exposure to extreme temperatures, the $AgCl_x$ layer remained intact. Density functional theory (DFT) indicated that the equilibrium coverage of Cl on the Ag monolayer was ~0.5 ML, and that the barrier for surface reorganization of the overlayer was low. It is proposed that this facile mobility of the overlayer imparts a protective property that allows the $AgCl_x$ layer to withstand extreme temperatures and attack by oxygen.

1. Introduction

Atomically flat, clean, and ordered surfaces are vital for the detailed study of surface and interface phenomena. Single-crystal metal and semiconductor surfaces, which have well-defined atomic lattices that are continuous with few or no defects, are widely used in surface science. However, in order to analyze most metal and semiconductor surfaces, complex ultrahigh vacuum (UHV) or electrochemical procedures must be used to keep the surfaces clean and ordered at the atomic-level. In contrast to the vast number of surface facets of metals, oxides, and semiconductors available to the UHV surface scientist, only a relatively small set of atomically flat and ordered surfaces exist that remain stable and contamination-free under ambient conditions. A fairly exhaustive list of these substrates includes: highly oriented pyrolytic graphite [1], graphene on SiO_2 [2], sulfur on Mo(0 0 1) [3], TaSe₂ [4], TaS₂ [4], NbSe₂ [5], iodine on Pt and Au [6–8], carbon on Ni [9–10], Cr_2O_3 [11], and self-assembled thiol monolayers (SAMs) supported on noble metal surfaces [12]. These systems offer many applications in self-assembly [13–14], sensing [15], lubrication [16], X-ray optics [17], and corrosion protection [18]. Additionally, silver halide films have shown to be stable at room temperature. Kawasaki and Uchiki reported the formation of AgCl and AgBr layers on thin Au films that were formed via solid phase material transfer [19]. These layers were stable under ambient conditions, however, the thermal stability beyond room temperature of such films was not explored [19]. This paper reports the discovery of an ultra-stable $AgCl_x$ layer on Au(1 1 1) that is not only atomically ordered and contamination free at ambient pressures and temperatures, but remains intact after heating cycles as high as 1000 K.

In order to generate this atomically thin, metal halide film, under potential deposition (UPD) was employed [20–21]. UPD is a useful procedure as it allows for the controllable and reproducible deposition of up to a few atomic layers of a metal before the onset of bulk deposition, thus enabling the study of atomically thin, metal layers which may otherwise be difficult to generate outside the UHV environment [22–25].

The UPD of Ag on Au(1 1 1) has been studied extensively [20–21,26–30]. Gewirth and co-workers carried out one of the first atomic-scale studies on this surface using *in situ* atomic force microscopy (AFM) [21]. The UPD structure was found to depend on the composition of the electrolyte used in the deposition procedure. In sulfuric acid the Ag adlayer adopted a (3 × 3) overlayer, while in

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nitrate- and carbonate-containing electrolytes a (4×4) overlayer was observed. Although it was not possible to identify the exact structure of the overlayer in perchloric acid, it was determined that the structure was not close-packed like the sulfate and nitrate systems. The same system was studied with electrochemical scanning tunneling microscopy (EC-STM) by Ogaki and Itaya in 1995 [31]. In this study, the authors found that the UPD of Ag occurs in three steps on Au(1 1 1) in both sulfuric and perchloric acid. For the first adlayer of Ag on Au(1 1 1) in sulfuric acid solution, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure was observed. In the potential range between 0.85 V and 1.10 V vs. RHE, an open (4×4) structure of the Ag was formed in the perchloric acid electrolyte. The authors were also able to observe a (1×1) close-packed structure at less positive potentials. Furthermore, it was possible to detect the onset of bulk Ag deposition, which ultimately resulted in a Ag(1 1 1)-(1×1) structure. Kwak and co-workers also studied this system both with and without chloride in an effort to determine how chloride altered the Ag structures; however, no data on thermal stability was reported [32]. In addition to these studies, many STM experiments (UHV, ambient, and EC) have also been performed on the adsorption of Cl on bulk Ag(1 1 1) crystals [33–37]. Importantly, none of the aforementioned studies describe the high thermal stability observed in the following experiments.

In this paper, we describe the UPD of Ag on Au(1 1 1) with and without the presence of chloride using EC-STM, ambient STM, low-temperature STM, and *ex situ* X-ray photoelectron spectroscopy (XPS). We show how the presence of chloride on the Ag adlayer greatly affects both the structure and the properties of the $AgCl_x$ film in very unexpected ways. Surprisingly, $AgCl_x$ films were remarkably stable; they remained intact on the Au surface even after the surface was heated in air to a temperature of 1000 K. High-resolution STM imaging revealed that the atomic-scale structure after flame annealing was actually more perfect than the structure of the as-prepared film. On the other hand, when Cl was not present in the electrolyte solution, the Ag adlayer was not maintained after the high temperature treatment, thus pointing to the presence of chloride as the origin of the film's stability. The system was modeled using density functional theory (DFT) calculations, which predicted the equilibrium stoichiometry of the surface $AgCl_x$ layer to be Ag and Cl in a ∼9:5 ratio. DFT calculations also indicated that the barrier for translation of the Cl layer over the Ag monolayer was extremely low, thus pointing to a protective mechanism as the key to the unprecedented stability.

2. Experimental

2.1. EC-STM setup and measurements

The working electrode was a Au(1 1 1) single crystal with a 9 mm diameter (MaTecK). The surface was cleaned in pirana solution (1:3 H_2SO_4/H_2O_2) to remove any organics and boiled in concentrated HNO_3 (ACS grade) to remove any excess Ag after every experiment. The sample was rinsed in ultrapure water and cyclic voltammograms (CVs) were performed to ensure sample cleanliness. The electrodes and fluid cell were cleaned in a similar manner. Prior to each experiment, the single crystal was flame annealed in a H_2 (g) flame at 1000 K for 2 min, cooled to room temperature, and then quickly covered with a drop of ultrapure water (18.2 MΩ cm, Millipore-Q) to protect the surface against contamination. The electrode was then transferred to the STM electrochemical cell, which was subsequently filled with 0.1 M $HClO_4$ (OPTIMA grade, Fisher). In the electrochemical cell, Pt and Pt/Ir wires were used for the quasi-reference and counter electrodes, respectively. All potentials were subsequently quoted against a Ag/AgCl reference electrode. A PicoScan Molecular Imaging STM was used for all experiments. STM

imaging was performed *in situ* using etched Pt/Ir wire tips (80/20, 0.25 mm diameter) coated in Apiezon wax to reduce Faradaic currents at the tip/electrolyte interface below 70 pA (Agilent Tech.). All images were recorded using the constant current mode. Prior to each experiment, the condition of the Au(1 1 1)-(1×1) surface was verified with CVs and EC-STM imaging. Ag was deposited onto the Au surface through the addition of either 1 mM $AgClO_4$ or 0.1 μM saturated AgCl solution to the STM electrochemical cell depending on the type of monolayer to be studied. All solutions were prepared from Sigma ACS grade chemicals and ultrapure water.

2.2. Electrochemical measurements

Cyclic voltammetry was performed in an external EC cell using Pt wire mesh as the counter electrode and either Ag wire for the chloride-free data or Ag/AgCl for all other data as the reference electrode. The solutions were purged with N_2 (g) prior to running the electrochemical measurements. For all of the Ag deposition experiments, the scan rate was 0.1 V/s. Control of voltage sweeps was performed with a CH Instruments 830 Electrochemical Analyzer.

2.3. UHV STM study

The ultrahigh vacuum (UHV) STM experiments were performed in a low-temperature (LT-UHV) microscope built by OmicronNanotechnology^{TM}. The $AgCl_x$ layer was first formed electrochemically, then flame annealed in air with a H_2 (g) flame for 15 min, and finally transferred directly to the UHV STM ($<5 \times 10^{-10}$ mbar) chamber for imaging. In approximately 30 min, the sample cooled from room temperature to 78 K. All images were recorded using the constant current mode at 78 K with etched W tips, and voltages refer to the sample bias.

2.4. XPS measurements

In order to ascertain the chemical composition of the surface, *ex situ* X-ray photoelectron spectroscopy (XPS) was employed. Two XPS instruments at independent user facilities were used for the XPS experiments. The instruments had load-lock entry, and the UHV analysis chambers were maintained at a base pressure below 5×10^{-10} mbar during experiments. Table 1 shows the relevant details describing the XPS instruments and experiments. For the spectra taken at the MIT facility, a grazing take-off angle of 70° was used. For the data taken at Harvard, a take-off angle of 55° was used. All peaks were adjusted using a Shirley type background. Accurate binding energies (BE) were determined by referencing to the Au 4f peak at 84.0 eV. Atomic ratios were computed from peak intensity ratios and reported atomic sensitivity factors [38] by the CasaXPS software package (version 2.3.15).

2.5. Computational details

DFT calculations were performed using the Vienna Ab inito Simulation Program (VASP) [39–42]. Vanderbilt ultra-soft pseudopotentials (USPP) [43–44] were used to describe the core electrons. Unless otherwise specified, the electron exchange and correlation effect was modeled using the Perdew and Wang 91 (PW91) exchange and correlation functional [45]. The simulation box contained 4 layers of Au with 9 Au atoms in each layer in a 3×3 super cell arrangement. On top of the Au layer, one full monolayer of Ag was adsorbed in the face-centered threefold hollow (FCC) positions of the underlying Au surface. The Cl overlayer was modeled in the plane above the Ag layer. The bottom two layers of Au were fixed at their bulk locations, and the z dimension of the simulation box was 28.98 Å. A $2 \times 2 \times 1$ k-point mesh