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Surface Science 592 (2005) 150–158
SURFACE SCIENCE
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Structural transitions of chemisorbed iodine on Au(100): A STM and LEED study

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Received 30 April 2005; accepted for publication 7 July 2005
Available online 25 July 2005

Abstract

We have studied the chemisorption of molecular iodine on a reconstructed Au(100) surface by means of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) in an ultra high vacuum environment at 300 K and at temperatures down to 115 K. Several structural phases are observed during iodine adsorption. At 300 K, a low iodine coverage of $\theta_I \sim 0.1$ ML is sufficient to lift the "hex" reconstruction, producing the substrate's (1×1) diffraction pattern with a diffuse background. The first stable structure defined as $c(p\sqrt{2} \times 2\sqrt{2})R45°$, is formed at coverages slightly higher than 0.4 ML that uniaxially compresses with increasing iodine coverage. For higher coverages $\theta_I > 0.5$ ML the iodine layer transforms to a rotated hexagonal structure with a maximum angle of 3.5° with respect to the [001] substrate direction. An iodine structure not previously reported for this system was observed to form at $T \sim 120$ K when $\theta_I \sim 0.33$ ML, and only observable under certain adsorption/cooling conditions. The findings are discussed in terms of the subtle competition between adsorbate–substrate and adsorbate–adsorbate interactions in determining the adsorbate structure.

Keywords: Iodine; Gold; Scanning tunneling microscopy; Electron diffraction; Chemisorption; Surface structure; Solid–vacuum interfaces

1. Introduction

Halogen adsorption on metal surfaces has been investigated extensively in the past using low energy electron diffraction (LEED) and surface X-ray scattering (SXS) techniques in ultrahigh vacuum (UHV) and electrolyte solution respectively, and more recently with in situ scanning

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doi:10.1016/j.susc.2005.07.004

tunneling microscopy (STM) [1–4]. Iodine adsorption on Au(1 0 0) has not been so extensively studied as Au(1 1 1), and only limited information can be found in the literature about structural transitions in UHV conditions. Neumann et al. [5] studied iodine adsorption on Au(1 0 0) using LEED and thermal desorption spectroscopy (TDS), where they reported the formation of an incommensurate c($p\sqrt{2}\times 2\sqrt{2}$)$R45°$ structure beginning at $\theta_I = 0.42$ ML that transforms to a so-called "compression" structure as θ_I approaches 0.5 ML, with a saturation coverage reaching a maximum value of 0.56 ML. They also reported that upon adsorption at a slightly lower temperature or by annealing the $\theta_I = 0.5$ phase the formation of a commensurate c($\sqrt{2}\times 2\sqrt{2}$)$R45°$ phase was possible. No detailed explanation of the observed diffraction patterns in terms of real-space structural models was presented by the authors.

An in situ STM study in an electrochemical environment revealed a series of potential-dependent iodine phases, beginning at $\theta_I = 0.46$ with a compressible incommensurate c($p\sqrt{2}\times 2\sqrt{2}$)$R45°$ structure which reverted to a commensurate c($\sqrt{2}\times 2\sqrt{2}$)$R45°$ at $\theta_I = 0.5$. At higher potential (increased coverage) a pseudo-hexagonal adlayer formed with a slight rotation with respect to the Au(1 0 0) substrate [6].

Here we report a variable temperature study of the adsorption of iodine on Au(1 0 0) using a combination of LEED and STM techniques that complements the above cited studies, with the hope that it will provide a better understanding of the differences and similarities between the solid/vacuum and solid/electrolyte interfaces concerning halogen adlayers on metal surfaces. We also present results of a new iodine structure stable at low temperatures and observable only under certain adsorption/cooling conditions. The results are discussed in terms of competing adsorbate–substrate and adsorbate–adsorbate interactions mediated by substrate temperature.

2. Experimental details

Experiments where carried out in an ultra high vacuum system equipped with a quick sample introduction load-lock, a reverse view LEED (VG Instruments) and a lab-built ambient temperature STM. Working pressure during iodine adsorption was kept below 1×10^{-10} mbar. A special heating/cooling sample stage was constructed for the multi-axis manipulator (VG Instruments) that permitted transfer of the sample between the different instruments with the help of a long travel wobble-stick. The sample holder was made of a molybdenum sheet that included its own thermocouple welded close to the sample, with the gold single crystal fixed to this plate using tantalum wire. Heating was achieved by direct filament radiation and electron bombardment. For cooling the sample, nitrogen gas flowed through a copper coiled tubing immersed in a Dewar filled with liquid nitrogen and then through a heat-transfer unit inside the chamber that included a heavy copper braid and plate where a second thermocouple was fixed.

For the iodine source we constructed a solid state electrochemical cell following a reliable design that uses a Ag_4RbI_5 pellet: a high ionic-conductivity compound sandwiched between two Pt electrode meshes that serve as electrodes [7]. The use of this design presents several advantages: dosing amounts are highly controllable since they are proportional to the Faraday current in the cell. Also exposure and coverage calibration is less complicated than gas admission into the chamber, and operates at room temperature. Typical cell currents in our experiments range between 25 and 100 μA, enough to complete a full iodine monolayer in less than a minute. During operation of the cell only a slight increase of background pressure was detected.

The Au(1 0 0) single crystal was supplied cut and polished by a commercial vendor (SPLabs, Holland), and no further treatment was done except for ultrasonic cleaning in acetone and annealing in UHV. For STM imaging electrochemically etched W tips were used, with typical tunneling parameters of: below 25 mV for the sample bias and currents from one up to several nA. All STM images presented here where taken in topographical/constant current mode.