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Adsorption and desorption of thermally generated hydrogen atoms on Au(111) and Ag/Au(111)

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ABSTRACT

To explore the possibility of employing thermally generated H atoms to determine the chemical composition of a metallic surface, we investigated the adsorption and desorption of H atoms generated with a thermal cracker on surfaces Au(111) and Ag/Au(111). Angle-resolved photoemission spectra showed that the noble-metallic surfaces deteriorated upon exposure to a flux of H atoms at ~100 K. Upon subsequent annealing, the order of the surfaces was mostly recovered when H atoms on the surfaces desorbed, but the recovery was incomplete even with annealing at a temperature much higher than that at which H atoms desorb. X-ray photoemission spectra showed that O-containing contaminants existed on the surfaces after the H dosing. The evolution of O 1s during annealing indicated that the O-containing contaminants were H_2O and its moieties generated during thermal cracking; the disturbances of the surfaces remaining above the desorption temperature of H atoms were likely caused by chemisorbed O. Our results show that it is possible to employ thermally generated H atoms to determine the chemical composition of a metallic surface, but a small proportion of H_2O in a H_2 gas line might be unavoidable; precautions against possible O contamination are required when a thermal cracker is employed.

1. Introduction

The manipulation and characterization of the surface of a nanostructure attract great interest because the physical and chemical properties of a nanostructure depend strongly on the chemical composition of its surface. Surface states are electronic states confined between a surface vacuum barrier and a bulk-projected band gap [1]; they have been utilized for surface characterization because their properties, such as binding energy, intensity and line width, are sensitive to the surface order and composition [2–5]. It was recently demonstrated [5] that it is feasible to characterize the chemical composition of the topmost layer of a nanostructure on monitoring the evolution of its surface states. In that work, the chemisorption of H atoms on a metallic surface was induced with ultraviolet irradiation, causing the surface states to deteriorate. The surface composition was explored on determining the temperatures at which the surface states recovered, assuming that the H atoms desorbed from the surface at the same temperature. Although the dosage and dosing location of H atoms are controllable, photon-induced dosing is tedious and might be unsuitable for many applications.

A thermal cracker is a popular instrument to generate a flux of H atoms. Hydrogen molecules pass through a hot capillary and dissociate, producing a stream of H atoms that can rapidly dose a large surface area. One might wonder whether these thermally generated H atoms chemisorbed on metallic surfaces behave in a manner similar to that of photon-induced chemisorbed H atoms. To address the issue, we investigated in detail the adsorption and desorption of H atoms generated with a thermal cracker on noble-metallic surfaces, such as Au(111) and Ag/Au(111), with angle-resolved photoemission spectra (ARPES) and x-ray photoemission spectra (XPS). Our ARPES results demonstrated that the surface deteriorated significantly on H dosing at ~100 K, and recovered mostly when the chemisorbed H atoms desorbed from the surface, but the surface did not recover fully even when annealed at a temperature much higher than that at which H atoms desorb. The XPS results showed that O-containing contaminants existed on the surface exposed to a flux of thermally generated H atoms. The evolution of the core level O 1s spectra lines during annealing indicated that the O-containing contaminants were H_2O and its moieties originating from H_2O vapor in the H_2 gas line; the surface disorder remaining at an elevated temperature observed in the ARPES measurements was likely caused by chemisorbed O atoms on the surface. Our work shows that

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precautions are required on employing a thermal cracker; the stream of H atoms so generated might inevitably contain a small amount of H_2O and its moieties that are likely detectable in sensitive measurements and produce misleading results.

2. Experiments

Our experiments were conducted at two beamlines in the National Synchrotron Radiation Research Center, Taiwan. The ARPES measurements were performed on an ultra-high-vacuum end station located at beamline BL21B1. This end station consisted of a main chamber and a preparation chamber; the latter was for sample sputtering and high-temperature annealing. Photoemission spectra were recorded with an analyzer (Scienta SES R4000) equipped with a microchannel plate and a charge-coupled device (angular resolution set at 0.05°). All spectra were measured with photons of energy 21 eV, and shifted to have zero binding energy at the Fermi level. A Au(111) single crystal was cleaned with repetitive sputtering and annealing until the surface showed a sharp and split Shockley state at $\overline{\Gamma}$ [6]. The sample was mounted on a transferable sample holder and transferred onto a motorized six-axis manipulator for data acquisition. With sample cooling with liquid nitrogen, the sample temperature, measured with a silicon diode, was variable between 90 and 400 K. Silver films were grown in two steps: Ag was evaporated from a *k*-cell evaporator and deposited when the sample was at ~100 K, and subsequently annealed to ~270 K to yield atomically flat films [7].

The XPS were measured at an end station installed at beamline BL24A1. The photoemission spectra were collected with an analyzer (SPECS PHOIBOS 150). With the grating of the beamline employed in this work, the photon energy was variable from 120 to 350 eV, mixed with high-order harmonics in substantial proportion. All XPS spectra were measured with photons of energy 326 eV and its second harmonic (652 eV); with these photons, all core levels of interest in this work, such as C 1s (~270 eV), O 1s (~530 eV), Ag 3d (~368 eV) and Au 4f (~84 eV), were accessible. A Au(111) single crystal was mounted with W wires at the bottom of a Cu cooling tube; its temperature, variable from 100 to 1000 K, was measured with a thermocouple junction (type K) directly attached to the sample. The sample was sputtered and annealed repetitively until the surface showed an effective LEED pattern of $(22 \times \sqrt{3})$ and no contaminant was detectable in XPS spectra. The atomically flat Ag films were grown with the two-step method mentioned above. The Ag was evaporated from a *k*-cell evaporator; the rate of deposition was calibrated with a quartz–crystal microbalance in a separate vacuum system.

Dosing H atoms was performed with a thermal cracker (TC50 from Oxford Applied Research Ltd.). A flux of H atoms was generated on passing H_2 through a hot capillary heated with an electron beam. The cracker was outgassed thoroughly after the vacuum system was baked. Before the H dosing, the power to the cracker was switched on for 10 min to stabilize its temperature. The dosage of H atoms was controlled on adjusting the chamber pressure and the duration of exposure. The duration of the H exposure was controlled on operating a shutter before the opening of the capillary. The H_2 gas was admitted into the cracker through a leak valve. The actual dosage of H atoms for a given chamber pressure and duration of exposure depended greatly on the capability of the system pumping. Because there was no mass spectrometer installed in our experimental apparatus, thermal desorption spectra were not measured; a comparison of the H dosage between separate vacuum systems is not trivial. The XPS results indicated that H_2O vapor existed in the H_2 gas line. Upon repeated baking and

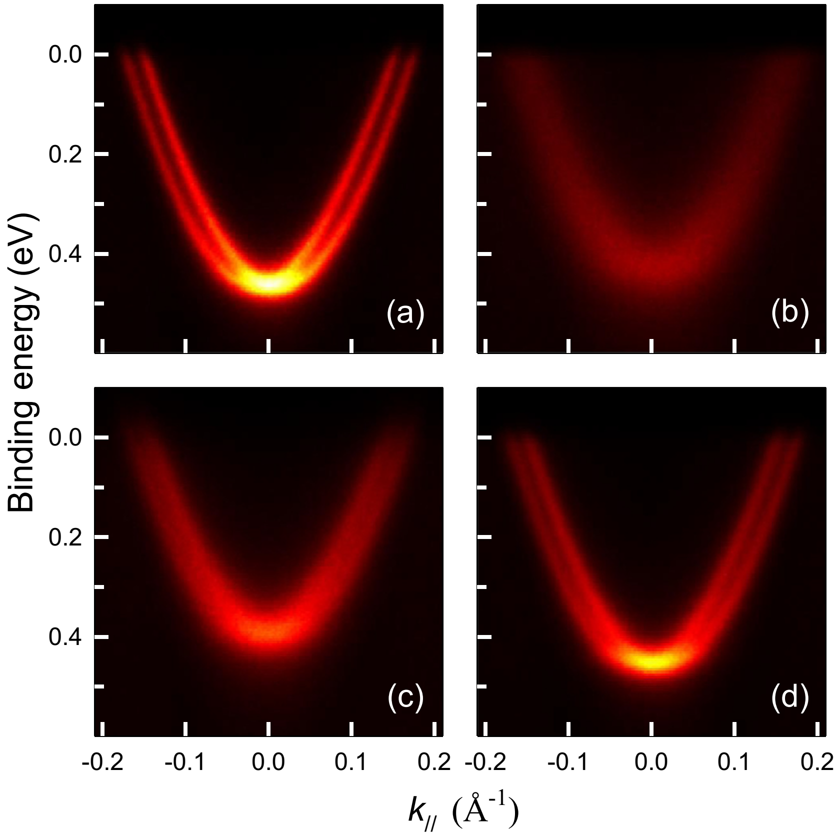

Fig. 1. Photoemission intensity at $\overline{\Gamma}$ measured on (a) clean Au(111) at 98 K; (b) Au(111) with H dosing at 98 K; (c) H-dosed Au(111) annealed at 334 K; (d) annealed sample at 105 K.