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Oxygen induced facet formation on Rh(2 1 0) surface

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ABSTRACT

Oxygen induced nanometer-scale faceting of the atomically rough Rh(2 1 0) surface has been studied using Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). The Rh(2 1 0) surface completely covered with nanometer-scale facets when annealed at $\geq$550 K in the presence of oxygen. LEED studies reveal that the pyramidal faceted surface is characterized by three-sided nanoscale pyramids exposing (7 3 1), (7 3 −1) and (1 1 0) faces. A clean faceted surface was prepared through the use of low temperature surface cleaning method using the reaction with H_2 while preserving ("freezing") the pyramidal facet structure. The resulting clean faceted surface remains stable for $T \sim 600$ K and for higher temperatures; the faceted surface irreversibly relaxes to the planar surface. STM measurements confirms the formation of nanopyramids with average pyramid size ranging from 12 to 21 nm depending upon the annealing temperature. The nanopyramidal faceted Rh surface may be used as a potential template for the growth of metallic nanoclusters and for structure sensitive reactions.

1. Introduction

Atomically rough clean metal surfaces generally have lower surface atom density and higher surface free energy than close-packed surfaces of the same metal. A variety of atomically rough clean metal surfaces can be prepared as stable orientations, but the presence of (strongly interacting) adsorbate can cause changes in surface morphology through mechanisms such as reconstruction and facet formation [1–6]. These morphological changes are usually explained in terms of changes in surface free energy due to the presence of adsorbate [7,8]. There are many overlayer/substrate systems that exhibit faceting, including oxygen and metal covered e.g., bcc W(1 1 1), Mo(1 1 1), fcc Cu(2 1 0), Ir(2 1 0), Pt(2 1 0) and Ni(2 1 0) and hcp Re(1 2 −3 1) and Re(1 1 −2 1) surfaces [3–11]. It has been observed that changes in morphology can be accompanied by changes in electronic structure and surface reactivity [12,13].

In the present study, we discuss the oxygen induced morphological change of Rh(2 1 0) surface which is an important substrate for catalytic processes and has potential applications in surface chemistry. Previous studies on fcc(2 1 0) surfaces [5–9] indicate that the facets formation can be induced by the presence of various gaseous adsorbates for example oxygen and nitrogen can induce faceting on Cu(2 1 0) and Ni(2 1 0) while oxygen and CO provide favorable conditions to restructure the Pt(2 1 0) surface to form facets. Ir(2 1 0) [8] shows the formation of pyramidal type facets with {3 1 1} and (1 1 0) facets, when annealed in the presence of oxygen above 600 K. In a recent study, Govind et al. [14] has studied the oxygen induced faceting of Rh(2 1 0) and revealed the various condition for the formation of faceted surface.

Rhodium is an fcc metal of the platinum group with melting point (Tm − 2239 K) and an ideal model of its surface is illustrated in Fig. 1. The bulk truncated surface is atomically very open and rough, with four exposed layers of atoms. The top layer has C_{2v} symmetry (180° rotation, with the [2 1 0] vector as the *z* axis and principal axis, as well as one vertical reflection plane defined by the [2 1 0] and [−1 2 0] vectors). The *z*-periodicity of the structure is 10 layers – the atoms of the 11th layer are in the same *x* and *y* positions as the atoms in the top layer. In this paper, motivation is to study the oxygen induced morphological instability of atomic rough Rh(2 1 0) metal surface and study the oxygen induced facet formation, destruction and freezing of the clean faceted Rh(2 1 0) surface. The paper is arranged in following manner: the experimental procedure is presented in Section 2 while results of AES, LEED and STM are presented in Section 3. Further the conclusions of the present study are presented in Section 4.

2. Experimental

The experiments were carried out in two different ultrahigh vacuum (UHV) chambers denoted as LEED and STM chambers,

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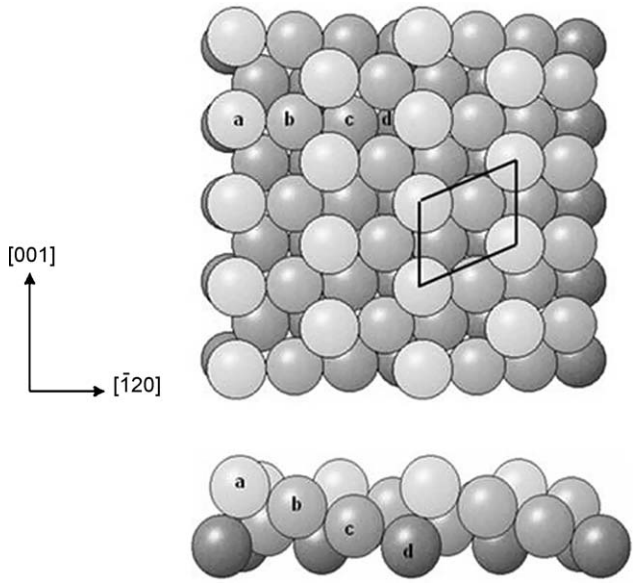

Fig. 1. Hard sphere model of fcc(2 1 0) surface (top and side view) showing top four exposed layer.

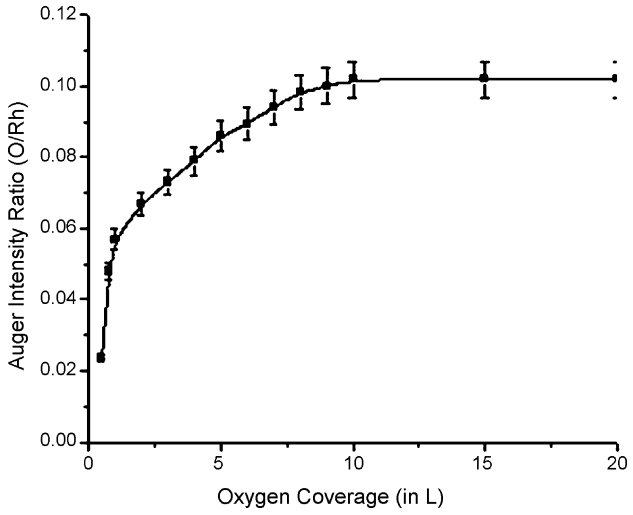

Fig. 2. The oxygen uptake curve on Rh(2 1 0) at room temperature measured by AES.

respectively. All LEED images are obtained in the LEED chamber that also contains a quadrupole mass spectrometer (QMS) for residual gas analysis and a cylindrical mirror analyzer for AES. STM experiments were performed in a chamber at room temperature using a hybrid variable temperature Omicron STM with tungsten tips. The Rh(2 1 0) crystal is cut from a single crystal Rh (99.99%) rod ~ 10 mm in diameter, ~1.5 mm thick, aligned within 0.5° of the (2 1 0) orientation and polished to a mirror finish. The sample is supported by two rhenium leads where a high current (up to 30 A) can be passed through the leads to achieve temperatures up to 1600 K. A C-type (W–5 at.% Re/W–26 at.% Re) thermocouple is spot welded directly to the rear of the sample for accurate temperature measurement. The sample support assembly also includes a tungsten filament for electron bombardment heating; a temperature up to 2000 K can be achieved by flashing the sample in UHV. The sample was cleaned by repeated cycles of 1 KeV Ar+ ion bombardment initially at 300 K and then at increasingly higher temperature (<650 K), annealing in UHV at 1200 K, annealing in O_2 (2×10^{-8} Torr) at 1000–1200 K followed by rapid flashes to ~1600 K in UHV to desorbs the excess oxygen from the surface. The oxygen gas deposition was achieved by back-filling the chamber by O_2.

3. Results

We study the adsorption of oxygen on planar Rh(2 1 0) at room temperature (Fig. 2). The curve shows the O/Rh Auger peak intensity ratio as a function of oxygen dose at room temperature; the oxygen dose is expressed in units of Langmuir (L, 1L = 1×10^{-6} Torr s = 1.33×10^{-4} Pa s). The O/Rh Auger ratio increases with oxygen dose and reach at the saturation at 10L of oxygen dose, which indicate the formation of one physical monolayer of oxygen at room temperature.

The low energy electron diffraction pattern obtained from clean Rh(2 1 0) is shown in Fig. 3a. The observed LEED pattern is consistent with the presence of an unreconstructed bulk fcc(2 1 0) plane. When electron beam energy (Ee) is increased the electron wavelength and, consequently, the diffraction angles decrease, and an apparent motion of the diffraction beams toward the specularly reflected (0, 0) beam is observed (Fig. 3b). For the clean Rh(2 1 0) surface the (0, 0) beam is perpendicular to the macroscopic surface plane and is in the center of the LEED pattern. The behavior of the LEED beams indicates that the surface is microscopically planar. No additional beams appear in the LEED pattern as a result of oxygen adsorption at room temperature. However, an increase in the background intensity is observed upon oxygen deposition which can be attributed to additional diffuse scattering from the oxygen overlayer and oxygen induced disorder in the topmost Rh layer.

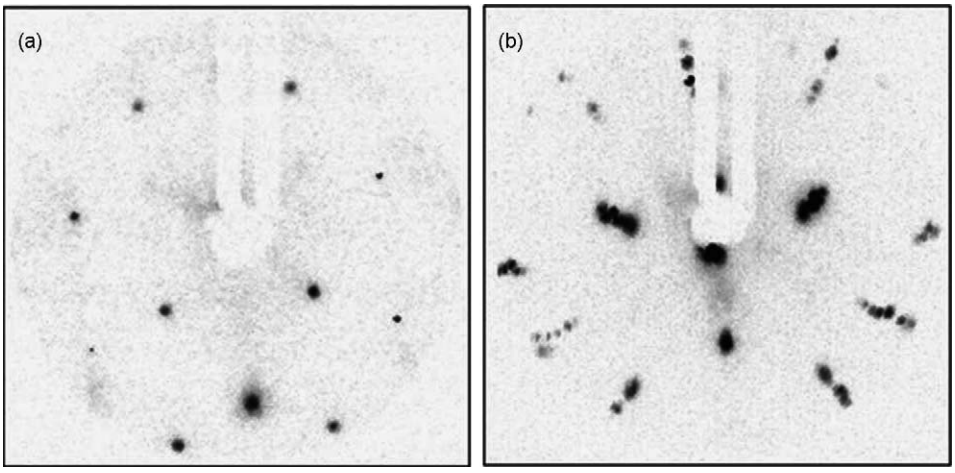

Fig. 3. (a) LEED pattern of Rh(2 1 0) clean surface at incident electron beam energy 160 eV. (b) LEED pattern from planar Rh(2 1 0) with energy 20–80 eV.