Surface Science 605 (2011) 1454–1458

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/ locate/susc

Growth of gold nanoparticles on faceted O/Ru(11–20) nanotemplate

Quantong Shen *, Wenhua Chen, Robert A. Bartynski

Department of Physics and Astronomy, and Laboratory for Surface Modification, Rutgers, The State University of New Jersey, Piscataway, New Jersey, 08854, United States

A R T I C L E I N F O

Article history:
Received 6 February 2011
Accepted 11 May 2011
Available online 18 May 2011

Keywords:
Ruthenium
Gold
Faceting
Nanotemplate
Nanoparticle
Scanning tunneling microscopy (STM)

A B S T R A C T

The growth of gold nanoparticles on the oxygen-covered faceted Ru(11–20) surface is investigated by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). By depositing gold onto the faceted surface held at room temperature, gold nanoparticles with regular spacings are fabricated. Gold nanoparticles are found to nucleate preferentially within valleys of the faceted surface. Our work demonstrates that the faceted metal surfaces are promising templates for the growth of metal nanoparticles.

1. Introduction

There is increasing evidence that the shape and size of supported metal nanoparticles affect the rate and selectivity of catalytic reactions [1,2]. Supported gold nanoparticles have been shown to be exceptionally active for several reactions, including low-temperature CO oxidation [3,4]. Some authors believe that metallic gold play the role for the activity and that the gold particle size is a critically important parameter in determining its catalytic behavior [5–7]. Others suggest that nonmetallic gold species are responsible for the activity [8,9]. Gold nanoparticles have been prepared on oxide surfaces, such as $TiO_2(110)$ and $CeO_2(111)$, and the NiAl(100) alloy surface [5,10,11]. On these surfaces, gold first decorates step edges, or point and line defects on terraces, and then grows into large nanoparticles. Only after saturation of these nucleation sites do gold nanoparticles start to grow on terraces. Moreover, as it is difficult to control spatial distributions of step edges, point and line defects and nucleation sites on terraces, the gold nanoparticles are distributed randomly on these surfaces. One promising way to prepare metal nanoparticles, with controlled size and arrangement, over a large surface area is to use a template for the self-assembly of nanoparticles. Various templates with ordered rippled structures grown on metal single crystal surfaces have been exploited for growing metal nanoparticles [12–17]. One such template is the moiré patterns formed when graphene is grown on Ir(111), on which the growth of monodispersed Ir clusters has been achieved [12]. On the hexagonal boron nitride nanomesh over Rh(111), arrays of Co nanoparticles have been fabricated [16].

Here we report on the growth of gold nanoparticles on a different template: the oxygen-covered faceted Ru(11–20) surface. Faceting of the Ru(11–20) surface by NO_2 dosing at elevated temperatures has been studied in detail elsewhere [18]. In this study, the faceted O/Ru (11–20) surface, composed of parallel ridges, is used as a template for the growth of gold nanoparticles. By depositing gold onto the faceted Ru(11–20) surface held at room temperature, gold nanoparticles are observed to nucleate preferentially within valleys of the faceted surface. The size distributions of gold nanoparticles are narrow and their average size can be controlled by changing the gold coverage.

2. Experimental

All experiments were performed in an Omicron ultra high vacuum (UHV) chamber with a base pressure of about 2×10^{-10} Torr. The chamber contains scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The Ru(11–20) sample used in this study is approximately 10 mm in diameter and 1 mm thick. The clean Ru(11–20) surface was prepared by cycles of electron beam heating in oxygen (1×10^{-7} Torr) followed by flashing to 1650 K. The cleanliness of the Ru surface was checked by AES and the residual species such as carbon, oxygen, and nitrogen were below 1% of a monolayer of atoms. NO_2 and O_2 were used in the experiment by backfilling the chamber. All exposures shown here are in Langmuir ($1\ L=10^{-6}$ Torr•s) and are uncorrected for ion gauge sensitivity. The sample temperature was monitored using an infrared pyrometer.

The fully faceted Ru(11–20) surfaces were prepared by dosing the clean and planar surfaces with $\geq$20 L NO_2 at 800 K. The structure and

* Corresponding author.
E-mail address: shenq@physics.rutgers.edu (Q. Shen).

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.05.011

chemical composition of faceted surfaces were determined by STM, LEED, and AES after preparation. The faceted surfaces were held at room temperature when depositing gold onto these surfaces for growth of gold nanoparticles. A freshly prepared faceted O/Ru(11–20) surface was used for gold deposition for each gold coverage. Gold was evaporated from a home-made thermal evaporator. The gold coverage was calibrated based on the Auger Au(NVV, 69 eV)/Ru(MNN, 273 eV) peak-to-peak height ratio obtained when depositing gold onto clean and planar Ru(11–20) surface. The gold dose is expressed in units of monolayer (ML), and 1 ML is the areal atom density of the planar Ru(11–20) surface. The deposition rate of gold is estimated to be ~0.017 ML/min, and various gold coverages were obtained by changing the deposition time onto the oxygen-covered faceted Ru(11–20) surface with this fixed deposition rate.

3. Results and discussions

The faceted Ru(11–20) surface presents a "hill and valley" structure, exposing new crystalline faces, compared with the initially planar surface. These new faces are (10–11), (10-1-1), (01–11), and (01-1-1), identified by comparing LEED diffraction patterns with the prediction of a kinematical simulation [18]. All of the facets share the same surface structure. Fig. 1(a) shows a large-scale (500 nm × 500 nm) STM image of the faceted surface prepared by dosing the Ru surface with 60 L NO_2 at 800 K. The faceted surface consists of uniform ridges running along the [0001] direction with four facets forming the ridges. The parallel ridges can extend as long as several hundred nanometers without interruption. The morphology of faceted surfaces prepared at higher NO_2 doses (<1000 L) does not show any significant differences.

Fig. 1(b) is a 20 nm × 20 nm X-slope image of the faceted surface, which was obtained by differentiating the height of the original STM image along X direction (scanning direction). In this way, details of the surface topology are enhanced at the cost of losing height information. Two facets are arranged on each side of the ridge. The average width of the ridges (bottom to bottom distance) is approximately 6 nm [18]. The ridge structures of the faceted surface can be removed by flashing the sample to 1650 K. The preparation and removal of the faceted surface is reversible. The faceted surface is covered only with oxygen as confirmed by AES measurements [18].

Fig. 2(a) is a 20 nm × 20 nm STM image obtained from the faceted surface after deposition of 0.3 ML gold onto the oxygen-covered faceted Ru(11–20) surface held at room temperature. Fig. 2(b) is the profile of the line scan "AB" in Fig. 2(a). The height of the gold nanoparticle is lower than that of adjacent ridges as shown by the profile. Fig. 2(c) is an X-slope image produced from the original STM image, establishing better definition of gold nanoparticles and substrate ridges. Gold nanoparticles have formed on the faceted surface and nucleate preferentially in valleys. Fig. 2(d) is a 50 nm × 50 nm X-slope image of the gold-covered O/Ru(11–20) surface, illustrating the uniformity of nanoparticle size but also regular spatial distributions of gold nanoparticles.

If the dimensions of ridge structures are comparable to those of tips, the accuracy of STM images can be significantly affected by tip-surface convolutions. However, the facets and Au nanoparticles are clearly resolved in Figs. 1(b) and 2(c), which indicates that the tips are sufficiently sharp so as not to cause significant distortion of the surface morphology. Fig. 2(e), (f), and (g) contain histograms of the gold particle size distributions for 0.3 ML gold coverage. The mean length, mean width, and mean height of the gold nanoparticles are 2.82 nm, 1.70 nm, and 0.54 nm, respectively, without considering the effect of tip-surface convolutions.

Metal nanoparticles with various sizes prepared on supports have different shapes. Not only do large nanoparticles exhibit well-defined structures [19], but small nanoparticles (~1 nm) on oxidized surfaces also have the high degree of atomic ordering as shown by a recent study [20]. For small gold nanoparticles confined within valleys in our study, however, the STM images obtained here do not reveal well-defined Wulff-like structures. Therefore, to calculate volume of nanoparticles we have chosen to take their shape to be a prism of a triangular cross section and of dimensions equal to the mean length, width, and height of the nanoparticle ensemble. With these assumptions, the volume of a gold nanoparticle with the mean dimensions is determined to be 1.29 nm^3. Based on the average nanoparticle size and the number density of nanoparticles, the amount of gold contained in nanoparticles is estimated to be 0.26 ML, which is in good agreement with the surface coverage as determined using AES. From this we conclude that most of the gold atoms deposited onto the oxygen-covered faceted surface forms nanoparticles.

Previous studies indicate that gold wets the clean Ru(0001) surface, forming a pseudomorphic monolayer first, followed by a layer-by-layer growth mode. In contrast, gold grows in three-dimensional islands on the O/Ru(0001) surface [21–26]. The difference of the growth behavior of gold on the clean and oxygen-covered Ru(0001) surface is attributed to the significant lowering of the surface energy of Ru by adsorbed oxygen [21–23,25]. The faceted Ru(11–20) surface in this study is covered by ~1.2ML oxygen, which exceeds the saturated oxygen coverage obtained by dosing the planar surface with O_2 at room temperature [18]. Based on the similarity to the behavior of gold on Ru(0001), we attribute experimentally observed three-dimensional growth of gold on the oxygen-covered faceted surface to the reduced surface free energy induced by covered oxygen.

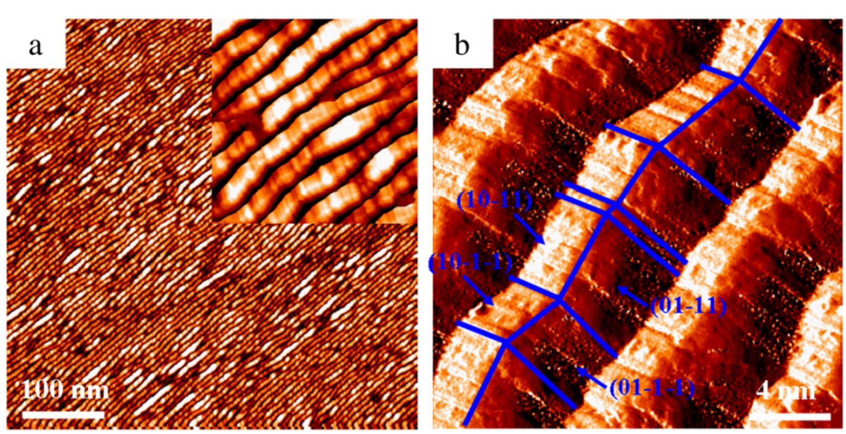

Fig. 1. STM images of the faceted O/Ru(11–20) surface prepared by dosing 60 L NO_2 onto the planar Ru(11–20) surface at 800 K. (a) A large-scale (500 nm × 500 nm) STM image of the fully faceted surface. The inset (50 nm × 50 nm) shows ridges on the faceted surface. (b) X-slope image (20 nm × 20 nm) obtained from its original STM image, showing that the facets (10–11) and (10-1-1) are arranged alternately on one side of a ridge while the other two facets (01–11) and (01-1-1) on the other side of the ridge.