Preparation and characterization of hexagonal shaped nanostructures on Au (111) in UHV

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〈ABSTRACT〉

The nanostructure fabrication with energetic ions is a critical tool in the laboratory and industry. The ion-solid collision process at the elevating temperature contains fascinating surface physics, chemistry, and material science. In this article, we report fabrication methods of hexagonal shaped nanostructures by using neon and oxygen ion bombardment at different temperatures. By adjusting ion energy, flux, and sample temperature, we were able to control the depths and diameters of the nanostructures. The morphology and bonding configurations of the nanostructures were monitored by STM and XPS. Oxygen ion bombardments of Au (111) result in Au-O complex structures, which represent activated gold nanoparticles for CO oxidation reaction and can give a clue to solve their unusual catalytic activities.

1. Introduction

Gold has been treated as an inert material for many years. However, since the studies of Haruta et al., demonstrated unusual catalytic activities of oxide supported Au nanoparticles for CO oxidation even at temperature below 200K, lots of efforts to understand underlying reasons for the enhanced catalytic activity have been being made. One of the primary explanation is that the gold nanoparticles possess lots of undercoordinated gold atoms, which act as binding sites for CO or dissociated sites for O₂ atoms. Goodman research group suggested that catalytic activity of gold nanoparticles is due to the different electronic properties where the gold nanoparticles less than 3 nm in diameter present a band gap between conduction and balance bands. An alternative explanation of the origin of the catalytic activity is the charge transfer to/from the oxide support from/to gold nanoparticles which result in positive or negative oxidation states in gold.

In surface science approach for the catalytic

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process, well-defined model systems are usually employed. Either metal nanoparticles can be vapor deposited on oxide single crystal or nanocrystalline oxide can be prepared on the metal surface, called inverse model catalysts. This approach allows the exploitation of all the surface analysis techniques for precise characterization of the model catalytic system. The scanning tunneling microscopy (STM) is known as a primary tool for this approach since it can visualize 3-D images of catalytic system and provide electronic information in atomic scale.

Recently, we demonstrated that the density of the undercoordinated sites on Au (111) are directly proportional to CO adsorptions by using STM, infrared reflection absorption spectroscopy (IRAS), and density functional theory (DFT) calculation. Hexagonal shaped nanostructures on Au (111) surface were carefully prepared by ion bombardments and CO gas was dosed on this surface. The weakly bound CO at the undercoordinated sites induced irreversible morphological changes of the surface even at temperature below 180K and very low CO pressure ($5 \times 10^{-9}$torr). However, we haven’t explained the detailed preparation methods and physical property of the surface.

In this present work, we report on STM studies of nanostructures on Au(111) surface prepared by using neon and oxygen ion bombardments. In particular, we focus on the fabrication methods of the hexagonal shaped nanostructure by controlling the ion energy, flux, duration time and temperatures. And we explored the underlying reasons for the morphological changes as a function of annealing temperatures.

2. Experimental

All experiments were performed in ultrahigh vacuum (UHV) system, with a base pressure of $5 \times 10^{-11}$ mbar, equipped with a variable temperature scanning tunneling microscope (VT–STM), ion gun, and x-ray photoelectron spectroscopy (XPS). Clean Au (111) surface was prepared after Ne$^+$ ion sputtering and subsequent annealing at 700K. Ne$^+$ and O$^+/O_2^+$ ion bombardments for nanostructure fabrication were performed at the surface normal and the ion flux was determined by measuring the grounding current. STM measurements were done with electrochemically etched tungsten tips. All of the images shown here were taken at room temperature in the constant current mode with a tunneling current of 1 nA at sample biases, ranging from $-2.0$ V to $+2.0$ V. After image acquisition, a background plane fit was applied to all of the images.

3. Data and results

The clean Au(111) surface as shown in Figure 1(a) exhibits the well known herringbone $2 \times \sqrt{3}$ reconstruction, which contain 4% more atoms than Au (111) plane in the bulk. The herringbone reconstruction consists of two surface domains; periodic arrangement of stressed domain separated by soliton wall and partially dislocated soliton wall, called herringbone. The main reasons for the surface reconstruction have been known to minimize the tensile stress and an elastic energy related to anisotropy of the stress relief in the soliton reconstruction.

Low energy Ne$^+$ ion bombardments of Au (111) led to tiny pits (nanopits) with the diameter of 1~2 nm [Figure 1(b)]. The number density of the pits is pretty comparable to the impinging ion flux, suggesting that single ion impact is most likely responsible for the each nanopit. The depth profiling of the nanopits clearly shows one layered deephole, whereas tiny bumps were also observed as indicated by dashed arrow. A possible explanation of why those pits and bumps can be generated on the surface would be following. When