



Formation of bismuth nanodot in (4×4) vanadium oxide nanomesh on Pd(111)

S. Hayazaki^a, T. Matsui^{a,b}, H.L. Zhang^c, W. Chen^c, A.T.S. Wee^c, J. Yuhara^{a,*}

^aSchool of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

^bEcotopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

^cDepartment of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

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ABSTRACT

The formation of bismuth (Bi) nanodots on a well ordered (4×4) vanadium oxide nanomesh on Pd(111) has been investigated by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). At very low Bi coverage of 0.01 ML, a Bi atom locates in the vanadium oxide nanomesh and every Bi atom forms an isolated Bi nanodot. At the Bi coverage of 0.06 ML, two different heights of Bi nanodots are observed by STM. When the Bi coverage increased to 0.2 ML, most of the nanoholes in the nanomesh are occupied by Bi nanodots, and the remaining Bi atoms form Bi clusters on the vanadium oxide surface.

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1. Introduction

The fabrication of single-molecular devices, conductive molecular nanowires, etc. has received much attention recently. So far, electrical properties of single molecules on metal and semiconductor surfaces have been investigated experimentally as well as theoretically by means of scanning tunneling spectroscopy (STS) with scanning tunneling microscopy (STM) or atomic force microscopy (AFM) [1–10]. To identify the electrical properties of single molecules, interactions between molecules also have to be taken into account because of the many equivalent adsorption sites close to each other, on the crystalline surface. In addition, the bigger molecules sometimes contact on the metal surface at several places.

The fabrication of surface nano-templates that are artificially or naturally patterned has been recently studied for the purpose of preferential adsorption of molecules, atoms, and nano-clusters [11–22]. Using the nano-templates, nanodots can be fabricated periodically at the nanoscale in a self-assembly process. Reactive molecules may adsorb to these nanodots as a single molecule without any inter-molecular interaction, resulting in the possibility of the measurement of the electrical properties of a single molecule on a metal surface even at room temperature. A vanadium surface oxide on Pd(111) has been studied recently, and is found to form a (4×4) nanomesh structure [23–26]. The detailed surface structure of the nanomesh has been identified by low-energy electron dif-

fraction (LEED) analysis and ab initio density functional theory (DFT) calculations [26]. Therefore, it will be interesting to examine the metal nanodot formation at the (4×4) nanomesh for the purpose of controlled metal contact of single molecule devices.

In the present paper, we report bismuth (Bi) nanodot formation at the (4×4) vanadium surface oxide nanomesh on Pd(111) and analyze the geometric and electronic structure by STM, low-energy electron diffraction (LEED), and X-ray photoemission spectroscopy (XPS).

2. Experiment

The experiments were carried out under ultrahigh vacuum (UHV) conditions with a base pressure less than 5×10^{-10} mbar in the sample preparation chamber, and $<4 \times 10^{-11}$ mbar in the analysis chamber. To prepare a clean Pd(111) surface, the crystal was sputtered by 2-keV Ar⁺ ions at room temperature, followed by an annealing to 700 °C. The sample was heated by electron bombardment from the backside. Additionally, the Pd(111) surface was exposed to molecular oxygen (3×10^{-8} mbar) at 500 °C, followed by a flash to 700 °C to get rid of impurities such as hydrogen. The cleanliness of the sample was checked by Auger electron spectroscopy (AES) and LEED observation, showing no contaminations and a distinct (1×1) LEED pattern, respectively.

A vanadium film was deposited on Pd(111) at room temperature in UHV from a well degassed water-cooled electron beam evaporator at a deposition rate of about 0.2 monolayer/min measured by a quartz crystal microbalance. The amount of deposited

* Corresponding author. Tel.: +81 52 789 3792; fax: +81 52 789 3779.

E-mail address: j-yuhara@nagoya-u.jp (J. Yuhara).

vanadium was fixed at ~ 0.3 ML. After deposition, the vanadium films on Pd(111) were annealed at 300 °C in O₂ at a partial pressure of 2×10^{-7} mbar and cooled to room temperature at the same oxygen pressure. This vanadium oxide surface on Pd(111) exhibited a distinct (4×4) pattern. Bismuth was then deposited onto the (4×4) vanadium surface oxide nanomesh at room temperature using a boron nitride crucible in a water-cooled evaporator at a deposition rate of 0.1 monolayer/min. The amount of Bi deposited was determined by the quartz crystal microbalance and was varied between 0.01 and 0.2 ML.

The STM experiments were performed in the UHV analysis chamber equipped with a customized Omicron room temperature STM-1, four-grid LEED optics, an electron gun, an X-ray source and hemispherical analyzer for AES and XPS, and a mass spectrometer for residual gas analysis. All STM images were obtained in constant current mode with positive sample bias voltage. XPS data have been recorded with a VG CLAM2 analyzer that uses Mg K α X-ray source ($h\nu = 1253.6$ eV). The overall resolution of the spectrometer was 0.1 eV.

3. Results and discussion

Fig. 1a and b shows STM images of the (4×4) vanadium oxide on Pd(111) at the vanadium coverage of 0.31 ML. From the large scale STM image, the (4×4) structure was observed all over the surface at this vanadium coverage, in good agreement with Ref. [26]. The LEED pattern shows very sharp (4×4) spots as shown in the inset at the lower right corner of Fig. 1a. The high-resolution STM image in Fig. 1b shows a honeycomb (4×4) structure. Since the vanadium oxide forms a (4×4) structure, the distance between nanoholes is estimated to be 1.1 nm. These nanoholes are

used in the present study as a nano-template to fabricate Bi nanodots periodically spaced at intervals of 1.1 nm.

Bismuth was deposited onto the (4×4) vanadium oxide nanomesh on Pd(111) at room temperature in order to examine the Bi nanodot formation. Fig. 1d and e show STM images after 0.01 ML Bi deposition onto the (4×4) nanomesh at room temperature. It is seen from Fig. 1d that the nanomesh is stable against Bi deposition. No difference could be observed in the LEED spots, as shown in the inset at the lower right corner of Fig. 1d. The Bi nanodots can be seen as the large protrusions with uniform height at the position of nanoholes. They are isolated from each other at this Bi coverage. The coverage of the nanodots is in good agreement with the Bi coverage deposited. Therefore, it is concluded that each nanodot contains one Bi atom at this lowest coverage. Since a uniform and large (~ 1 nm) protrusion is observed at each Bi nanodot in the STM image although there is only one Bi atom inside, the Bi atom might be mobile in the nanohole. At this lowest coverage, no bismuth locates on-top of vanadium atoms. Moreover, the nanodot positions did not change at all during the STM observation. It is concluded that the Bi atoms deposited locate inside the nearest nanohole and do not move beyond the nanohole at room temperature.

Fig. 1c and f shows a cross-sectional profile along the solid white line in Fig. 1b and e, respectively. The vanadium at the on-top site (V1) that is the brightest spot is found to be slightly higher than the vanadium in the threefold hollow site (V2). The height of the Bi nanodot is almost the same as the vanadium in the threefold hollow site (V2). Since the height of the vanadium in the threefold hollow site (V2) is reported to be 0.32 above the Pd(111) surface [26] and the atomic size of Bi is 0.31 nm, Bi seems to directly bond with Pd in the nanohole.

Since the vanadium oxide nanomesh has a (4×4) structure and each unit cell has one nanohole, the ratio of nanoholes to Pd atoms

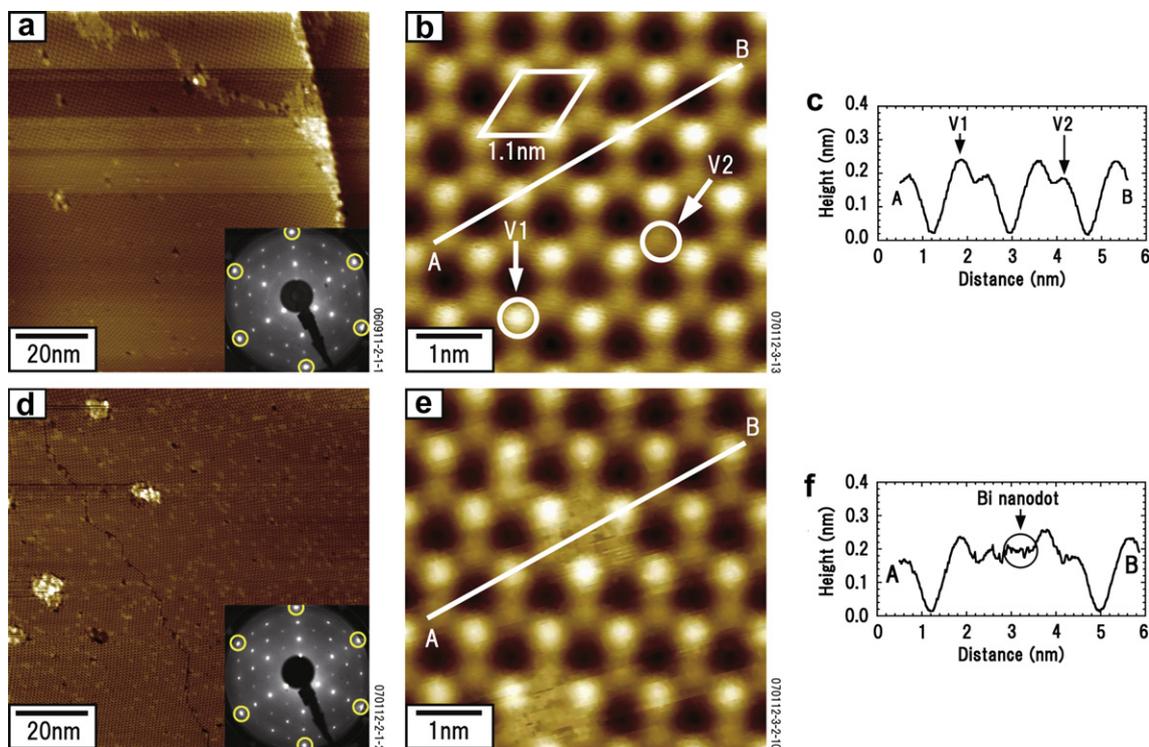


Fig. 1. STM images of the (4×4) vanadium oxide nanomesh on Pd(111): (a) large scale image, $V_s = 1.0$ V, $I = 0.5$ nA, and (b) high-resolution image, $V_s = 2.0$ V, $I = 0.6$ nA showing 4×4 unit cell. Two different vanadium positions are marked by V1 and V2. The inset at the lower right corner in (a) shows LEED pattern taken after STM observation. (c) Cross-sectional profile as marked by the solid line in panel (b). STM images of 0.01 ML Bi deposition onto the (4×4) vanadium oxide nanomesh on Pd(111): (d) large scale image, $V_s = 1.0$ V, $I = 1.0$ nA and (e) high-resolution image showing the Bi nanodots isolated from each other, $V_s = 2.0$ V, $I = 0.6$ nA. The inset at the lower right corner in (d) shows LEED pattern taken after STM observation. (f) Cross-sectional profile as marked by the solid line in panel (e).

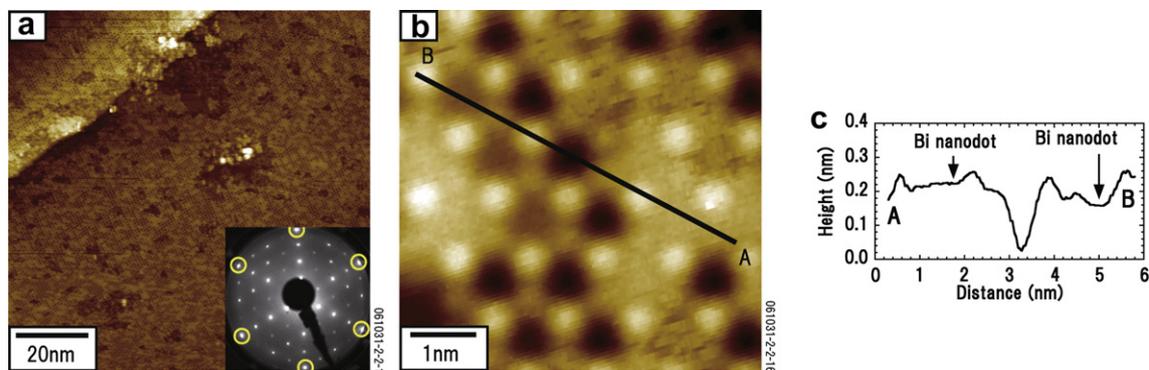


Fig. 2. STM images of 0.06 ML Bi deposition onto the (4×4) vanadium oxide nanomesh on Pd(111): (a) large scale image, $V_s = 1.5$ V, $I = 1.0$ nA and (b) high-resolution image showing the adjacent Bi nanodots on VO nanomesh, $V_s = 2.0$ V, $I = 1.0$ nA. (c) Cross-sectional profile as marked by the solid line in panel (b).

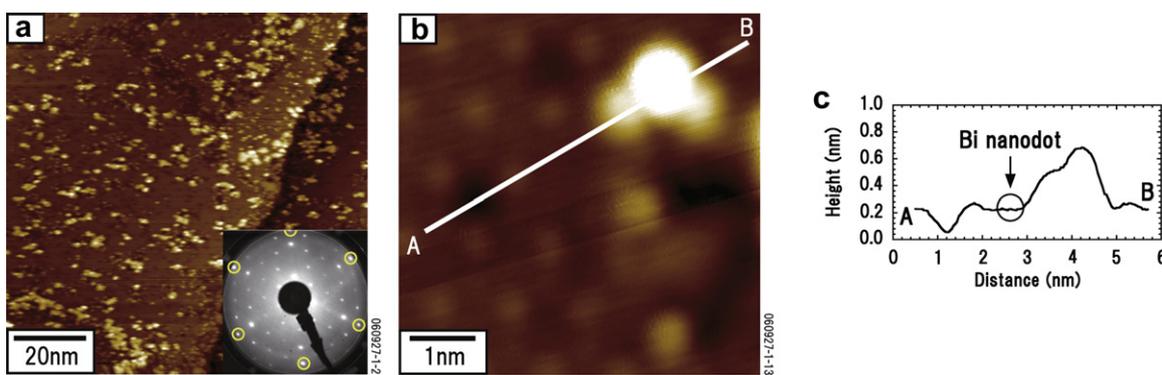


Fig. 3. STM images of 0.2 ML Bi deposition onto the (4×4) vanadium oxide nanomesh on Pd(111): (a) large scale image, $V_s = 2.0$ V, $I = 0.6$ nA and (b) high-resolution image showing the Bi clusters on VO nanomesh, $V_s = 2.0$ V, $I = 0.6$ nA. (c) Cross-sectional profile as marked by the solid line in panel (b).

in the first layer is 1/16, namely a coverage of 0.06 ML. Therefore, to investigate multiple Bi adsorptions in a single nanohole, a Bi coverage of 0.06 ML was deposited on the (4×4) vanadium oxide nanomesh. As shown in Fig. 2, the STM images identified empty nanoholes as well as Bi nanodots that are adjacent with each other. All Bi atoms deposited are located in the nanoholes and no Bi islands are observed. The STM images at the Bi nanodots show two levels of brightness (Fig. 2b). Fig. 2c shows a cross-sectional profile along the black line in Fig. 2b. We can see two different heights of Bi nanodots. These results indicate the single and multiple Bi adsorptions in the nanoholes. No spatial correlation was observed between nanoholes or nanodots.

It is also interesting to note that the (4×4) vanadium oxide nanomesh becomes more stable against subsequent Bi adsorption. It is reported that the (4×4) nanomesh is completely decomposed after dosing 2 L of molecular hydrogen [26]. From the experiment of molecular hydrogen exposure at the (4×4) vanadium oxide with Bi adsorbates, it is found that Bi stabilize the (4×4) vanadium oxide against hydrogen gas at least ten times. Since it is reported that molecular hydrogen dissociates on Pd(111) [27,28], Bi adsorption at the nanoholes may prevent molecular hydrogen from dissociation at the first Pd layer in the nanoholes.

Next, we increased the Bi coverage up to 0.2 ML to examine the stability of the vanadium oxide nanomesh against multiple Bi adsorptions. Fig. 3 shows the STM images after the 0.2 ML Bi deposition onto the vanadium oxide nanomesh. Most of the nanoholes are now filled with Bi atoms and some Bi atoms form Bi clusters on-top of the vanadium in the threefold hollow site (V_2), as shown in Fig. 3b. The height of the Bi cluster is 0.3–0.5 nm. Since some nanoholes are not filled with Bi atoms even at such a high Bi

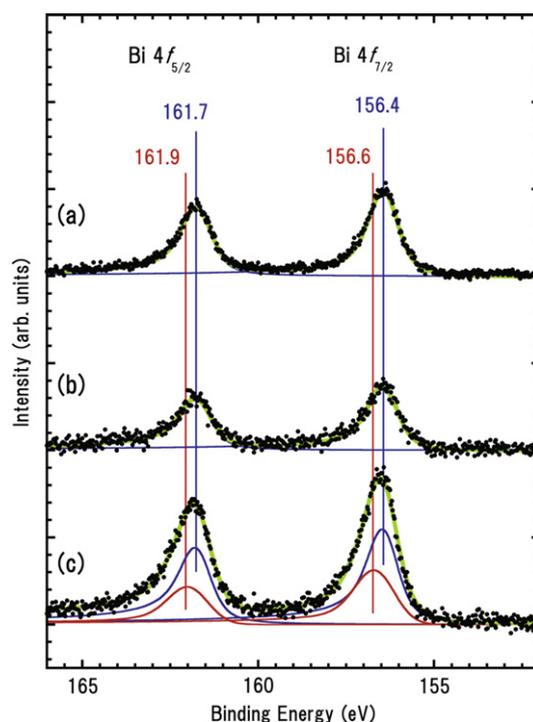


Fig. 4. XPS spectra at Bi 4f core level of (a) 0.2 ML Bi film on Pd(111), (b) 0.06 ML Bi deposition onto the (4×4) vanadium oxide nanomesh on Pd(111), and (c) 0.2 ML Bi deposition onto the (4×4) vanadium oxide nanomesh on Pd(111).

coverage, the Bi mobility on vanadium oxide with Bi-filled nanoholes does not appear to be high at room temperature.

Typical XPS spectra of the Bi 4*f* core levels of the Bi film on clean Pd(1 1 1) and Bi nanodots at the (4 × 4) vanadium oxide nanomesh on Pd(1 1 1) are shown in Fig. 4. The Bi 4*f* 7/2 peak for the Bi film on Pd(1 1 1) is at a binding energy of 156.4 ± 0.05 eV. Since the Bi 4*f* 7/2 peak for pure Bi is 157.0 eV ± 0.05 [29], the Bi 4*f* peak for the Bi film shifts 0.6 eV towards lower binding energy. The Bi 4*f* 7/2 peak for the 0.06 ML Bi coverage at the (4 × 4) nanomesh on Pd(1 1 1) is consistent with the Bi peaks for the Bi on Pd(1 1 1). It is proposed that Bi atoms do not adsorb at the vanadium oxide nanomesh, but directly adsorb on the first Pd layer in the vanadium oxide nanoholes. On the other hand, the Bi 4*f* peaks for the 0.2 ML Bi coverage at the (4 × 4) nanomesh on Pd(1 1 1) are broader, and they can be fitted by two components, namely the original peak position (156.4 eV) and a higher binding energy component which has 156.6 ± 0.05 eV. This new peak shift is attributed to Bi clusters at the vanadium oxide nanomesh.

We have studied other foreign metal adsorption, e.g. Au, Ag, Cu, Co, and Sn, at the (4 × 4) vanadium oxide nanomesh at 0.2 ML coverage. Interestingly, none of the metals adsorbed in the nanoholes. Moreover, the (4 × 4) nanomesh was completely destroyed by the foreign metal depositions, except for Cu. For Cu deposition, the (4 × 4) nanomesh was partly destroyed and Cu atoms form clusters at the edge of (4 × 4) domains. Therefore, it is found that the Bi adsorption at the (4 × 4) vanadium oxide nanomesh is a specific phenomenon.

4. Conclusions

The adsorption of very low coverages (<0.2 ML) of bismuth on the (4 × 4) vanadium oxide nanomesh on Pd(1 1 1) has been investigated by STM. At the lowest coverage of 0.01 ML, the formation of isolated Bi nanodot was observed. At the Bi coverage of above 0.06 ML, two different heights of Bi nanodots were observed with Bi atoms occupying most of the nanoholes. From XPS measurement, it is found that Bi atoms deposited at very low coverage go into the nanoholes and directly adsorb on first Pd layer. When the Bi coverage increased, some Bi atoms form clusters at the vanadium oxide nanomesh.

Acknowledgments

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