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Scanning tunnelling microscope studies of growth of $RuO_2(110)$ thin layer on Ru(0001)*

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This paper reports that the growth of $RuO_2(110)$ thin layer growth on Ru(0001) has been investigated by means of scanning tunnelling microscope (STM). The STM images showed a domain structure with three rotational domains of $RuO_2(110)$ rotated by an angle of 120°. The as-grown $RuO_2(110)$ thin layer is expanded from the bulk-truncated $RuO_2(110)$ due to the large mismatch between $RuO_2(110)$ and the Ru(0001) substrate. The results also indicate that growth of $RuO_2(110)$ thin layer on the Ru(0001) substrate by oxidation tends first to formation of the Ru-O (oxygen) chains in the [001] direction of $RuO_2(110)$.

Keywords: ruthenium oxide, growth, scanning tunnelling microscope
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1. Introduction

In recent years, the study of oxide formation on transition metal (TM) surfaces have attracted much interest since it is of great importance in many disciplines such as surface coatings in materials science and supported metal particles in heterogeneous catalysis. Considerable advances have recently been made in the microscopic understanding of oxide formation on TM surfaces.[1−4] As a member of TM, the oxygen-rich Ru(0001) surfaces with thin layers of RuO_2 are considered as a model system for CO oxidation.[5−8] In such a system, the CO oxidation increases drastically when the chemisorbed oxygen species is replaced by oxygen.[7] Therefore, the growth of RuO_2 thin layers and the existence of a clean view of the oxidation structure of Ru(0001) surface are very important.

In this paper, we report our investigations on growth of RuO_2 thin layers, the morphological and structural features of the RuO_2 thin layers, and on the Ru(0001) surface by mean of scanning tunnelling microscope (STM).

2. Experimental

The experiments were performed in a multifunctional ultrahigh-vacuum system (Omicron) with a base pressure less than 2×10^{-5}mPa. The system has been described in detail elsewhere.[9−11] In brief, it consists of a fast entry lock for sample and tip loading, a preparation chamber, an analysis chamber, and a STM/AFM (atomic force microscope) chamber. The system is equipped with a few of resistive-heating and electron-beam-heating evaporators, an electron-bombardment sample heater, an argon-ion sputter gun, a low-energy electron diffraction (LEED) optics, ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS).

The cleaning of the Ru(0001) surface was achieved by several cycles of argon-ion sputtering and annealing, and the sample cleanliness was verified by LEED, STM and XPS measurements. The thin layers of RuO_2 were prepared by exposing the well-prepared Ru(0001) surface to high doses of O_2 at the sample temperature of about 700 K. Oxygen doses were done through a doser (a tube of about 150 mm long and 1.5 mm in diameter, directed to the sample with a dis-

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tance of about 5 mm from the end to the sample). The typical pressure in the chamber is about 5×10mPa during O_2 exposing. After the preparation, the sample was annealed to 600 K (about 10 min) for removing any contamination. All the STM measurements were taken at room temperature.

3. Results and discussion

Figure 1(a) shows the structure of RuO_2(110) thin layer, the outermost oxygen chains are aligned in the [001] direction. Figure 1(b) gives a brief top view for epitaxial growth of RuO_2(110) thin layer on Ru(0001), and the lattice constant of the bulk-truncated RuO_2(110) surface is given in comparison with the substrate lattice. Apparently the mismatch between RuO_2(110) and Ru(0001) is large, especially in the [10-10] direction of Ru(0001) (or [-110] of RuO_2(110)).

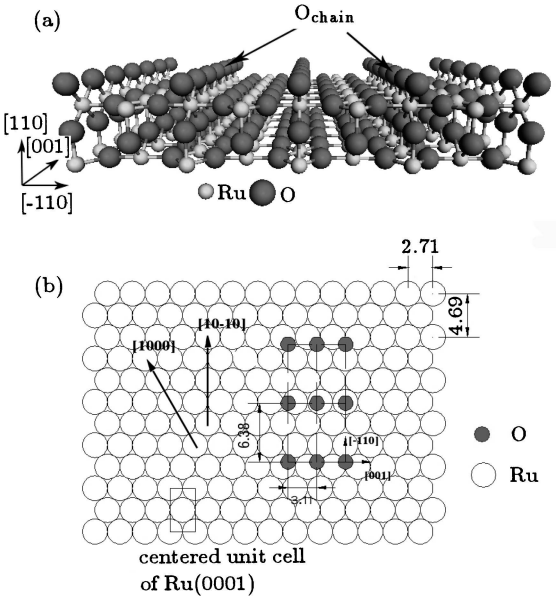


Fig.1. (a) Schematic diagram of the structure of RuO_2(110) thin layer, the oxygen chains aligned in [001] are indicated, and (b) top view of the domain of RuO_2(110) on the Ru(0001)substrate, the lattice constants of Ru(0001) and RuO_2(110) are indicated for comparison.

Figure 2 shows the STM image of the as-grown RuO_2(110) thin layer on Ru(0001) prepared by a high dose of O_2 (O_2 pressure of 5×10mPa, 3 min) to Ru(0001) at a sample temperature of 700 K, and apparently the surface was very rough. Two typical areas were found as shown in this figure. The under-layer which was marked as area A is the well-grown RuO_2(110) (also see the image in Fig.3), while the upper-layer marked as area B showed some chain-structures that along the [1000] direction of Ru(0001), and the chain-structures in the STM image can be recognized as the outer-most oxygen chains along the [001] direction of RuO_2(110) (as shown in Fig.1) at the present tunnelling condition[1,10,12]. The chain structures of the upper-layer are not regularly defined, especially the distributions of the chain length (see detailed discussions about this below).

As we know, the RuO_2(110) has twofold axes, while the substrate Ru(0001) has threefold symmetry. On the basis of symmetry, the thin layer of RuO_2(110) grown on Ru(0001) should exhibit a domain structure with three rotational domains of RuO_2(110) rotated by an angle of 120°. In our experiment, the domain structures of as-grown RuO_2(110) with the oxygen chains along the equivalent [1000] direction of the Ru(0001) substrate were found.

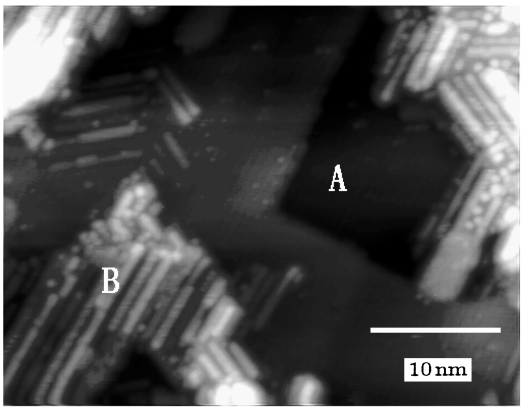


Fig.2. STM image of a RuO_2(110) thin layer grown on Ru(0001) with a high doses (O_2 pressure of 5×mPa, 3 min) of O_2 at a sample temperature of 700K. The image was taken at tunnelling conditions of I=1.2 nA, and V_s=–1.0 V.

Figure 3 shows a STM image of the well-grown RuO_2(110) thin layer, a typical region of area A as shown with better resolution in Fig.2. The unit cell (about 7.63×3.25Å^2) of RuO_2(110) is indicated. The bulk-truncated RuO_2(110) surface has a rectangular unit cell with dimensions of 6.38×3.11Å^2, while the centred unit cell of Ru(0001) is 4.69×2.71Å^2[12] (as shown in Fig.1). Apparently the substrate lattice is too small to allow a pseudomorphic growth of RuO_2(110) thin layer. As a consequence, the thin layer of RuO_2(110) can grow incommensurately, and the as-grown RuO_2(110) would be distorted to match the small Ru(0001) substrate lattice. To our sur-

prise, the grown $RuO_2(110)$ layer is expanding instead of shrinking in comparison with the bulk-truncated $RuO_2(110)$ surface. We think that the strain energy arising from mismatch between $RuO_2(110)$ and the Ru(0001) substrate may play an important role in this incommensurate (expanding) growth. The strain energy could be reduced by this elongation of $RuO_2(110)$ lattice in the [-110] direction from 6.38Å to 7.63Å (expanded by 19.6%). It should be noticed that the expansion along the [001] direction (from 3.11Å to 3.25Å, expanded by 4.5%) of the $RuO_2(110)$ lattice is not as large as that of the [-110] direction. This is due to the strong Ru–Ru attraction when the coordination of Ru is reduced in an ultrathin $RuO_2(110)$ layer and the misfit between the bulk-truncated $RuO_2(110)$ and the substrate Ru(0001) in the [001] direction (from 3.11Å to 2.71Å) is not as large as that in the [-110] direction of $RuO_2(110)$ (6.38Å to 4.69Å).

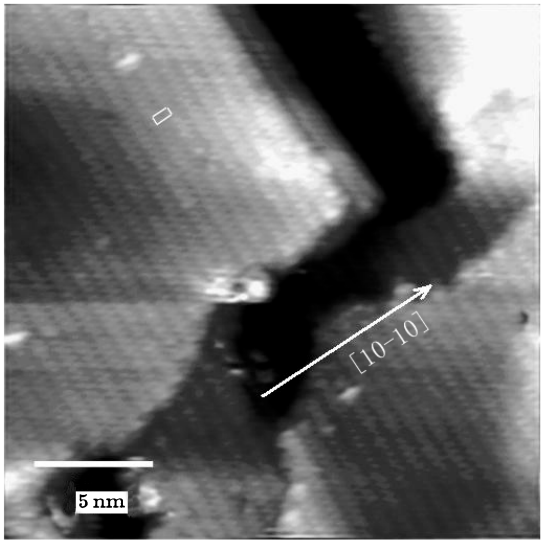


Fig.3. High resolution STM image of a well-grown $RuO_2(110)$ surface taken at tunnelling conditions of I=0.87 nA, and V_s=–0.55 V; the rectangular unit cell of $RuO_2(110)$ is indicated.

Figure 4 shows a STM image taken on an as-grown $RuO_2(110)$ thin layer by a higher dose of O_2 (O_2 pressure of 5×10mPa, 5 min) to Ru(0001) at a sample temperature of 700 K. Similar to the upper layer shown in Fig.2, The surface is full of these 3-fold domain structures with the oxygen chains along the equivalent [1000] direction of Ru(0001). It is clear that with a higher O_2 dose the surface becomes much rougher. Apparently, with higher O_2 dose, i.e., with a longer exposure duration at the same O_2 pressure, for growth $RuO_2(110)$ thin layer, the O atoms have more chance for diffusing into the bulk. Since the $RuO_2(110)$ lattice is larger than that of Ru(0001), there is not enough space to accommodate Ru atoms, and some Ru atoms may be lifted up to the outermost surface, which makes the surface rougher. However, at a certain temperature and partial oxygen pressure, the diffusion depth of O atoms is limited.

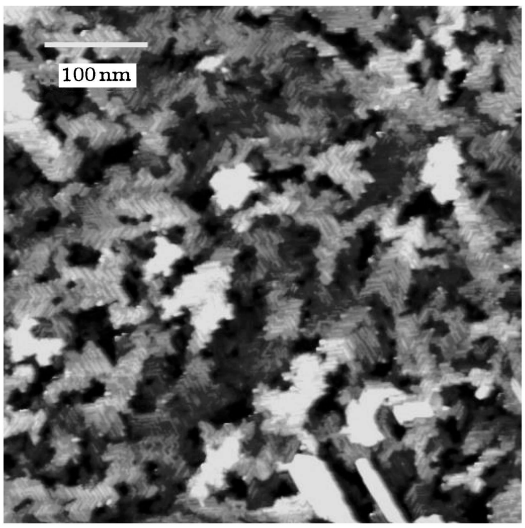


Fig.4. STM image of a $RuO_2(110)$ thin layer grown on Ru(0001) with a higher doses (O_2 pressure of 5×mPa, 5 min) of O_2 at a sample temperature of 700K. The image was taken at tunnelling conditions of I=0.35 nA, and V_s=1.0 V.

Figure 5 shows an enlarged STM image with better resolution. The most common distance between the oxygen chains are 9.32Å and 12.1Å, which are

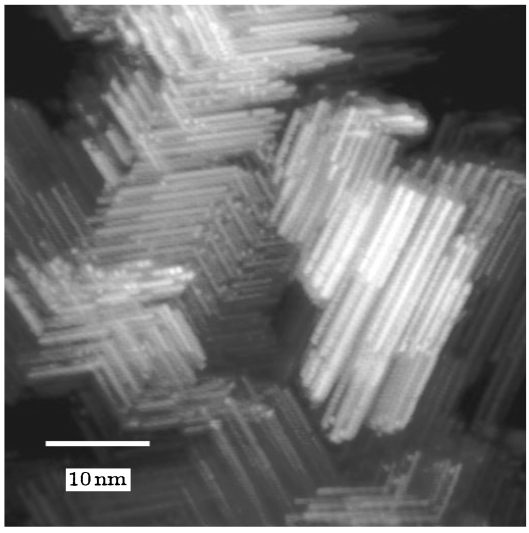


Fig.5. An enlarged STM image of a $RuO_2(110)$ thin layer is prepared with the same conditions as in Fig.4; it shows the chain structures with better resolution (I=0.66 nA, and V_s=–0.45 V).

about 3 and 4 times of the lattice constant of $RuO_2(110)$ in the [-110] direction(3.25Å). This im-

plies that some outermost oxygen chains are accommodated; the reason for this may be related to the repulsive interaction between the oxygen chains since formation of dipoles at the outermost surface can be imaged due to the change transfer between Ru atoms and outermost O atoms. As well as the oxygen chain structures shown in Fig.5, we also know that the lengths of the chains are not regular, i.e. the formation of the chain structure is not started from a step, or not from a defect. The results also indicate that growth of RuO_2(110) thin layer on the Ru(0001) substrate by oxidation tends first to grow Ru–O (oxygen) chains in the [001] direction.

4. Conclusion

We have carried out STM measurements for RuO_2(110) thin layer grown on Ru(0001) by high O_2 doses at substrate temperatures of 700 K. The results showed three rotational domains of RuO_2(110) with a rotational angle of 120° The as-grown RuO_2(110) thin layer is expanded from the bulk-truncated RuO_2(110) of $6.38\times3.11\text{Å}^2$ to $7.63\times3.25\text{Å}^2$ because of the large mismatch between RuO_2(110) and the Ru(0001) substrate. This results also showed that the growth of RuO_2(110) thin layer on the Ru(0001) substrate by oxidation tends first to form Ru–O (oxygen) chains in the [001] direction.

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