Epitaxial growth of \( \text{WO}_x \) nanorod array on \( \text{W}(001) \)

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Abstract

Nanorods of substoichiometric tungsten oxide (\( \text{WO}_x \)) were grown on \( \text{W}(001) \) substrates. Two methods for the growth of nanorods were used: oxidation of the substrate under appropriate conditions and the deposition of tungsten oxide from a tungsten foil heated in the presence of oxygen. The grown nanorods were observed using a scanning electron microscope and an atomic force microscope. The diameters of the nanorods were 5–20 nm. The nanorods were slightly inclined from the directions parallel or normal to the surface. The inclination of nanorods was explained in terms of the epitaxial relationship between \( \text{WO}_3 \) crystals and the \( \text{W}(001) \) substrate. The \( \text{WO}_3 \) crystals formed at the initial stage of growth act as the nuclei of \( \text{WO}_x \) nanorods. We observed selective enhancement of the growth in a certain epitaxial direction depending on the method of growth, and an array of \( \text{WO}_x \) nanorods was produced on the \( \text{W}(001) \) substrate.

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1. Introduction

Recently, various kinds of nanomaterials such as nanowires, nanorods, nanotubes and nanobelts have been fabricated using metal oxide [1–3]. These one-dimensional (1D) nanomaterials have become increasingly important due to their potential use in nanoelectronics for interconnections and field emitters, for example. These metal oxide nanomaterials with large aspect ratio are also considered to be applicable to tips for scanning probe microscopy. One of the most important issues in all these applications is to establish well-defined connections between the nanostructures and supporting substrates. It is also indispensable to control the orientations of 1D nanomaterials for various applications.

Rodlike structures of tungsten oxide having nanometer-scale diameter were formed under appropriately chosen growth conditions [4–7]. The rodlike structures showed various substoichiometries. In this paper, we report the techniques of growing tungsten oxide nanorods on single-crystal tungsten, and the epitaxial relationships between the nanorods and the \( \text{W}(001) \) surface. We also propose a method of enhancing the growth in a selected epitaxial direction.

2. Experimental

The growth of \( \text{WO}_x \) nanorods was performed in an ultrahigh-vacuum (UHV) chamber. The base pressure of the UHV chamber was \( 1.0 \times 10^{-10} \) torr. Tungsten (body-centered cubic structure) was used as a substrate. A single-crystal \( \text{W}(001) \) plate (4.8×4.8×0.5 mm) was cleaned by oxidation as follows. The substrate was oxidized by heating at 1000 K in \( 1 \times 10^{-5} \) torr \( \text{O}_2 \) and annealed at 1600 K under UHV conditions to remove tungsten oxides. By repeating this procedure several times, a clean \( \text{W}(001) \) surface to be used as a substrate for \( \text{WO}_x \) nanorod growth was prepared.

Two different growth methods were used for the formation of \( \text{WO}_x \) nanorods. The first method was nanorod
growth using tungsten oxide generated on the substrate surface, as shown in Fig. 1 (a) (growth method 1). The substrate was heated to 900–1000 K in 1×10⁻⁵ torr O₂ for 5 min to 3 h, resulting in the growth of nanorods. The second method (growth method 2) was the deposition of tungsten oxide from a tungsten foil as follows. The tungsten foil (5.0×10.0×0.025 mm) was placed in front of the substrate at a distance of 10 mm, as shown in Fig. 1(b). The substrate was heated to 900–1000 K in 1×10⁻⁵ torr O₂, and the tungsten foil was heated to 1200–1300 K. The grown nanorods were observed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) and an atomic force microscope (AFM, SII SPA-400) operated in air.

The grown nanorods were identified as WOₓ (x=2−3) on the basis of the contrast in the microscope images and the electron energy loss spectra obtained using an energy filtered transmission electron microscope (TEM). The value of x depends on the density of crystallographic shear (CS) planes that correlate with planar defects of oxygen layers [4]. It is known that various kinds of CS planes can be formed in WO₃ crystal [8,9]. Under the growth conditions adopted in this study, {001}-type CS planes were mainly formed in the nanorods.

3. Results and discussion

Fig. 2 (a) shows an SEM image of the WOₓ nanorods grown on the W(001) substrate using growth method 1. The angle between the incident electron beam and the substrate surface is 45°. Most of the nanorods were grown approximately parallel to the surface. The nanorods grown parallel to the surface were aligned in four directions along W{110}. The diameters of the grown nanorods are about 10 nm.

The nanorods were not grown precisely parallel to the surface, as we see in Fig. 2(a). In order to observe the angle between the nanorods and the surface in detail, AFM measurements were carried out. Fig. 2 (b) shows a typical contact-mode AFM image of the WOₓ nanorods grown on the W(001) surface. The growth condition was similar to the case of Fig. 2(a). The inset in Fig. 2(b) shows the height profile corresponding to the line in the AFM image. As measured from the height profile, the angle between the nanorod and the surface was 6.5° which is a typical value for nanorods grown on W(001).

The observed deviation from the surface parallel direction can be understood on the basis of the epitaxial relationships between WO₃ crystals and the W(001) surface. Although WO₃ belongs to a monoclinic system, the deviation from a simple cubic structure is small. Therefore, for simplicity, we treated WO₃ as a simple cubic structure in
the following discussion. The oxidation process of the tungsten surface at a temperature of about 1000 K was investigated by low-energy electron diffraction (LEED) [10] and reflection high-energy electron diffraction (RHEED) [11]. It has been reported that WO₃ crystals form at the initial stage of oxidation. On the W(001) surface, as WO₃ crystals grow, the original metal surface becomes less important in determining the epitaxy, and the crystals grow such that WO₃{111} planes becomes parallel to the W{011} facet planes lying 45° to the surface [11]. As a result, WO₃ crystals are formed with the WO₃{001} face inclined about 9.7° from the original W(001) surface, and an inclination of 9.7° is expected for vertically grown nanorods when they are elongated in the WO₃{001} direction, as shown in Fig. 2(c). For the nanorod grown in the direction nearly parallel to the surface, it is expected to be inclined 6.9° from the surface plane, as shown in Fig. 2(d). The observed orientations of the WO₃ nanorods agree well with those of the WO₃ crystals. The results strongly suggest that the WO₃ crystals act as the nuclei for the subsequent growth of nanorods.

An SEM image of nanorods formed using growth method 2 is shown in Fig. 3. The substrate was W(001) and the angle between the incident electron beam and the substrate surface was 45°. In contrast to the case of Fig. 2(a), most of the nanorods grew perpendicular to the surface, and an array of WO₃ nanorods was produced. The sizes of nanorods were about 20 nm in diameter and about 1000 nm in length. The growth directions of the nanorods were not exactly normal to the surface. The slight inclination of the nanorods can be explained by the same epitaxial relationships as we have discussed already. The density of the nanorods is considerably different between Figs. 2(a) and 3, probably due to a difference in the flux of tungsten oxide molecules which contribute to the growth of the nanorods.

The difference between Figs. 2(a) and 3 clearly indicates that selective enhancement of the epitaxial growth direction is possible. In the case of growth method 1 (grown nanorods are observed in Fig. 2(a)), tungsten oxide molecules are produced at the substrate surface. Therefore, it is reasonable to conclude that these molecules would not contribute to the growth of the nanorod if the growth front is away from the surface. Indeed the nanorods prepared by growth method 1 mainly grew in the direction nearly parallel to the surface, as seen in Fig. 2(a). When growth method 2 was used, tungsten oxide molecules were additionally supplied from the tungsten foil placed in front of the substrate surface. Therefore, the growth front of the nanorod growing in the surface normal direction had a higher probability to incorporate tungsten oxide molecules than in the case of growth method 1. Actually, Fig. 3 clearly shows such enhanced growth of the nanorods in the surface normal direction.

4. Conclusions

We developed two techniques for the epitaxial growth of WO₃ nanorods on a W(001) surface. We achieved the enhancement of growth in a selected epitaxial direction. When tungsten oxide was supplied from the substrate itself, the nanorods mainly grew in the direction parallel to the substrate surface. On the other hand, an array of free-standing nanorods grew in the surface normal direction when tungsten oxide was deposited from tungsten foil. All nanorods obtained in this study showed slight inclination from the surface parallel and surface normal directions. The inclination of the nanorods can be explained in terms of the epitaxial relationship between the WO₃ crystals and the W(001) surface. The results indicate that initially formed WO₃ crystals act as nuclei for WO₃ nanorod growth.

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