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Evidence for two growth modes during tungsten oxide vapor deposition on mica substrates

Karel Mašek*, Marcel Gillet, Vladimír Matolín

Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-180 00 Prague 8, Czech Republic

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ABSTRACT

The morphology, the structure and the orientation of tungsten oxide nanorods grown on mica are investigated as a function of the deposition time. The previous results are recalled to point out the changes with the nanorod thickness. The investigations were conducted by Atomic Force Microscopy (AFM) and Reflection High Energy Electron Diffraction (RHEED). The results evidence two successive growth modes. In the first stage thin and long nanorods were formed. They grew layer by layer with a hexagonal tungsten bronze structure and two different (1 – 10) and (2–10) planes parallel to the mica surface. In the second stage, as the deposition time increased thin nanorods with the (1 – 10) orientation grew in thickness when the others preserve their morphology and structure.

In the discussion the difference between the two growth modes is emphasized. In the first stage the nanorod growth proceeds mainly by the surface diffusion of K_xWO_3 species. In the second stage the growth is due to the by direct impinging of WO_3 molecules on some thin nanorods having already the (1 – 10) orientation, leading to growth of thick nanorods with a monoclinic structure.

1. Introduction

In the past we have synthesized tungsten oxide nanostructures by evaporation and condensation of WO_3 vapors on mica substrates and we have investigated their morphology, orientation and structure in the first stages of growth. The main objective of this paper is to characterize the growth of such nanostructures and to point out the changes in morphology and structure which occur when their size increases during longer times of deposition.

Our previous studies have been mainly conducted by Transmission Electron Microscopy (TEM) and Transmission Electron Diffraction (TED) so they were performed on nanostructures with thicknesses smaller than 100 nm. In this paper we report investigations by Reflection High-Energy Electron Diffraction (RHEED) on nanorods with thickness more than 50 nm obtained with longer deposition time.

We will show that the thicker nanorods are formed by pure WO_3 with a monoclinic structure while the thin nanorods grown in the first stage of the growth contain K^+ ions (K_xWO_3) and have a hexagonal structure. We expect that the properties of the pure WO_3 nanorods are different from those of the K_xWO_3 ones, in particular, the sensing properties which depend on the crystallographic structure and surface composition of the sensing material.

The first part concerns of the present paper the materials and the growth procedure. The preparation of the nanorods is briefly recalled and we present the methods of investigation of their morphology and crystallographic structure by AFM and RHEED.

In the second part we resume the results already obtained on the thin nanorods. The results on thick nanorods are given in the third part. From the AFM images we characterize their morphology and from the RHEED patterns we deduce their orientation and structure. In the last part we discuss the results and emphasize evidence of two nanorod growth modes which successively take place during the tungsten oxide vapor deposition.

2. Materials

2.1. Tungsten oxides

During the last decades tungsten oxides have attracted interest mainly due to their applications in electrochromic devices [1], photocatalysts [2] and gas sensors [3–9].

The tungsten oxides have different stable crystallographic structures in defined temperature ranges. For increasing temperature the structures are successively: monoclinic (ε-WO_3), triclinic (δ-WO_3) monoclinic (γ-WO_3), orthorhombic (β-WO_3), tetragonal (α-WO_3) and cubic [10–12]. In the temperature range from 300 to 600 K the monoclinic structure is the most stable for the bulk

* Corresponding author. Tel.: +420 22191 2753.
E-mail address: karel.masek@mff.cuni.cz (K. Mašek).

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oxide [13]; a hexagonal structure HWO_3 has been also reported [14]. The HWO_3 can be obtained from dehydration of tungsten oxide hydrate [15] or by hydrothermal synthesis [16,17]. The HWO_3 has also synthesized by vapor phase deposition [18]. The hexagonal structure exhibits large tunnels along the c axis through which cations like K^+ can easily intercalate leading to the formation of an hexagonal tungsten bronze K_xWO_3 [19–21], the composition of which can vary in a composition range $0.13 < x < 0.33$ [19]. The crystallographic parameters of KWO_3 are $a=b=0.73$ nm and $c=0.77$ nm for $x=0.27$; these parameters are independent of the composition in the limit $(0.13 < x < 0.33)$ and they are quasi identical to those of HWO_3. In the last twenty years the interest concerning the tungsten oxides was oriented toward the oxides with nanometric dimensions such as nanowires and nanorods. Due to their specific properties related to a large surface to volume ratio and anisotropic shape, the nanowires or nanorods have attracted special attention and a lot of studies were devoted to the synthesis of such nanomaterials. Their investigation revealed very good sensing properties in detection of toxic and hazardous gases for applications in environmental and industrial pollution monitoring. Size reduction is an important factor enhancing the gas-sensing properties of semiconducting devices and increase of sensitivity is expected when the crystal size decrease to the nanometer scale. Tungsten oxide self-assembled nanorods are promising for fabrication of gas nanosensor by the electron beam lithography technique [22]. Tungsten oxide nanostructures have been prepared by thermal evaporation or sublimation of tungsten metal or oxides with or without catalysts or reactants in various atmosphere conditions [23–35]; various substrates were used [36–39] and different chemical ways were proposed including soft chemistry processes [40–43], thermal dissociation of tungsten salts [44] and hydrothermal processes with additives or precursors [45–47]. These examples show that a variety of methods and processes were used to prepare one dimensional nanostructures. They also evidence that, in spite of a lot of studies, the growth mechanism of such materials is not well understood so far. The understanding of the growth mechanism of such nanomaterials is the key point for controlling their formation and properties in a reproducible manner and remains a scientific challenge.

2.2. Mica substrate

The tungsten oxide nanorods were grown on mica muscovite cleavages. Mica muscovite has a layered structure formed of SiO_4 tetrahedral- Al_2O_6 octahedral- SiO_4 tetrahedral (TOT) sheets of one nanometer thick stacked in a monoclinic structure along the c axis [48,49]. Its crystalline parameters are: $a=0.518$ nm, $b=0.899$ nm, $c=2.0$ nm and $\beta=95.11^\circ$. The TOT sheets are separated by a potassium plane. Due to the weak bonding between the silicate layers and the potassium atoms the cleavage is easy along atomically flat (001) plane. During cleavage the ions K^+ are shared between the two created surfaces [50]. The K^+ ions are relatively mobile on the cleaved surfaces and can be incorporated into the nanorods during the WO_3 vapor deposition.

3. Experimental details

3.1. Preparation of the tungsten oxide nanorods

The tungsten oxide nanorods were prepared by a very simple vapor-solid growth process under air at atmospheric pressure on a (001) freshly cleaved mica surface [35,51]. The tungsten oxide vapors are produced by heating a thin WO_3 layer. The nanostructures are formed by condensation of the WO_3 vapors on the mica cleavages fixed above the oxide vapor source at a distance which can be varied between 1 and 5 mm resulting in a mica substrate temperature modulation between 340 and 390 °C. The experimental results given in this paper were obtained in the following conditions: temperature of the WO_3 vapor source $T_a=620$ °C, temperature of the mica substrate $T_s=370$ °C, deposition time $t_d=10$–60 min.

3.2. Methods of investigation

After cooling to room temperature the samples were examined by AFM in tapping mode and then transferred into an UHV chamber equipped with RHEED. The RHEED investigations were performed with a 25 keV electron beam. A movable sample holder allows changing the incidence as well the direction of the incident electron beam. Due to the small surface area of the nanorods exposed to the electron beam the RHEED pattern intensity was relatively low and the contrast so poor that we used, if necessary, an intensity profile performed across the RHEED pattern to determine the position of the diffraction spots.

To be sure that no artifact due to the surface electrical charges created during observation, we have deposited a thin carbon film on the sample surfaces. This carbon film eliminated the electrical charges and it was possible to observe the patterns without charging perturbations. Such samples gave patterns a little more diffuse than without carbon and the comparison between the patterns show that the possible charges of the mica substrate do not perturb the RHEED results.

In order to test the nanostructure stability some samples have been annealed in situ in the RHEED chamber under the following conditions: annealing temperature $T_A=400$ °C, time of annealing $t_A=30$ min. The patterns from annealed samples were identical to those obtained on unannealed ones and they have better quality due to the outgassing of the sample surface. So, the RHEED interpretations can be indifferently performed on patterns obtained on annealed and unannealed samples.

4. Our previous results

In the last years we have investigated the morphology, composition, structure and epitaxial orientations of thin WO_3 nanorods during the first stages of growth on mica substrates [35,51–56]. The nanorods grew in two well-defined directions with an angle of 60° between them. Their thickness, width and length varied in the ranges of 1–30 nm, 40–100 nm and 1–20 μm, respectively. The thickness analysis evidenced that they grew layer by layer [52]. Energy-Dispersive X-ray (EDX) spectroscopy and image mapping with K and O elements evidenced the presence of potassium in the whole nanorods [54] resulting in the formation of a K–W–O compound such as a tungsten bronze K_xWO_3 [35,53–56].

In the previous experiments we have shown that depending on the preparation conditions of the mica substrate we could obtain nanorods or three-dimensional particles [35,54]. Such results evidenced that the potassium plays a key role in the formation of tungsten oxide nanorods.

The crystallographic structure of the WO_3 nanorods with thickness in the range from 2 to 30 nm were investigated by HRTEM (High Resolution TEM) and SAED (Selected Area Electron Diffraction) [35,54]. The nanorods were elongated along two of the three [010], [130] and [1–30] mica axes and they have a hexagonal structure corresponding to the hexagonal tungsten bronze (HTB) [33–55]. This HTB compound grew on the (001) mica surface with two different deposit – substrate interfaces: either (1–10) parallel to the substrate surface plane (zone axis [1–10]) or (2 – 10) parallel to the surface plane (zone axis [100]). It results in the following epitaxial relationships:

(1 – 10) HTB or (2-10) HTB//(001) mica
[001] HTB//[010] or [130] or [1–30] mica