

Synthesis of Self-aligned Tungsten Nanowires on Tungsten Substrate

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ABSTRACT

Self-aligned tungsten nanowires were grown on single crystalline tungsten substrates with Ni as the catalyst material by hot-wall chemical vapor deposition (CVD) at 850°C. The diameter of the resulting nanowires is in the range of 10-100 nm, and the lengths can be up to several microns. These tungsten nanowires have a bcc crystal structure growing along the [100] direction. Since the synthesis temperature 850°C is significantly lower than the eutectic point 1495°C of the bulk Ni-W binary system, the vapor-solid-solid mechanism is likely responsible for the growth of Ni-catalyzed W nanowires in our experiment.

Keywords: tungsten nanowire, alignment, chemical vapor deposition, vapor-solid-solid.

1 INTRODUCTION

Metallic nanowires have attracted much attention due to their unique mechanical, magnetic, optical and electronic properties, and their function as well-defined building blocks for nanodevices.[1-3] Tungsten (W), in particular, is of great interest, being promising in applications such as emitters for field emission and field ionization, interconnection lines, and gate electrodes for integrated circuits.[4-7] To realize these applications, considerable effort has been devoted to the synthesis of W nanowires. However, very limited results have been reported on the precise control of the position and orientation of W nanowires on substrates. Aligned β -phase W nanorods having square-base pyramidal apexes were grown on oxidized Si substrate using glancing angle deposition technique by Singh et al. [5,6], and these nanorods were used as cold field emitters and gas ionizer. Through a directional solidification on eutectic NiAl-W alloy, Hassel et al.[8] formed W nanowire arrays and W nanowires with a wire diameter of ~200 nm. This solidification was carried out at 1700°C, and an etching process in a mixture of HCl: H₂O₂: H₂O was needed to get the product. A vapor phase technique for the bulk synthesis of W nanowires was introduced by Vaddiraju et al.[9], in which condensation of oxide species above their decomposition temperatures leads to the growth of metal nanowires. Wang et al. [10]

synthesized single-crystalline W nanowires with length up to 20 μ m by nickel-catalyzed vapor-phase methods at a low temperature of 850°C, which was significantly below the eutectic temperature of Ni-W binary system (1495°C). In this work, we report the growth of self-aligned W nanowires directly from single crystalline W substrates. The sample was prepared by heating a Ni-coated W substrate with tungsten oxide powder at upstream as source at 850°C in a conventional horizontal tube furnace. The diameter of the resulting nanowires is in the range of 10-100 nm, and the lengths can be up to several microns.

2 EXPERIMENTAL DETAILS

Aligned growth of W nanowires was completed in a conventional horizontal tube furnace. The furnace was 30 cm long and has a zone of 10 cm of uniform temperature. The W substrates were cut from a [100] W single crystal rod. A 3 nm Ni film was deposited on single crystalline W substrates using an electron beam evaporator. WO_{2.9} powder (Alfa, 99.99% in purity) at upstream of the W substrate as source materials were placed into an alumina boat and located in the uniform-temperature zone of the tube furnace. High purity H₂ (10 sccm, standard cubic centimeter per minute) and N₂ (100 sccm for bubbling DI water at room temperature) were passed through the tube as the furnace was first heated to 850°C at a heating rate of 20°Cmin⁻¹, and kept at this temperature for 3 h. After this, the temperature was allowed to descend gradually to room temperature in the protection of H₂ and Ar. W nanowires were finally produced on the substrate. The as-prepared sample was examined by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). Selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) investigations were also conducted during the TEM experiments.

3 RESULTS AND DISCUSSION

The SEM images in Figure 1 show a typical sample of W nanowires grown on W substrates. The diameter of the nanowires ranges from 10 to 100 nm, depending on the size of Ni nanoparticles, and the length up to a few microns.

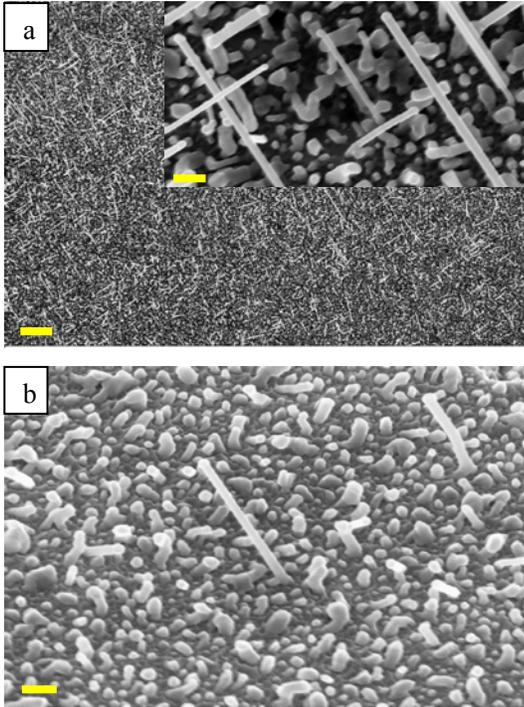


Figure 1: SEM images of self-aligned W nanowires grown on W substrate. (a) Top view. Inset image is in high magnification. The scale bars are 2 μm, 200 nm inset, respectively. (b) 45° side view. The scale bar is 200 nm.

Alignment is observed with nanowires growing along two major directions. From the side view in figure 1(b), nanoparticles and nanorods can also be found. The most of nanowires have a bead-shape tip on the end, which was expected as catalyst in the growth of nanowires in vapor-liquid-solid or vapor-solid-solid modes.

The structure and morphology of the W nanowires were further studied by TEM. Figure 2(a) and (b) present the bright field TEM image and high resolution TEM image of the nanowires, respectively, while the corresponding SAED pattern was given in the inset of figure 2(a). The nanowire is straight and uniform in the diameter along its axis and its lattice spacing is determined to be 0.316 nm. Both the SAED pattern in the inset of figure 2(a) and the high resolution TEM results demonstrate that the synthesized nanowires are W with a bcc crystal structure growing along the [100] direction. The chemical composition of the W nanowires was characterized by the EDS spectrum shown in figure 3, which reveals that the nanowires consist of pure W. The observed oxygen signal may result from the oxidation of the nanowire surface.

With the presence of water vapor and H₂, complicated chemical reactions happen in W ↔ WO_x process, involving oxidation and reduction. Two fundamental chemical reactions have been well applied to this process: oxygen diffusion in the solid state (oxygen transport) and chemical

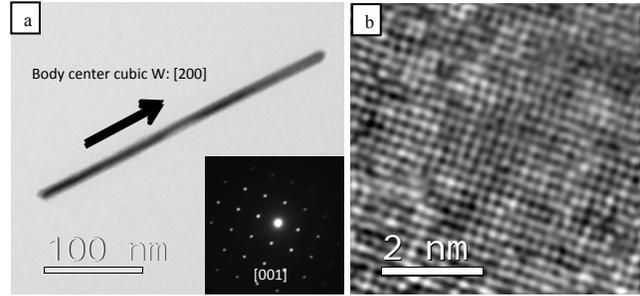


Figure 2: Plane view TEM images of W nanowires. (a) Low magnification image. The inset SAED pattern, taken from the nanowires, can be well indexed based on structural data of bcc W. (b) HRTEM image.

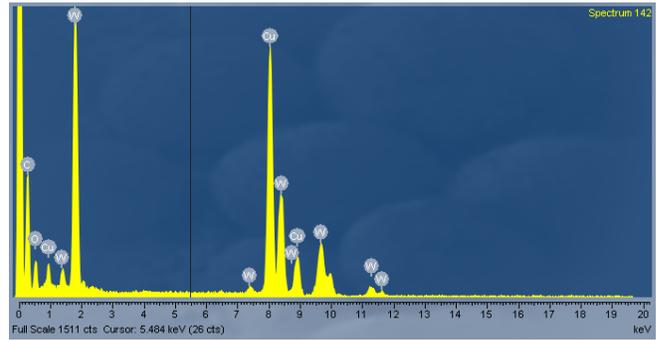
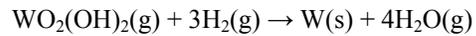
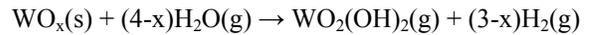


Figure 3: EDS data of W nanowires. The Cu and C signals are initiated from the TEM grid.

vapor transport (tungsten transport) [11]. In the oxygen transport mechanism, oxygen is directly removed from the solid oxides (solid-state diffusion). Generally the reduction sequence could be, (for example, from WO₃ to W), WO₃ → WO_{2.9} → WO_{2.72} → WO₂ → W. While, the chemical vapor transport is the reduction process with transport of tungsten via the volatile tungsten compounds WO₂(OH)₂. Following two reactions can illustrate this process.



It should be noticed that the synthesis temperature 850°C is significantly lower than the eutectic point 1495°C of the bulk Ni-W binary system.[12] Therefore, the vapor-solid-solid mechanism is likely responsible for the growth of Ni-catalyzed W nanowires in our experiment.

Based on the above characterization and discussion, a growth model for generating W nanowires in the present experiment is proposed here. At elevated temperatures, the Ni nanoparticles form first, which serve as catalysts for the growth of the nanowires. Under the set reduction atmosphere, volatile tungsten compound WO₂(OH)₂, generated by the reaction between WO_x and water vapor, decomposes preferentially on the surface of Ni particles to into W atoms and water vapor. Solid Ni-W alloy particles

are then formed by the diffusion of W atoms. With the continued presence of $\text{WO}_2(\text{OH})_2$ vapor, its reduction products W atoms diffuse through and along the catalytic alloy particles, and then condense at the interfaces between Ni-W and W, resulting in nucleation and directional W nanowires growth. During the growth, the W substrate may also behave as source materials, providing W atoms through surface diffusion at high temperature.

To verify the importance of water for the W nanowires growth in our experiment, we have prepared samples using the same condition as previously described except that instead of N_2 , Ar (100 sccm) was introduced directly without bubbling DI water. No nanowires could be found by SEM after the treatment. It suggests that the existence of $\text{WO}_2(\text{OH})_2$ formed by the reaction between water vapor and WO_x is necessary for the nanowire growth.

4 CONCLUSIONS

In summary, we have fabricated self-aligned W nanowires on single crystalline W substrates using a CVD method at 850°C . TEM results demonstrate that these nanowires are W with a bcc crystal structure growing along the [100] direction. The likely growth mechanism vapor-solid-solid has also been discussed. The volatile W compound $\text{WO}_2(\text{OH})_2$ formed by the reaction between water vapor and WO_x plays an essential role during the nanowire growth in our experiment.

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Alloys, and Chemical Compounds. Kluwer Academic / Plenum Publishers, New York, 1999.
[12] SGTE Alloy Phase Diagrams.