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Controllable synthesis of Ni-catalyzed tetragonal tungsten nanowires via chemical vapor deposition

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Abstract Tetragonal single-crystal tungsten nanowires were successfully synthesized by chemical vapor deposition (CVD) catalyzed by Ni particles. The influences of the catalysts, temperature and growth time on the formation of the nanowires were investigated. It was found that the tetragonal tungsten nanowires (WNWs) arrays were obtained by deterministic growth from the ordered Ni catalyst particles with one-to-one relation in size and position between the catalysts and nanowires. The large-scale tungsten nanowire arrays were synthesized at the low temperature of 950 °C. Samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Increasing growth time at 950 °C, the tip of the WNWs changed from four (211) planes to four (110) planes. Good controls of the orientation and structure of WNWs arrays were important for adjusting their properties to satisfy different requirements of potential nanodevices.

1. Introduction

Tungsten nanostructures arouse great interest from both scientific and technological areas of research because it has well-known chemical [1–3], physical [4], electrical [5], and mechanical [6–8] properties. High conductivity and chemical stability of tungsten nanostructures have made it an attractive candidate for future applications in ideal cold-cathode materials and high-temperature devices [9,10]. Some performance of tungsten and the oxide in many applications could also be

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potentially enhanced by fabricating it into 1D nanostructure with controllable dimensions and aspect ratios [11–14]. In particular, for the application of field emission (FE), it is especially useful to synthesize large-scale arrays of W nanowires (WNWs) with the desired surface work function and FE behavior [4,5]. So far, to our knowledge, tungsten nanowires have been fabricated by electron-beam-induced deposition [12,15,16], or chemical vapor methods [4,17–19], but the arrays of tetragonal single-crystal WNWs over a large area have not been synthesized by metal-catalysts. In our previous work [20], the tetragonal WNWs arrays were successfully fabricated on tungsten substrate using Ni catalysts, and the possible formation mechanism was proposed. However, how to control the nanostructure and to synthesis single-crystal WNW arrays remains a big challenge.

In this paper, we report the successful low-temperature synthesis of high-density, large-scale single-crystal WNW arrays by using Ni-catalyst at as low as 950 °C in a deterministic manner. It was found that the Ni nanoparticles played a critical role in controlling the aspect ratios of the W nanowires. By controlling the size and distribution of the catalyst nanoparticles, the diameter of WNWs is uniformly distributed at 80–120 nm. Furthermore, a new detail of the WNWs structure changes was unveiled with increasing growth time at 950 °C.

2. Experimental

WNWs were grown on the tungsten substrates by Ni-catalyzed chemical vapor deposition (CVD). Tungsten substrates were firstly washed to remove the impurities by ultrasonic washing for 20 min. Magnetron sputtering was used to realize a Ni film on the substrates. The base pressure was about 4.5×10^{-4} Pa and the pressure of the Ar gas was 12 Pa without intentional heating of the substrate. The sputtering power is 60 W and the sputtering rate is 1.6 nm/min. After Ni film was deposited, the substrate was annealed at 950 °C for 30 min in H_2 atmosphere to form Ni nanoparticles. The size of the resulting Ni nanoparticles was investigated by SEM. For WNWs growth, the WO_3 powders (10 g) were placed in a quartz tube which was placed inside a horizontal tube furnace, and the substrates were placed on the exit of the quartz tube. At the stage of synthesis, H_2 gas with a constant flow of 30 sccm (standard cubic centimeters per minute) was entered into the tube furnace, and N_2 (flow rate of 100 sccm) with water vapor (10 sccm) was used as the carrier gas flowing from left to right in the furnace (Fig. 1). The WNWs were grown at 750–1050 °C.

The synthesized products were characterized by FE-SEM (Nova Nano SEM 230) equipped with an energy dispersive spectroscopy (EDS) system to study the microstructures and the compositions. The surface topography was measured using a Digital Instruments Dimension V AFM. XRD (Dmax 2500VB) with a Cu Kα source was used to determine the phase composition of the product. TEM (JEM-2100, 200 kV) was used to analyze the structure of the WNWs.

3. Results and discussion

The as-deposited substrates were firstly examined by FE-SEM. A low-magnification FE-SEM image of the obtained substrates is shown in Fig. 2a. The image showed that the dense and wirelike nanostructures formed in large-scale. Because the lengths are up to several micrometers, the wires had a high aspect ratio more than 50. A typical XRD pattern of the nanowires is shown in the inset. The diffraction peaks are indexed to a body-centered cubic structure of W with the lattice parameter $a = 0.316$ nm (JSPDF: 04-0806). Furthermore, the high-magnification FE-SEM images (Fig. 2b) indicated that the nanowires seem to be tetragonal structure and the diameters are about 100 nm.

A TEM image of a single nanowire is shown in Fig. 3a. It had a nearly uniform diameter of 80 nm along its entire length. A corresponding HRTEM image taken from the top region of the nanowire is shown in Fig. 3b. The observed lattice fringes in Fig. 3b revealed that the WNWs were highly single-crystalline. And observed interplanar spacings marked representatively were about 0.16 nm and 0.22 nm, corresponding to the (200) plane and (110) plane of bcc tungsten crystal, respectively. The growth direction of the WNWs was [100] which was perpendicular to the (200) plane. The SEAD pattern (Fig. 3c) provided more evidence of the oriented growth of the WNWs on the W substrate. The WNWs had a single-crystalline tetragonal structure. This was consistent with the results of XRD.

Generally, the growth process of the crystals can be separated into two steps: an initial nucleating stage and a subsequent crystal growth process. At the initial nucleating stage, the crystalline phase of the seeds is critical for directing the intrinsic shapes of the crystals due to its characteristic symmetry and structure. In the subsequent step, the crystal growth stage is a kinetically and thermodynamically controlled process that can yield 1D and other more complicated shapes with some degree of shape tenability through changes in the reaction parameters such as temperature, reaction time and concentration. In the present study, it was found that the

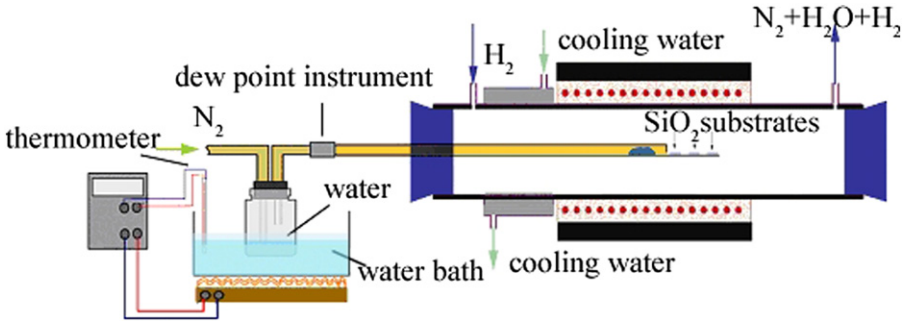

Fig. 1 Schematic diagram of the setup used for the synthesis of WNWs.