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The Influence of Oxygen Concentration in the Sputtering Gas on the Self-synthesis of Tungsten Oxide Nanowires on Sputter-deposited Tungsten Films

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1. Introduction

In recent years, nanostructured materials have attracted much attention due to their outstanding features as compared to bulk counterparts. Among them, transition metal oxide nanowires are of great importance because of their distinctive electrochromic, optochromic, and gaschromic properties for applications in gas, humidity, and temperature sensors.

Recently, the ways for the synthesis of tungsten oxide nanowires based on thermal treatment have been proposed [1, 2]. Gu *et al* [1] successfully obtained tungsten oxide nanowires on tungsten (W) tips/plates by thermal annealing at 700-750^{o}C in Ar ambient, and concluded the growth of nanowires resulted from the oxygen leakage of their system. Liu *et al* [2] synthesized tungsten oxide nanowires by heating a tungsten filament in vacuum with some room air leakage. In addition, some other approaches to obtain tungsten oxide nanowires, such as vapor phase growing [3] and synthesized by CVD with precursors [4] have also been proposed. Especially noteworthy is that all the thermal annealing methods [1, 2] are not in an oxygen-rich condition of O_2 ambient. On the contrary, it was done only under the circumstance of a trace amount of oxygen impurities introduced unintentionally during the thermal growth of tungsten oxide nanowires through oxygen leakage [1] or room air leakage [2].

Recently, Cho *et al* [5] prepared tungsten oxide whiskers by a short period pre-treatment of the tungsten film in steam of H_2O then subsequently annealed at above 1000^{o}C in vacuum. It reveals that the incorporation of oxygen in the tungsten film prior to the thermal treatment might be very crucial for the growth of tungsten oxide nanowires. In this study, a simple method for growing dense tungsten oxide nanowires from sputter-deposited tungsten films by thermal annealing in nitrogen ambient at relatively low temperatures (700-850^{o}C) is proposed. Due to the fact that the growth of tungsten oxide nanowires is very sensitive to the amount of oxygen impurities, oxygen in this study was introduced to tungsten films during thin film deposition. By the way of precisely controlled the flow rate ratio of O_2/Ar in the sputtering gas, the influence of oxygen concentration in the sputtering gas on the self-growth of tungsten oxide nanowires from sputter-deposited tungsten films through thermal annealing is investigated.

2. Experiment

Wafers of *n*-type Si (100) were used as substrates. A dc magnetron sputtering system of a power of 200 watt was used to deposit tungsten films of about 60 nm in thickness. The base and sputtering pressure were held at 2×10^{-6} and 7.6×10^{-3} Torr, respectively. In order to introduce different amount of oxygen impurities into the sputter-deposited W films, the flow rate of O_2 was changed from 0-8 sccm and the Ar gas was kept at 24 sccm for all cases. The higher flow ratio of O_2/Ar is expected to introduce more oxygen impurities into W films. After deposition, samples were annealed at 700-850^{o}C for 15 min in N_2 ambient. The surface morphology of samples and density of nanowires were examined by scanning electron microscopy (SEM). Diameter and nano-structure of nanowires were inspected by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) patterns.

3. Results and Discussion

Figure 1 shows the typical SEM photo of samples deposited with O_2/Ar flow rate ratio of 0/24 (abbreviated as the 0/24-sample) after annealed at 700-850^{o}C for 15 min in N_2 ambient. As estimated from the figure, wire density on the 700, 750, 800, and 850^{o}C-annnealed sample was about 320, 240, 120, and 90 μm^{-2}, respectively. Length and diameter of the self-synthesized nanowires were in the range of 0.1-0.45 μm and 10-30 nm, respectively. Our results showed that, as the thermal annealing temperature was increased from 700 to 850^{o}C, the shape of nanowires changed from cylinder-type to ribbon-type, in addition, the dimension of nanowires also increased appreciably.

Figure 2 shows the TEM image and SAED pattern of a single nanowire obtained from the 0/24-sample after annealed at 800^{o}C. It has a length and diameter of ~0.35 μm and ~17 nm, respectively. As revealed by the SAED pattern shown in the inset of the figure, the value of d-space along

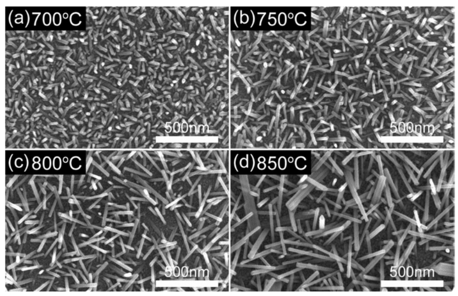

Fig. 1 SEM images of annealed samples prepared by O_2/Ar ratio of 0/24. Samples were annealed at 700-850^{o}C for 15 min in N_2 ambient.

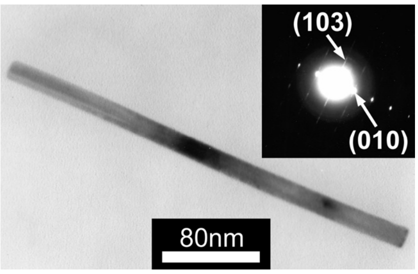

Fig. 2 TEM image for a single nanowire obtained from the 0/24-sample after annealed at 800^{o}C for 15 min in N_2 ambient. The inset shows the SAED pattern of the wire.

the wire growth direction and its transverse direction is about 0.38 and 0.37 nm, respectively, which could be indexed as the crystallite of monoclinic $W_{18}O_{49}$ (010) and (103), respectively. Similar results have also been obtained from the other samples with different O_2/Ar flow rate ratio (not shown). The source of oxygen impurities in the 0/24-sample might originate from target impurities, residual oxygen of the working chamber, or moisture and O_2 contamination when the sputter-deposited films were exposed to the open air.

Figure 3 and 4 show the high and low resolution SEM images of the 1/24-sample after the thermal annealing, respectively. As compared to Fig. 1(a) and (b), nanowires obtained from the 1/24-sample after thermal annealed at 700 and 750^{o}C were shorter in length. The decrease in the wire length became much more obvious as the temperature was increased above 800^{o}C. As was indicated in Fig. 4, the increase in the oxygen concentration exerted an adverse effect on the uniformity of the wire growth. It implied the growth of tungsten oxide nanowires was sensitive to oxygen impurities, and even though a low doping level of oxygen into W films would be harmful to the growth of nanowires.

For the 2/24 and 4/24-samples, the relatively higher oxygen concentration resulted in the disappearance of nanowires or, more precisely, inability for the growth of tungsten oxide nanowires after annealed at 700-850^{o}C as shown in Fig. 5. The surface of these samples turned into grains. As the O_2/Ar flow rate ratio was further increased to 8/24, tungsten oxide sheets with a relatively large size appeared. Similar sheet structure of tungsten oxide was also seen in researches of Gu *et al* and Cho *et al* [1, 5].

4. Conclusions

In this study, tungsten oxide nanowires with $W_{18}O_{49}$ (010) and (103) phases were synthesized on sputter-deposited W films by a simple thermal annealing at 700-850^{o}C in nitrogen ambient. Length, diameter and density of nanowires were in the range of 0.1-0.45 μm, 10-30 nm and 90-320 μm^{-2}, respectively. The influence of the oxygen concentration introduced in the sputtering gas on the growth of tungsten oxide nanowires has been analyzed. Results implied dense nanowires could be obtained with the existence of native oxygen impurities in 0/24-sample. The increase in the oxygen concentration has been found exerting an adverse effect on the uniformity of the wire growth.

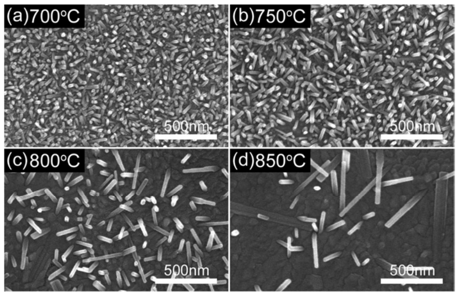

Fig. 3 High-resolution (×70k) SEM images of 1/24 (O_2/Ar)-deposited samples. Samples were observed after annealed at 700-850^{o}C for 15 min in N_2 ambient.

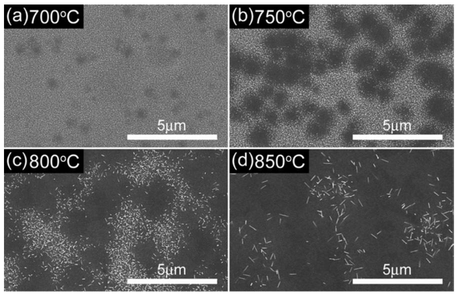

Fig. 4 Low-resolution (×10k) SEM images of 1/24 (O_2/Ar)-deposited samples. Samples were observed after annealed at 700-850^{o}C for 15 min in N_2 ambient. Dark zones represent the degrading area of tungsten oxide nanowires

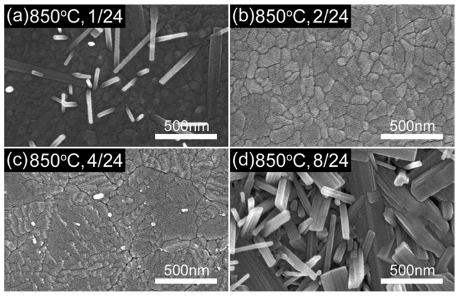

Fig. 5 SEM images of the 1/24, 2/24, 4/24, and 8/24-sample. All the samples were subjected to thermal annealing at 850^{o}C for 15 min in N_2 ambient.

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