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To cite this article: Yohei Yomogida et al 2021 Jpn. J. Appl. Phys. 60 SCCD02

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Synthesis of relatively small-diameter tungsten ditelluride nanowires from solution-grown tungsten oxide nanowires

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Received November 30, 2020; accepted February 1, 2021; published online February 22, 2021

Tungsten ditelluride (WTe₂) is a semi-metallic transition metal dichalcogenide (TMDC). WTe₂ has attracted a lot of interest for topological properties and various applications such as batteries. In this study, we developed a method to obtain WTe₂ nanowires from solution-grown tungsten oxide nanowires. By optimizing the supply of Te vapor, which strongly influences sample composition and structure, and using small-diameter solutiongrown nanowires as precursors, we finally synthesized relatively small-diameter WTe₂ nanowires with diameters of 15–50 nm. Interestingly, nanowire structures are mainly obtained via tellurization, but when sulfurization and selenization are applied on the same precursors, nanotube structures are obtained. We assume that the volume increase via chalogenization is a key parameter that determines the formation of nanotubes and nanowires. © 2021 The Japan Society of Applied Physics

1. Introduction

Transition metal dichalcogenides (TMDCs) represented by MX_2 (M = Mo, W, Nb; X = S, Se, Te) have attracted much attention due to their remarkable electronic and optical properties.¹⁻⁴⁾ Unlike usual semiconducting TMDCs, such as WS_2 and WSe_2 , which are stable in the 2H structure, WTe_2 is stable in the distorted 1 T structure (Td structure),^{5,6)} which gives it semi-metallic properties and allows for unique applications. For example, WTe₂ is expected to have applications in next-generation batteries, such as sodium- and potassium-ion batteries.^{7–9)} This is because WTe₂ has larger interlayer spacing than similar semi-metallic graphite, and large ions can be diffused more efficiently. The electrochemical performance is reported to depend on the morphology of WTe₂.⁸⁾ For that purpose, smaller nanostructures will cause more interfaces and have more electrochemically active edges, resulting in higher electrochemical performance. Furthermore, such edge structures are very important for their topological properties¹⁰⁻¹³⁾ and optical properties due to inversion symmetry breaking.¹⁴⁾ The physical properties of WTe2 strongly depend on the morphology and the edge structure, and thus its control is important for both basic science and applications.

One of the typical methods to control the nanostructure of TMDCs is chalcogenization of metal oxide precursors.¹⁵⁾ In chalcogenization, oxygen atoms in the precursors are replaced by chalcogen atoms to obtain TMDCs that follow the morphology of the precursors. For example, it has been reported that planar layered nanowires (nanoribbons),^{16–18)} coaxial layered (core/shell) nanowires^{19–21)} and coaxial layered nanotubes^{22–26)} can be obtained from nanowire precursors (see Fig. 1). The formation of such nanostructures is affected by parameters during chalcogenization. In particular, the chalcogen supply is considered to be an important factor that promotes chalcogenization and influences the morphology of TMDCs,^{27–29)} and its effects have been systematically investigated in the synthesis³⁰⁾ and sulfurization and selenization, few studies have been reported on

tellurization,^{8,18}) and it is not clear how the conditions of tellurization affect the structure and composition of the products. This may be due to the experimental difficulties in tellurization, such as low thermal stability of tellurides and low activity of tellurium (Te). In order to control the nanostructures of tellurides, it is important to clarify how the tellurization conditions influence the structure and composition of synthesized products.

In this study, we investigated the effects of the Te supply and the tellurization temperature on the structure and composition of tellurized samples. Solution-grown tungsten oxide nanowires, which are usually used for the synthesis of TMDC nanotubes, were used as precursors for tellurization. The morphology and composition of the telluride sample were found to strongly depend on the Te supply and tellurization temperature, and through their optimization, Td-WTe₂ nanowires were finally synthesized successfully. Reflecting the structure of the solution-grown nanowire precursors, relatively small-diameter WTe₂ nanowires with diameters of 15-50 nm were obtained. Interestingly, the obtained WTe₂ has planar layered nanowire structures. The result is different from those when sulfurization and selenization are applied on the same precursors. In the case of the WS_2 and WSe_2 , we obtain the coaxial layered nanotube structures. This indicates that tellurization is very different from sulfurization and selenization.

2. Experimental methods

The tungsten oxide ($W_{18}O_{49}$) nanowire precursors were synthesized via the solvothermal reaction of tungsten hexachloride (WCl₆) in ethanol, as described in the previous study.^{25,26)} First, 50 mg of WCl₆ (99.9%, Sigma-Aldrich) was suspended in 40 ml of ethanol by stirring. This suspension was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. The obtained suspension was gently filtered using a PTFE membrane (0.2 μ m pore size, Merck Millipore) without drying out, washed with ethanol, and deposited onto SiO₂/Si substrates to prepare precursor samples for tellurization.



Fig. 1. (Color online) Candidate TMDC structures that can be obtained by chalcogenization of metal oxide nanowires. (a) Planar layered nanowires (nanoribbons). (b) Coaxial layered (core/shell) nanowires. (c) Coaxial layered nanotubes.

Figure 2 shows the experimental setup for tellurization using a quartz tube and two independent tube furnaces. Inside the quartz tube, a quartz boat with the oxide samples and an alumina boat with Te powder (99.99%, Sigma-Aldrich) were placed downstream and upstream, respectively. First, the entire system was vacuumed and the downstream side was heated at 200 °C. The system was then filled with Ar, and the oxide samples were heated to 650 °C-700 °C in the downstream furnace with Ar flowing at a flow rate of 200 sccm under atmospheric pressure. Once the temperature of the downstream furnace reached the set temperature, the Te powder was heated in the upstream furnace with Ar/H₂ flowing at a flow rate of 192/8 sccm. Te is not reactive compared to Se and S. Thus, we controlled the supply of Te vapor by varying the temperature of the upstream furnace (T_{Te}) between 600 °C and 700 °C to investigate its effect on tellurization. The temperature was maintained for 30 min, and the system was rapidly cooled.

The obtained samples were evaluated by scanning electron microscopy (SEM, Phenom ProX, Thermo Fisher Scientific Inc.), transmission electron microscopy (TEM, JEM-3200FS and JEM2500SE, JEOL Ltd.), energy-dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), and Raman spectroscopy.

3. Results and discussion

3.1. Effect of Te supply and tellurization temperature Figures 3(b) and 3(c) show typical SEM images of the samples tellurized at 650 °C under different Te supply conditions, compared to the oxide sample [Fig. 3(a)]. The macroscopic morphology of the samples did not change much via tellurization. To discuss the detailed structure, typical TEM images of these samples are shown in Figs. 3(d)–3(f). The low Te supply condition ($T_{Te} = 600$ °C) typically yielded nanowire samples (15–50 nm in diameter), with a similar diameter to that of the precursors (5–40 nm in diameter). On the other hand, the high Te supply condition ($T_{Te} = 700$ °C) yielded not only the nanowire samples but also the flake samples with relatively large width (60–120 nm in width). These results indicate that tellurization has changed the microscopic structure of the precursor during the synthesis.

The tellurization conditions also affect the compositions of the sample. Figures 4(a) and 4(b) indicate Raman spectra of the telluride and oxide samples. The positions of the Raman peaks and spectra of the telluride samples strongly depend on the tellurization conditions, unlike the peaks of $W_{18}O_{49}$.³¹⁾ The samples tellurized under the high Te supply conditions ($T_{Te} = 650$ and 700 °C) exhibited the peaks at 113, 131, 161, and 209 cm⁻¹, corresponding to the modes of Td-WTe₂ (112, 133, 164, and 212 cm⁻¹).³²⁾ On the other hand, the samples



Fig. 2. (Color online) Experimental setup for tellurization with two independent tube furnaces.

tellurized under the low Te supply conditions ($T_{Te} = 600$ and 620 °C) exhibited the peaks at 153 and 192 cm⁻¹, which correspond to the Raman modes of WTe.³³⁾ EDS spectrum [Fig. 4(c)] indicates that the sample tellurized under $T_{Te} = 650$ °C is WTe₂ with the W/Te ratio of 1/2. In contrast, the sample tellurized under $T_{Te} = 600$ °C has the W/Te ratio of 1/1.5, which suggests the presence of Te-deficient compounds, such as WTe. Therefore, the supply of Te vapor is important in promoting tellurization and in determining the composition of tungsten tellurides. The W/Te ratio under $T_{Te} = 700$ °C indicates the presence of Te-rich structures, which is discussed later.

Next, we discuss the results for the sample tellurized at a higher temperature (700 °C) while maintaining a high Te supply condition ($T_{\rm Te} = 700$ °C). A typical TEM image [Fig. 5(a)] show that the structure of the nanowires with diameters of ~10 nm has been broken. This is considered to be due to the thermal decomposition of WTe₂, which is reasonable considering that the low thermal stability of tellurides.³⁴⁾ Furthermore, the Raman spectrum of the sample [Fig. 5(b)] show the peaks of WTe, despite the sample tellurized under high Te supply condition. This suggests that de-tellurization occurs at higher temperatures due to the low thermal stability of WTe₂.

3.2. Structures of WTe₂ nanowires

Figures 6(a) and 6(b) shows high-resolution TEM images of the WTe2 nanowires, tellurized at 650 °C under the high Te supply conditions ($T_{\rm Te} = 650$ and 700 °C). The nanowires have clear lattice fringes parallel to their longitudinal direction. The spacing of 0.72-0.74 nm between the fringes corresponds well to the interlayer spacing of 0.704 nm for WTe_{2} , ^{35,36)} and the lattice fringes correspond to the (002) planes of Td-WT₂. Thus, the obtained samples are not the coaxial layered nanowires, but rather the planer layered nanowires. Interestingly, this is different from WS_2 and WSe_2 , which form the coaxial layered nanotubes.^{24–26)} Furthermore, the SAED pattern of the WTe₂ nanowire [Fig. 6(c)] is shown in Fig. 6(d). From the SAED pattern, the lattice spacing can be estimated to be 0.32 nm and 0.62 nm, corresponding to the interplanar spacing between the (100) and (010) planes of Td-WTe₂, respectively.^{35,36}) These results indicate that the obtained nanowires are composed of planar layered WTe₂.



Fig. 3. Morphologies of the tungsten oxide ($W_{18}O_{49}$) nanowire sample and the samples tellurized at 650 °C under different Te supply conditions. (a)–(c) Typical SEM images of the oxide sample (a) and the samples tellurized under low Te supply condition ($T_{Te} = 600$ °C) (b) and high Te supply condition ($T_{Te} = 700$ °C) (c). (d)–(f) Typical TEM images of the oxide sample (d) and the samples tellurized under low Te supply condition ($T_{Te} = 600$ °C) (e) and high Te supply condition ($T_{Te} = 700$ °C) (f).



Fig. 4. (Color online) Compositions of the samples tellurized at 650 °C under different Te supply conditions. (a), (b) Raman spectra of the oxide sample and the samples tellurized under $T_{\text{Te}} = 600$ °C, 620 °C, 650 °C, and 700 °C. (c) EDS spectra of the samples tellurized under $T_{\text{Te}} = 600$ °C, 650 °C, and 700 °C. The W/Te ratio for each sample is also shown.

3.3. Possible mechanism of nanowire formation

We discuss the results of tellurization compared to sulfurization and selenization. In this study, the planar layered structures of WTe₂ were mainly obtained, but the solutiongrown nanowires are usually used as precursors for the coaxial layered structures of WS₂ and WSe₂.^{24–26)} In the synthesis of such coaxial layered structures, it is known that the formation of an inert MX_2 outer shell first takes place, followed by a substitution reaction of the oxide core. Thus, the rapid formation of the outer shell is important. Such a situation can be achieved by increasing chalcogen activity, chalcogenization temperature, and chalcogen vapor supply. In this study, tellurization was promoted by increasing the supply of Te vapor, but the chalcogenization temperature and



Fig. 5. (Color online) Evaluation of the samples tellurized at a higher temperature (700 °C) under high Te supply condition ($T_{\text{Te}} = 700$ °C). (a) A typical TEM image of the sample. (b) Raman spectra of the sample.



Fig. 6. (Color online) Structures of the samples tellurized under high Te supply conditions. (a), (b) High-resolution TEM images of the samples tellurized under $T_{\text{Te}} = 650 \text{ °C}$ (a) and $T_{\text{Te}} = 700 \text{ °C}$ (b). (c), (d) TEM image (c) and SAED pattern (d) of the sample tellurized under $T_{\text{Te}} = 700 \text{ °C}$.

the chalcogen activity were relatively low. This may have prohibited the outer shell formation and promoted the nanowire formation. Also, the semi-metallic WTe_2 sheets are more active than the usual semiconducting MX_2 sheets, so the outer shell formation around the oxide core may not be stable.

We also discuss the effect of volume on the formation of nanowires and nanotubes. In the case of nanotube structures, it has been reported that if the volume increases by Li intercalation after the formation of the outer shell, the nanotube structures are broken and flake samples are formed.³⁷⁾ In this study, we observed the nanowire structures with an incomplete outer shell [Fig. 7(a)] and flake structures [Fig. 7(b)], suggesting a similar situation. Therefore, we estimated how much the volume changes via chalcogenization using the reported crystal structure data.^{35,38,39} Here, due to the low reaction temperature, we consider that the W atom is conserved in the substitution reaction. The volume of the compound containing the same number of W atoms can be compared by dividing the unit



Fig. 7. Morphologies of the samples tellurized under high Te supply conditions. (a), (b) Typical TEM image of the partially covered shell structure on the nanowire (a) and flake structures (b), which are contained in the samples tellurized under high Te supply conditions.

cell volume by the number of W atoms. The estimated volumes (Table I) were larger than that for the oxide precursor, for all chalcogenides. We estimated how much the volume increases by the volume ratio of each chalcogenide to oxide, the value of α (Table I). The α value of WTe₂ was 1.55, and the value was found to be higher than that of WS_2 (1.08) and WSe_2 (1.23). This suggests that the volume increase in the formation of WTe₂ is larger than that of WS₂ and WSe₂. It is noteworthy that the increase in volume (average diameter) has been observed experimentally.^{24–26)} In the case of WS_2 nanotubes, this increase of the volume is considered to be due to the formation of amorphous trichalcogenides such as WS₃, and the subsequent formation of the outer shell.²⁴⁾ Then, we can assume that if the increase of the volume by trichalcogenide formation is greater than the value of α , the hollow structure would be obtained. In this study, the presence of such chalcogen-rich structures is indicated [see Fig. 4(c)]. However, in the case of WTe2, it would be difficult to achieve nanotube formation due to the large value of the α . Therefore, the nanowire formation (no nanotube formation) via tellurization may be due to the large α value of WTe₂.

4. Conclusions

In this study, we clarified that the effects of Te vapor supply and tellurization temperature on tellurization and developed a method to synthesize relatively small-diameter WTe2 nanowires. The solution-grown tungsten oxide nanowires were used as precursors for tellurization. The tellurization temperature was set to 650 °C, above which the small-diameter samples would be broken. The Te vapor supply controlled by the temperature of the Te precursor was found to be important for determining the morphology and composition of the telluride samples, and Te vapor formation at 650 °C was considered suitable for the synthesis of WTe₂ nanowires. Then, finally, we obtained the relatively small-diameter WTe_2 nanowires with diameters of 15–50 nm. The WTe_2 nanowires exhibited defined crystal structure of Td-WTe₂ with interlayer spacing of ~0.7 nm. Furthermore, WTe2 has planar layered nanowire structures, which are different from the coaxial layered nanotube structures of WS₂ and WSe₂. The increase of the volume during the tellurization was relatively large compared with the cases in sulfurization and selenization, and thus we assume that this parameter prevented nanotube formation.

Table	I. Volume	e increase	ratio	of	each	compound.
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	W ₁₈ O ₄₉	WS ₂	WSe ₂	WTe ₂
Crystal structure	Monoclinic	Hexagonal	Hexagonal	Orthorhombic
Unit cell volume (10^{-24} cm^3)	882	106	121	303
Number of W atoms in a unit cell	18	2	2	4
Unit cell volume per the number of W atoms (10^{-24} cm^3)	49.0	53.1	60.4	75.8
Volume increase ratio α	—	1.08	1.23	1.55

Acknowledgments

This study was partially supported by JST CREST Grant Nos. JPMJCR1715, JPMJCR16F3; JSPS KAKENHI Grant Nos. JP19K15392, JP20H02573, JP17H01069, JP17H06124, JP18H01816, JP18H01832, and JP20H02573.

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