

Article

Recrystallization of Single-Crystalline VO₂ Microtube Arrays on V₂O₅ Substrate

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Abstract: Single-crystalline VO₂ microtube arrays on V₂O₅ substrate were fabricated through a thermal oxidation route based on resistive heating V foil in air. Four sheets of as-fabricated single-crystalline VO₂ microtube arrays on V₂O₅ substrate were then, respectively, heated to approximately 855 °C and 1660 °C to melt V₂O₅ or VO₂. Thereafter, the melted V₂O₅ or VO₂ was cooled rapidly or slowly to recrystallize the liquid V₂O₅ or VO₂. The morphologies and phases of the recrystallization products were characterized by scanning electron microscopy and X-ray diffraction. This study proposes that the peak temperature of heating and the cooling rate are responsible for the recrystallization products of single-crystalline VO₂ microtube arrays on V₂O₅ substrate.

Keywords: VO₂ microtube arrays; recrystallization; resistive heating

1. Introduction

VO₂ is characterized by a metal-insulator transition (MIT) [1], which Morin discovered in 1959 [2]. With an increased temperature to 68 °C from room temperature, a low-temperature monoclinic phase (insulator) of VO₂ transforms into its high-temperature tetragonal rutile phase (metal). Accompanying the MIT are the large changes in optical, electrical, and magnetic properties of VO₂. Based on the MIT, VO₂ can be applied in several modern devices, such as optical switching [3], smart window [4,5], oscillators, [6], and field-effect transistors [7,8]. Previous reports showed that the MITs of VO₂ are strongly related to its crystal quality and morphology, which are generally determined by the fabrication methods. Taking previous reports into consideration, many researchers have focused on the fabrication method of VO₂ in recent years. These fabrication methods primarily include hydrothermal synthesis [9–12], chemical vapor deposition [13], sol-gel deposition [14], vapor transport method [15], and so on. However, these methods suffer from many disadvantages, such as time-consuming, complex operation, expensive equipment, poor crystal quality, and waste generation. Thus, discovering an easy method to fabricate high crystal quality VO₂ is necessary.

Recently, a simple, fast, green, and low-cost fabrication method is developed for single-crystalline VO₂ microtube arrays on V₂O₅ substrate through a thermal oxidation route based on resistive heating V foil in air [16]. However, the recrystallization characteristic of the single-crystalline VO₂ microtube arrays on V₂O₅ substrate remains unclear. At present, at least 52 stable and metastable phases of the vanadium-oxygen system have been obtained [17]. These phases may transform from one-to-another via recrystallization [18,19], redox reaction [20], or thermal treatment [21]. For a further understanding of the microstructure and phase evolution characteristics of single-crystalline VO₂ microtube arrays on V₂O₅ substrate during heating and cooling, a recrystallization study of single-crystalline VO₂ microtube arrays on V₂O₅ substrate is carried out in this work.

2. Materials and Methods

Four bars of commercially available pure V foil (99.9 wt.%) with thicknesses of 0.2 mm, widths of 3 mm, and lengths of 20 mm were used in this work. First, these V foils were gradually heated to a temperature higher than 1700 °C by direct current (< 40 A) in several tens of seconds with a GW Instek PSB-2400L power supply followed by cooling rapidly to room temperature in a few seconds to fabricate single-crystalline VO₂ microtube arrays on V₂O₅ substrate (VO_x), which is located on the surface of each V foil (Figure 1). The detailed fabrication process of VO_x can be found elsewhere [16]. Then, each V foil was resistively heated again with a direct current to reach temperatures of approximately 855 °C or 1660 °C to melt the as-fabricated V₂O₅ substrate or single-crystalline VO₂ microtubes. Then, the liquid V₂O₅ or VO₂ were cooled at a rapid rate or a slow rate by controlling the direct current manually to recrystallize the liquid V₂O₅ or VO₂. The fabrication temperature was monitored by a pyrometer (LumaSense IGAR 6 Advanced with a temperature range of 250–2000 °C, a resolution of 0.1 °C, and a sampling rate of 60 s^{−1}). The obtained products were detached from V foil for morphology observation and microstructure analysis. The morphologies of obtained products were observed using a Hitachi TM3030 scanning electron microscope (SEM). The microstructures and phases of obtained products (without any further treatment) were examined using a Rigaku Ultima IV X-ray diffractometer at room temperature.

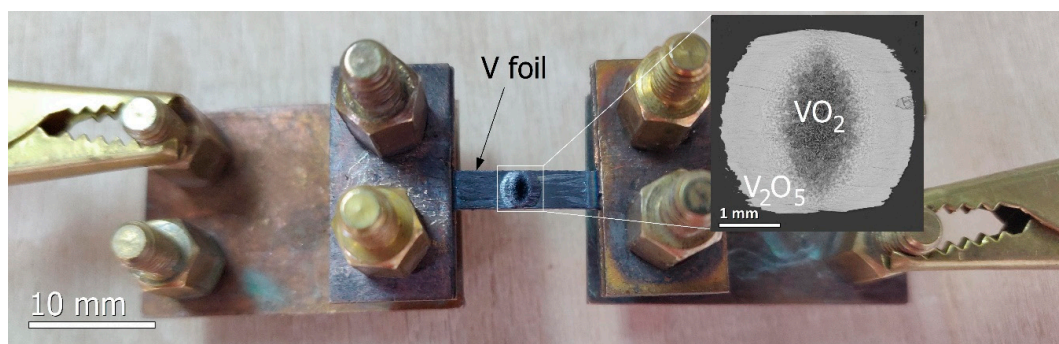


Figure 1. Photo of partial experimental setup. The inset is the SEM image of as-fabricated single-crystalline VO₂ microtube arrays on on V₂O₅ substrate.

3. Results and Discussion

3.1. Single-Crystalline VO₂ Microtube Arrays on V₂O₅ Substrate

The SEM images of the typical morphology of as-fabricated VO_x is depicted in Figure 2a. The single-crystalline VO₂ are straight, hollow, rod-like, rectangular cross sectional, and nearly vertically aligned on the V₂O₅ substrate. The temperature vs. time curves (Figure 2b) during fabrication clearly indicates that the peak temperature is 1816 °C, the average heating rate is 25 °C/s, the average cooling rate is 310 °C/s, the crystallization temperatures of VO₂, and V₂O₅ are 806 °C and 304 °C, respectively. The X-ray diffraction (XRD) pattern (Figure 2c) of as-fabricated VO_x demonstrates that only VO₂ and V₂O₅ presented. Apparently, the diffraction peaks of (200) and (211) of VO₂ are higher than the others, which indicate a preferential growth of single-crystalline VO₂ microtubes. Our previous transmission electron microscopy observations demonstrated that the as-fabricated microtube is in the [100] growth direction of the M1 phase VO₂ at room temperature with a thin layer of V₂O₅ on its surface [16].

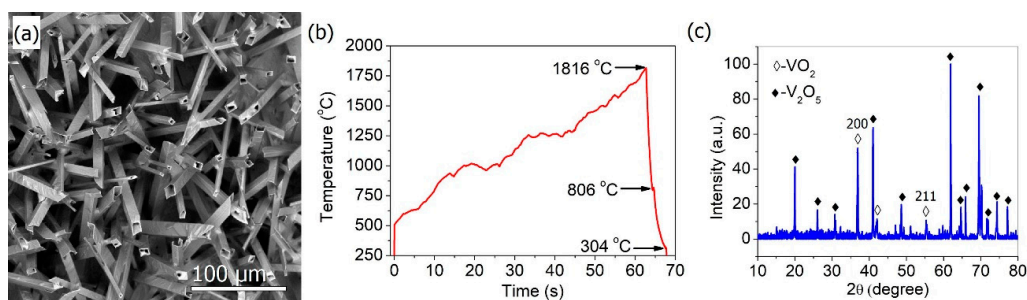


Figure 2. Characteristics of as-fabricated single-crystalline VO₂ microtube arrays on V₂O₅ substrate: (a) SEM image, (b) temperature vs. time curve during fabrication, and (c) XRD pattern.

3.2. Recrystallization of VO_x via Heating with Low Peak Temperature and Cooling Rapidly

One sheet of as-fabricated VO_x was gradually heated to a relatively low peak temperature with a heating rate of 40 °C/s to melt the V₂O₅ substrate, followed by cooling rapidly with a cooling rate about 169 °C/s by stopping resistive heating to recrystallize the liquid V₂O₅. The SEM image of obtained recrystallization product is depicted in Figure 3a. Hollow, rod-like, and nearly vertically aligned products still exist on the surface of a substrate. The microtubes shown in Figure 3a are covered with a thin layer, which are different from as-fabricated single-crystalline VO₂ microtubes. The corresponding temperature vs. time curve is shown in Figure 3b with a peak temperature of 855 °C and a crystallization temperature of 298 °C. The XRD pattern (Figure 3c) of the obtained product shows the existence of VO₂ and V₂O₅. When the temperature of as-fabricated VO_x is heated between 678 °C (the melting point of bulk V₂O₅ [22]) and 1542 °C (the melting point of bulk VO₂ [22]), only V₂O₅ substrate is melted into liquid and resulted in the single-crystalline VO₂ microtubes immersed in liquid V₂O₅. When the VO_x is rapidly cooled down to 298 °C, a part of the liquid V₂O₅ recrystallized on the surface of single-crystalline VO₂ microtubes and other parts of liquid V₂O₅ recrystallized as the substrate of the single-crystalline VO₂ microtube arrays again. The recrystallization process of liquid V₂O₅ is exothermic, which maintains the recrystallization starting temperature of V₂O₅ for a short time. As a result, a platform at 298 °C appears in the temperature vs. time curve—marked by an arrow in Figure 3b.

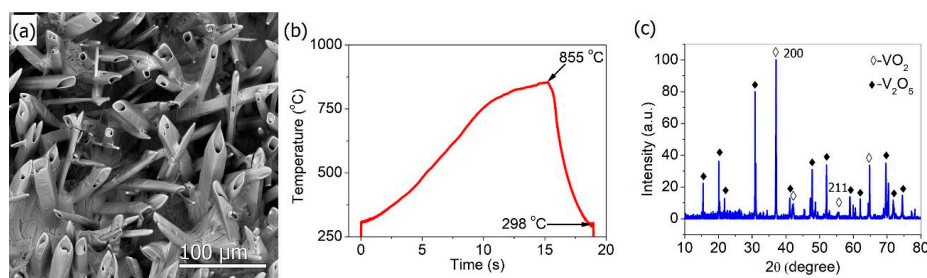


Figure 3. Characteristics of recrystallization product via heating with low peak temperature and cooling rapidly: (a) SEM image, (b) temperature vs. time curve during recrystallization, and (c) XRD pattern.

3.3. Recrystallization of VO_x via Heating with Low Peak Temperature and Cooling Slowly

One sheet of as-fabricated VO_x was heated to relatively low peak temperature with a heating rate of 11 °C/s to melt the V₂O₅ substrate, followed by slow cooling with a cooling rate of 24 °C/s. The direct current of resistive heating is gradually decreased, thereby inducing the liquid V₂O₅ to recrystallize. The SEM image of the obtained recrystallization product is depicted in Figure 4a. Hollow, rod-like products still exist, which are randomly aligned on the surface of a substrate. The microtubes shown in Figure 4a are covered with a thick layer, which are different from as-fabricated single-crystalline VO₂ microtubes. The corresponding temperature vs. time curve is shown in Figure 4b with a peak

temperature of 855 °C and a crystallization temperature of 298 °C. The XRD pattern (Figure 4c) of the obtained product demonstrates that only VO₂ and V₂O₅ are presented. Only V₂O₅ substrate is melted into liquid. The single-crystalline VO₂ microtubes are immersed in liquid V₂O₅ when heated. When the VO_x is slowly cooled down to 299 °C, a part of the liquid V₂O₅ recrystallized on the surface of single-crystalline VO₂ microtubes and other parts of the liquid V₂O₅ recrystallized as the substrate of the single-crystalline VO₂ microtube arrays again. Due to the slow cooling, some VO₂ microtubes cannot erect on the substrate, which results in a random distribution on the surface of the V₂O₅ substrate.

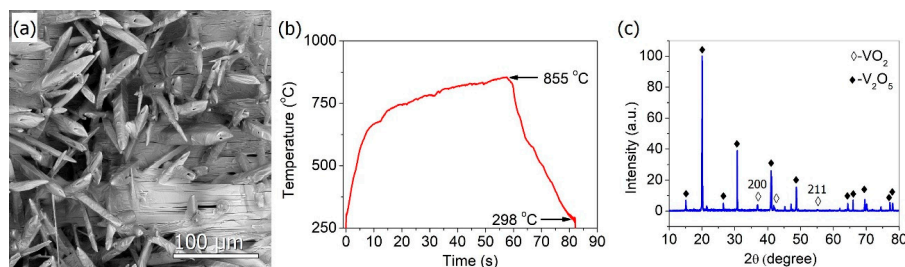


Figure 4. Characteristics of recrystallization product via heating with low peak temperature and cooling slowly: (a) SEM image, (b) temperature vs. time curve during recrystallization, and (c) XRD pattern.

3.4. Recrystallization of VO_x via Heating with High Peak Temperature and Cooling Rapidly

One sheet of as-fabricated VO_x was gradually heated to a relatively high peak temperature with an average heating rate of 46 °C/s to melt the V₂O₅ substrate and the single-crystalline VO₂ microtubes. Subsequently, rapid cooling with an average cooling rate of 288 °C/s, by stopping resistive heating, was performed to recrystallize the liquid V₂O₅ and VO₂. The SEM image of obtained recrystallization product is depicted in Figure 5a. Hollow, rod-like products that are nearly vertically aligned on the surface of a substrate still exist. Apparently, the microtubes shown in Figure 5a are the same as the as-fabricated single-crystalline VO₂ microtubes. The corresponding temperature vs. time curve is shown in Figure 5b with a peak temperature of 1663 °C, two crystallization temperatures of 826 °C and 299 °C. The XRD pattern (Figure 5c) of the obtained product demonstrates that only VO₂ and V₂O₅ are present. When the temperature of as-fabricated VO_x is heated to higher than 1542 °C, both the V₂O₅ substrate and single-crystalline VO₂ microtubes are melted into liquid, which results in a liquid mixture of VO₂ and V₂O₅. When the VO_x is rapidly cooled down to 826 °C, liquid VO₂ recrystallizes to form single-crystalline VO₂ microtube arrays standing in liquid V₂O₅. The crystallization process of liquid VO₂ is exothermic, which maintains the crystallization starting temperature of VO₂ for a short time. As a result, a platform at 826 °C appears in the temperature vs. time curve—marked by an arrow in Figure 5b. After completion of the VO₂ recrystallization, the temperature decreases again until 299 °C is reached. The liquid V₂O₅ is recrystallized to form a substrate of single-crystalline VO₂ microtube arrays again. As a result, a platform at 299 °C appears in the temperature vs. time curve—marked by an arrow in Figure 5b.

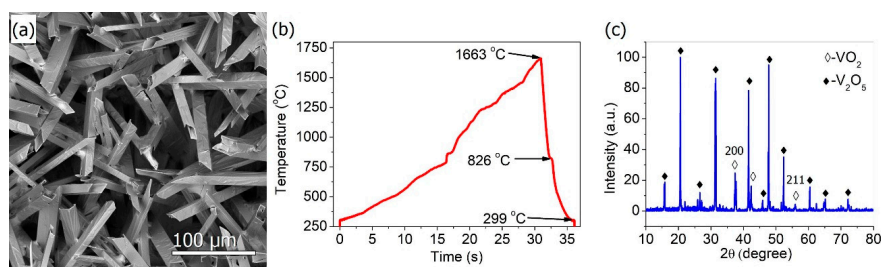


Figure 5. Characteristics of recrystallization product via heating with high peak temperature and cooling rapidly: (a) SEM image, (b) temperature vs. time curve during recrystallization, and (c) XRD pattern.

3.5. Recrystallization of VO_x via Heating with High Peak Temperature and Cooling Slowly

One sheet of as-fabricated VO_x was gradually heated to a relatively high peak temperature with an average heating rate of $87\text{ }^\circ\text{C/s}$ to melt the V_2O_5 substrate and the single-crystalline VO_2 microtubes. Subsequently, slow cooling with an average cooling rate of $49\text{ }^\circ\text{C/s}$ was performed by gradually decreasing the direct current of resistive heating to recrystallize the liquid V_2O_5 and VO_2 . The SEM image of the obtained recrystallization product is depicted in Figure 6a (top view) and Figure 6b (side view). Some plate-shaped solids exist on the surface of the V foil, although several microtubes (marked with two red ellipses in Figure 6b) can be found embedded in the plate-shaped solids. The corresponding temperature vs. time curve is shown in Figure 6c with a peak temperature of $1661\text{ }^\circ\text{C}$ and V_2O_5 crystallization temperature of $303\text{ }^\circ\text{C}$. A hump (marked with a blue arrow) around $860\text{ }^\circ\text{C}$ can be identified in the temperature vs. time curve, which means that VO_2 recrystallization may occur. However, the XRD pattern (Figure 6d) of the obtained product indicates that only V_2O_5 can be identified. When the temperature of as-fabricated VO_x is heated to higher than $1542\text{ }^\circ\text{C}$, both V_2O_5 substrate and single-crystalline VO_2 microtubes are melted into liquid, resulting in a liquid mixture of VO_2 and V_2O_5 . As the liquid VO_x is slowly cooled down, a large amount of VO_2 was re-oxidized to form V_2O_5 above the crystallization temperature of VO_2 along the following route: $4\text{VO}_2 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5$. With a gradually decreased temperature of $860\text{ }^\circ\text{C}$, a small amount of liquid VO_2 recrystallizes to form several microtubes. As a result, a hump appears in the temperature vs. time curve around $860\text{ }^\circ\text{C}$. However, the XRD peaks of VO_2 are too weak to be identified in Figure 6d. With a further decreased temperature to $303\text{ }^\circ\text{C}$, liquid V_2O_5 recrystallized to form plate-shaped solids.

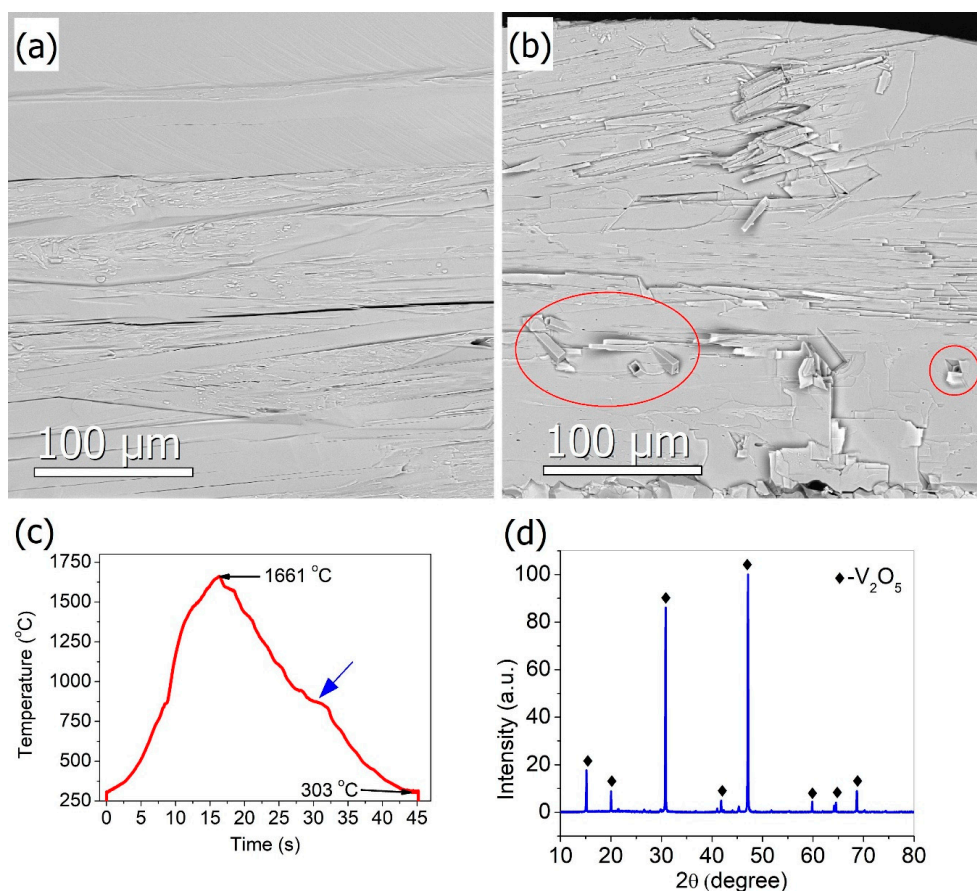


Figure 6. Characteristics of recrystallization product via heating with high peak temperature and cooling slowly: SEM image from (a) top view, (b) side view, (c) temperature vs. time curve during recrystallization, and (d) XRD pattern.

4. Conclusions

When single-crystalline VO₂ microtube arrays on V₂O₅ substrate are heated to a relatively low peak temperature to melt the V₂O₅ substrate, the recrystallization products are still single-crystalline VO₂ microtube arrays on V₂O₅ substrate through slow or rapid cooling. However, the single-crystalline VO₂ microtubes are coated with a V₂O₅ layer, which is apparently different from as-fabricated single-crystalline VO₂ microtubes. These products may be applied as V₂O₅ arrays for gas sensing, catalysts, and so on. The single-crystalline VO₂ microtube arrays on V₂O₅ substrate are heated to a relatively high peak temperature to melt the V₂O₅ substrate and the single-crystalline VO₂ microtubes. The recrystallization products retain the single-crystalline VO₂ microtube arrays on V₂O₅ substrate after rapid cooling because of the sequential recrystallization of VO₂ microtube and V₂O₅ substrate. However, the recrystallization product is mostly plate-shaped V₂O₅ by slowly cooling, due to the re-oxidization of VO₂ at high temperatures. Thus, the peak temperature of the heating and cooling rate are two key factors for recrystallization products of the single-crystalline VO₂ microtube arrays and V₂O₅ substrate.

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