Materials Chemistry and Physics 116 (2009) 527–531

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Formation of nano-rod sodium tungstate film by sodium ion diffusion

Chang-Yeoul Kim*, Seung-Hun Huh, Doh-Hyung Riu

Nanotechnology Convergence Lab., Korea Institute of Ceramic Engineering & Technology 233-5 Gasan-dong Geumcheon-gu, 153 801 Seoul, Republic of Korea

ARTICLE INFO

Article history:
Received 22 July 2008
Received in revised form 8 April 2009
Accepted 18 April 2009

PACS:
68.55.jm

Keywords:
Nanorod
Sodium tungstate
Tungsten oxide
Ion diffusion
Raman

ABSTRACT

Tungsten oxide (WO_3) and nano-rod sodium tungstate ($Na_2W_2O_7$) thin film was prepared by dip coating on slide glass (SG) and tin-doped indium oxide (ITO) coated glass in peroxotungstic acid (PTA) solution. Thermal analysis results showed that PTA is decomposed to tungsten oxide via multiple steps of $WO_3{\cdot}2/3H_2O$, $WO_3{\cdot}1/3H_2O$ and WO_3. Monoclinic phase appeared on ITO glass at 400 °C and crystal growth occurred at 500 °C. However, quite different crystallization behavior appeared on SG due to sodium ion diffusion. At 400 °C, rectangular shape crystals identified as $Na_2W_4O_{13}$ appeared in amorphous matrix, and grew to bundles of rod-shaped $Na_2W_2O_7$ and $Na_2W_4O_{13}$ phase at 500 °C. Raman scattering spectroscopy data confirmed the formation of $Na_2W_4O_{13}$ and $Na_2W_2O_7$ at 500 °C. The understanding of crystallization behavior and sodium ion diffusion into WO_3 thin film on different substrates may be helpful to the application area of electrochromic windows or photocatalyst.

1. Introduction

Tungsten trioxide and their alkali-tungstates, $M_xWO_{3+\delta}$, have attracted considerable attention because of the variety of crystalline structures and their electrochemical and electronic properties, which make it possible to be applicable as active electrodes in electrochromic displays and as catalysts. Tungsten oxide thin film could be prepared by a variety of methods such as evaporation, sputtering, chemical vapor deposition, electrodeposition, and sol–gel technique etc. [1,2]. The tungsten oxide coating solutions could be synthesized by using many kinds of starting materials of Na_2WO_4 [3,4], $WOCl_4$ [5], WCl_6 [6], W metal [7,8], tungsten alkoxide [9]. The tungsten oxide thin film prepared by sol–gel method was reported that it was comprised of micro-crystallites with a hexagonal-like structure when it was annealed at 190 °C. [10,11]

In the case of various alkali-tungstates with different structural families, they have drawn considerable attention in view of their wide ranging properties such as successive phase transitions over a range of temperatures, low dielectric constant, high dielectric loss and high electrical conductivity [12–15]. The presence of a vacant d-shell in the tungstate group facilitates charge transfer from oxygen atoms to the central tungsten atom in the excited state. It imparts a number of advantageous optical and electrical properties such as strong light absorption and luminescence, and so tungstates are considered as potential candidates for high-energy electromagnetic calorimetry and radiation detection [16]. Therefore, many researches have been conducted for the synthesis of sodium tungstates and their applications. The growth of Na_xWO_3 nanowhiskers was reported by varying heating time [17]. Anhydrous sodium pyrotungstate ($Na_2W_2O_7$) has been widely studied with regard to its synthesis through various methods [18–21], detailed structural characterization using X-ray diffraction (XRD) and vibrational spectroscopy (infrared/Raman) [22,23], thermal expansion [24,25] and luminescence properties [26]. The electrical properties of $Na_2W_2O_7$ prepared by solid state reaction were studied by a.c. impedance analysis [27]. However, there is no report about the formation of sodium tungstate thin film by sodium ion diffusion. Our research topic is concentrated on the formation of sodium tungstate on glass substrate by sodium ion diffusion. We used different substrates, slide glass (SG), tin-doped indium oxide (ITO) coated glass substrate and coated peroxotungstic acid on them. We investigated the sodium ion diffusion into tungsten oxide film and the crystallization behavior.

2. Experimental

Tungsten metal powders (99.9%, 0.6–1 μm, Aldrich) or tungstic acid (H_2WO_4, 99%, Aldrich) used as starting materials were dissolved into 30% hydrogen peroxide, which was very exothermic reaction so that it was conducted at 10 °C. Ethanol was added to that solution of which molar concentration was 1 M. WO_3 thin film was coated by dipping SG and ITO glass in the WO_3 coating solution and withdrawing at 100 mm min^{-1}. The withdrawing speed was fixed at 100 mm min^{-1}. The WO_3 coated glass was dried at 150 °C for 10 min and then heat-treated at 200–500 °C for 2 h in air. Thermal analysis of the solution dried at 100 °C for overnight in oven and H_2WO_4 commercial powders was carried out by differential thermal analysis (DTA) and thermogravimetric analysis (TG) method (TG-SDTA 851, Mettler Toledo). The crystal phase development of WO_3 thin film with heat-treatment temperature was

* Corresponding author. Tel.: +82 2 3282 2427; fax: +82 2 3282 7769.
E-mail address: cykim15@kicet.re.kr (C.-Y. Kim).

0254-0584/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2009.04.045

identified by powder X-ray diffraction (XRD, KFX-987228-SE, Mac Science) analysis. The microstructures and thickness of the thin film were measured by field emission scanning electron microscopy (FE-SEM, JSM6700F, JEOL, Japan). WO_3 and sodium tungstate formation by varying heat-treatment temperature were analyzed by micro-Raman scattering spectroscopy (NRS3200, Jasco, Japan).

3. Results

3.1. DTA and TG thermal analysis

In Fig. 1, we found that there was a large endothermic peak at 112 °C accompanying 13% weight loss, which is considered as a result of water molecule evaporation and hydrogen peroxide decomposition. In the range of 200–300 °C, there appears a endothermic peak at 238 °C and weight loss of about 2% follows, which is considered as a result of water decomposition from $WO_3 \cdot 2/3H_2O$. After that, there is an endothermic peak at 318 °C with 1.6% weight loss, which is thought as a result of bound water decomposition from tungstic acid (TA), $WO_3 \cdot 1/3H_2O$. Two exothermic peaks appeared at 411 and 451 °C with no weight loss. The exothermic peak at 411 °C is due to the phase transition of amorphous to monoclinic crystalline phase, and that at 451 °C due to the phase transition from monoclinic to rhombohedral phase. DTA and TG thermal analysis indicates that the precursor peroxotungstic acid (PTA) is $WO_3 \cdot 0.12H_2O_2 \cdot 2.4H_2O$, where the quantity of hydrogen peroxide was titrated by iodometric titration method. PTA was decomposed via three steps; (1) solvent water evaporation and hydrogen peroxide decomposition below 200 °C, (2) bound water decomposition at 200–300 °C, and (3) the decomposition of remaining bound water decomposition at 300–400 °C. The crystallization behaviors from PTA occur via three steps; (1) amorphous phase below 400 °C, (2) monoclinic phase at 400–430 °C and (3) rhombohedral phase at above 430 °C.

3.2. XRD analysis

The crystallization behavior of WO_3 thin film coated on ITO glass was shown in Fig. 2. Until 300 °C, WO_3 thin film was identified as an amorphous phase. At 400 °C, it could be known to be crystallized as rhombohedral phase, and the crystallinity became higher at 500 °C and the crystalline phase did not change. As seen in the DTA and TG thermal analysis, XRD data showed that there exists as amorphous below 400 °C, and crystallized at 400 °C. However, we could not find any evidence of monoclinic to rhombohedral phase transition at 400–500 °C. We guess that there is no distinction between monoclinic and rhombohedral phase of WO_3. For an electrochromic application, amorphous tungsten oxide is preferable to crystalline

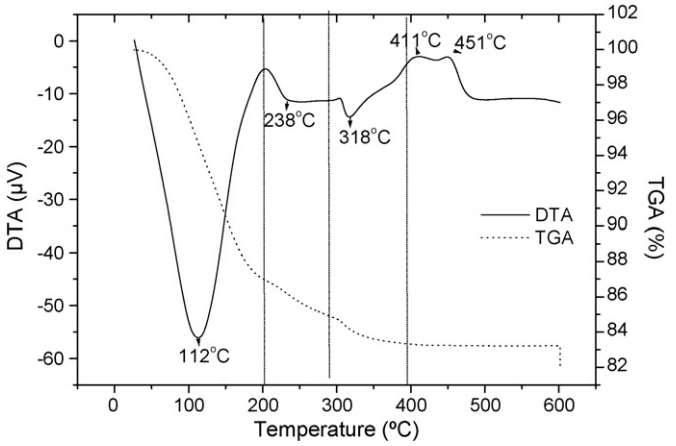

Fig. 1. DTA and TG analysis of PTA coating solution.

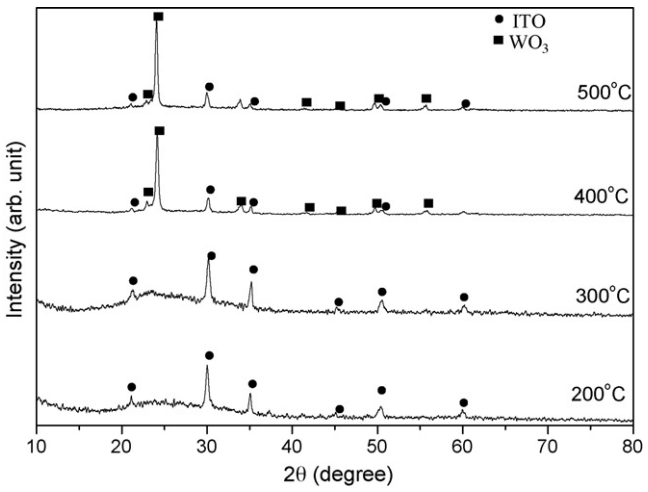

Fig. 2. XRD patterns of tungsten oxide thin film on ITO glass, heat-treated at 200, 300, 400, and 500 °C for 1 h.

phase because there are more active sites for lithium ion insertion or extraction, and so WO_3 thin film should be synthesized at below 400 °C. Anyway, the crystallization behavior on ITO glass occurs as guessed from the results of DTA and TG thermal analysis. However, it was different on SG, as shown in Fig. 3. Amorphous tungsten oxide also remained at 300 °C on SG. At 400 °C on SG, the crystallization behavior was different from that on ITO glass. Nanocrystalline WO_3 and sodium tungstate ($Na_2W_4O_{13}$) simultaneously existed, while rhombohedral WO_3 crystalline phase clearly identified on ITO glass. It indicates that sodium ion begins to diffuse into amorphous WO_3 phase and inhibits the formation of WO_3 crystalline phase. At 500 °C WO_3 crystal phases were identified as $Na_2W_4O_{13}$ and $Na_2W_2O_7$. Through these results, we guessed that sodium ions began to diffuse from SG to WO_3 thin film at 400 °C and form $Na_2W_4O_{13}$ and further sodium ion diffusion forms stable $Na_2W_2O_7$ phase at 500 °C. For ITO glass, ITO transparent conduction thin film layer is found to play a role as a barrier against sodium ion diffusion. Although we do not present the results of SiO_2 barrier formation, it plays the same barrier role. This sodium ion diffusion phenomenon is very interesting to understand sodium ion diffusion from substrate glass to a film.

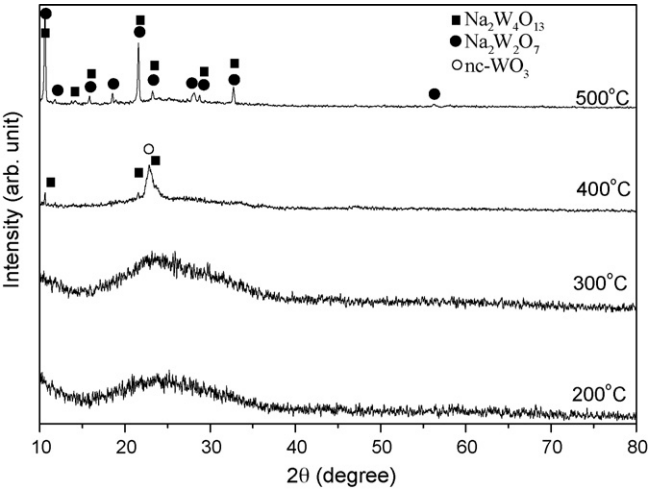

Fig. 3. XRD patterns of tungsten oxide thin film on SG, heat-treated at 200, 300, 400, and 500 °C for 1 h.