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Relationship between particle size and photochromic characteristics of tungsten oxide films prepared by electric current heating method using tungsten wire

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Abstract

Tungsten oxide films were deposited on glass substrates placed above tungsten wires heated by electric current in air. The film thickness in a region just above the wire (region A) was thinner than that in other region (region B). The observation using scanning electron microscope revealed that the films consisted of particles. The shapes of the particles were sphere in the region A while smaller octahedron shape was found in the region B. The amount of the particles in the region B was greater than that in A. The ratio of the number of small particles with a diameter ≤ 500 nm to the total particle number in the region A increased with decreasing applied voltage during the electric current heating, whereas, in the region B, the size of particles was ≤ 500 nm and had no applied voltage dependence. The films exhibited photochromism; the reflectance in the near-infrared region was decreased by the ultraviolet irradiation. In region A, the photochromic effects increased with decreasing applied voltage to the wire. On the other hand, in region B, the photochromic effects did not show the applied voltage dependence. Consequently, it was found that the obtained films showed positive correlation between photochromic effect and the ratio of the number of small particles (≤ 500 nm) to the total particle number. The particles in region B are suitable for mass production of the photochromic material because the photochromic effect and the amount of particles in region B are greater than those in A.

Keywords: Tungsten oxide; Electric current heating method; Photochromism; Near-infrared region

1. Introduction

Tungsten oxide (WO_3) is well known as a photochromic material and a promising candidate for a variety of optical applications such as optical data storage devices [1] and optical switching devices [2]. Takeda and Adachi [3] reported that the WO_{3-x} nanoparticles can be applied to solar control filters because the particles showed an absorption in the near-infrared region with high visible light transmittance.

The WO_3 have been prepared by various techniques such as sol–gel [4], chemical vapor deposition [2], spray pyrolysis [5], pulsed laser deposition [6] and gas-evaporation [7]. The photochromic behavior is thought to be influenced by the preparation methods because of the change in surface morphology and oxygen deficiency of WO_3.

We have succeeded in growing WO_3 films on glass substrate by the electric current heating method using metallic tungsten wire [8]. When a direct current flowed through a metallic tungsten wire at room temperature in air, the wire was heated by Joule heating. Then smoke rose and reached to glass substrate above the wire. After the heating, WO_3 film was obtained on a glass substrate. The film exhibited photochromism by UV irradiation. In this work, we investigated the relationship between the particle size of WO_3 and photochromic characteristics of the films prepared by the electric current heating.

2. Experimental procedure

A metallic tungsten wire (Nilaco Corp., 99.95% purity, 0.5 mm in diameter) was placed between copper electrodes kept 2 cm apart from each other. A glass substrate (Corning

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♯1737) was placed above the wire. The distance between the substrate and the wire was 1 cm. Constant voltages (1.4–3.0 V) were applied to the wire for 3 s using a dc power supply (Takasago Ltd., UX010-200). During the heating, the wire was observed using a video camera (Panasonic, NV-MX3000). Phase identification of the films was carried out using an X-ray diffractometer (XRD; RIGAKU, Multiflex) with CuKα radiation. The morphology of the films was observed using a scanning electron microscope (SEM; JEOL, JSM-5510). The particle size distributions were obtained by measuring the diameter of 1000 particles from the SEM images. The films were irradiated with an ultraviolet (UV) light in the wavelength range of 260–390 nm using a 500 W super high pressure mercury lamp (USHIO Inc., USH-500D) and a filter (SIGMA KOKI Co., Ltd., UTVAF-50S-34U). The relative diffuse reflectances of the films were measured before and after the UV irradiation using UV–vis–NIR spectrophotometer (Shimadzu, SolidSpec-3700DUV) with the Spectralon (Labsphere) as a reference.

3. Results and discussion

Fig. 1 shows sequence photographs which are the frames captured from the video taken from side of the wire during electric current heating at 2.0 V. The wire was perpendicular to the photographic plane. The wire incandesced just after the electric current heating was started. The smoke rose and reached to the substrate as shown in the photos for 0.10–0.17 s. At 0.21 s, the smoke branched into three parts symmetrically. After that, the smoke diffused (0.24–0.35 s). The mechanism for the generation of smoke is considered to be the following. The surface of the tungsten wire changes into WO_3 during the heating since metallic tungsten changes into WO_3 at temperature over 427 °C [9]. Then, the WO_3 is sublimated at temperature over 827 °C [9] and recrystallized between the wire and the substrate. The recrystallized WO_3 is thought to be observed as the smoke.

After the heating of wires, yellow films were obtained on the substrates. Fig. 2 shows the films prepared at 1.4, 2.0 and 3.0 V. The area of the film, which increased with increasing applied voltage to the wire, can be visibly classified into two regions; region A is an area just above the wire and region B is the other area.

Fig. 3 shows XRD patterns of each region of the films prepared with various voltages. The patterns of all films were attributed to two monoclinic WO_3 crystal phases with space groups of $P2_1/n$ and Pc. Any peaks attributed to Cu, CuO or Cu_2O were not detected.

Fig. 4 shows SEM images of cross sections in the regions A and B for the film prepared at 2.0 V. The thickness of the film was about 20 μm in region A while about 100 μm in B. The enlarged images of particles in the regions are shown on the right side of the figure. The shapes of the particles were sphere in region A and octahedron in B. The particle size in region A was bigger than that in B.

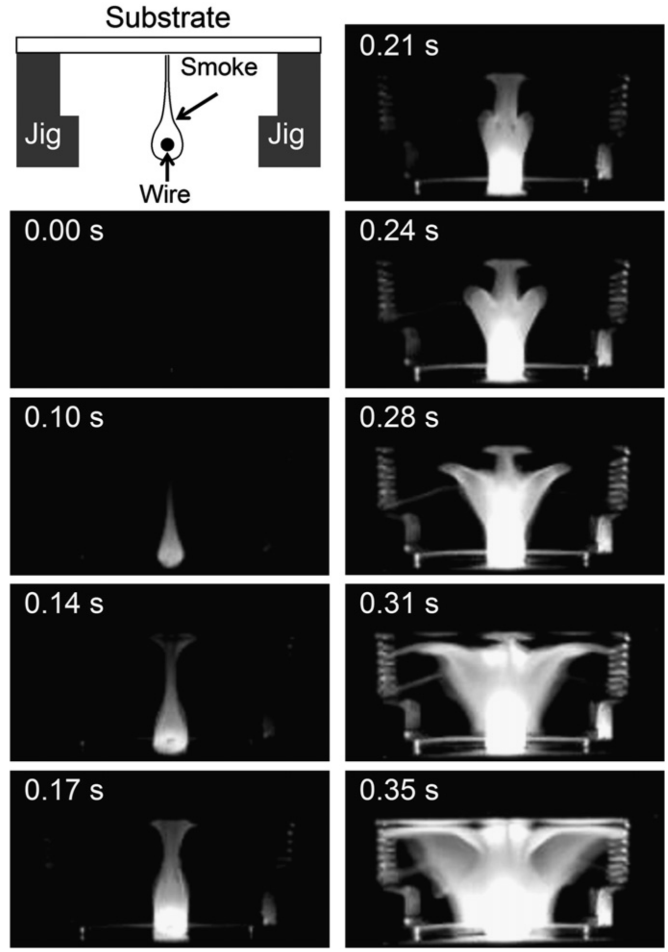

Fig. 1. Photographs of smoke during electric current heating of the wire heated at 2.0 V (side view). The wire was perpendicular to the photographic plane.

The differences of the particles shape in each region were considered to be caused by temperature differences. Region A is nearer to the wire than region B. It is thought that the temperature of region A was higher than that of B. Therefore, the spherical particles were supposed to be formed by the surface tension of melted WO_3. The octahedral particles, which were considered to reflect the WO_6 octahedron[10)], were formed by vapor phase growth.

Fig. 5 shows particle size distributions in region A for various applied voltages to the wire. The ratio of the number of small particles with a diameter ≤ 500 nm to the total particle number increased with decreasing applied voltage to the wire. As the applied voltage decreases, it is assumed that the temperature of the wire decreases and the amount of subliming WO_3 decreases, which results in the preferential formation of small particles. On the other hand, in region B, the size of particles was ≤ 500 nm and had no applied voltage dependence.

Fig. 6 shows the relative diffuse reflectance spectra in region A of the film prepared at 1.4 V. In the wavelength shorter than 480 nm, the reflectance decreased dramatically because of the band edge absorption for the WO_3 [10].