Microelectronics Reliability 79 (2017) 1–4

Contents lists available at ScienceDirect

Microelectronics Reliability

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

Effect of oxygen vacancy in tungsten oxide on the photocatalytic activity for decomposition of organic materials in the gas phase

Daisuke Fukushi [a,b,*], Akito Sasaki [b], Hideaki Hirabayashi [b], Masaaki Kitano [c]

[a] Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[b] Toshiba Materials Co., LTD. 8, Shinsugita-Cho, Isogo-Ku, Yokohama 235-8522, Japan
[c] School of Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form 2 September 2017
Accepted 29 September 2017
Available online xxxx

Keywords:
Semiconductor
Photocatalyst
WO_3
Organic compound
Buttery

ABSTRACT

The relationship between the oxygen vacancy of tungsten oxide and its ability to decompose organic materials under visible-light irradiation was investigated experimentally. In the field of rechargeable batteries, the highest charge-discharge rate is obtained when tungsten oxide is used as a negative electrode with an O/W ratio of 2.72. This result suggested that the number of oxygen vacancies in tungsten oxide affects the photocatalytic decomposition behavior of organic materials. Therefore, with the aim of increasing the photocatalytic activity of tungsten oxide to decompose organic materials, we attempted to clarify the role of the oxygen vacancy. WO_{3-x} nanoparticles, including $WO_{2.83}$ and $WO_{2.72}$ nanoparticles, were fabricated by changing the annealing temperature in a 10% H_2, 90% N_2 atmosphere to generate different densities of oxygen vacancies. Tungsten oxide with O/W ratios of 2.83 and 2.72 exhibited no photocatalytic activity for the photodecomposition of organic materials. The maximum decomposition rate was obtained for stoichiometric WO_3 (O/W = 3). The reason for the decrease or disappearance of the photodecomposition ability should originate in the increase in the number of electrons generated by the oxygen vacancies. These excess electrons promote the recombination reaction between electrons and holes in WO_{3-x}, and hence reduce the lifetime of electron-hole pairs.

© 2017 Published by Elsevier Ltd.

1. Introduction

Much research has been carried out on improving the photocatalytic activity of tungsten oxide, and its mechanism has also been investigated [1–8]. For example, Abe et al. reported the improvement of the decomposition reaction of acetaldehyde by using the platinum-added tungsten oxide photocatalyst [6]. Furthermore, Hashimoto et al. also reported the improved photocatalytic activity of Cu-added tungsten oxide [9]. Moreover, Su et al. fabricated the structurally modified hexagonal and monoclinic WO_3 and succeeded in increasing the photocatalytic activity by using flake- or filmlike shapes of tungsten oxide [10]. In addition, Chakrapani et al. reported that N doping into tungsten oxide narrowed the band gap, increased the visible light absorption, and improved the catalytic activity [11]. As described above, there is much research on improving the photocatalytic activity of tungsten oxide and elucidating its mechanism. However, few studies on the oxygen vacancies of tungsten oxide and the details of their influence on photocatalytic activity have been reported. In the strict sense, there are some reports on the oxidative decomposition of water as a similar application. Wan et al. reported that the WO_{3-x} with oxygen vacancies generated by heating in H_2 ambient at 250–500 °C for 20 min showed a high decomposition rate of water (liquid phase) [12]. However, in the above experiment, a xenon lamp was used as a light source that included ultraviolet illumination, but its irradiation power is too high for the photocatalyst experiment. In addition, a tungsten oxide photocatalyst used in deodorizing materials in indoor applications should be considered in the gas phase. However, the above reports describe only the decomposition behavior of water (liquid phase). On the other hand, there is much research on improving the photocatalytic performance of TiO_2 [9,13–15]. For example, when oxygen is extracted from TiO_2 by annealing treatment, defect levels caused by oxygen vacancies are formed in the band gap. Such defect levels act as recombination sites, and the recombination reaction between excess electrons and holes increases [16]. The number of holes, which act as oxidizers of organic materials, decreases tremendously because the excess electrons promote the recombination reaction between electrons and holes. It is also reported that visible light of long wavelength can be absorbed by defect levels generated by oxygen vacancies in TiO_2, and the photocatalytic activity is improved by irradiation with solar light [17]. These results indicated that the methods of generating oxygen vacancies and the experimental methods were varied, and thus, further detailed experiments are considered necessary. Unlike the atomic configuration of TiO_2, tungsten

* Corresponding author at: Toshiba Materials Co., LTD. 8, Shinsugita-Cho, Isogo-Ku, Yokohama 235-8522, Japan.
E-mail address: daisuke1.fukushi@toshiba.co.jp (D. Fukushi).

https://doi.org/10.1016/j.microrel.2017.09.025
0026-2714/© 2017 Published by Elsevier Ltd.

oxide has two different crystal structures, W_nO_{3n-1} and W_nO_{3n-2} ($n \geqq 4$), and oxygen vacancies are generated by a crystallographic shear structure. In short, tungsten oxide has more crystal structures than TiO_2. Therefore, we focused on the effect of oxygen vacancies in tungsten oxide nanoparticles on the photocatalytic activity for the decomposition of gas-phase acetaldehyde. Therefore, the effect on the photocatalytic activity of generating oxygen vacancies in tungsten oxide with an O/W ratio of 2.72–3 was examined.

2. Experiment

Tungsten oxide nanoparticles were prepared by the plasma vapor phase method using ammonium paratungstate as the starting material [18]. First, monoclinic tungsten oxide (Sample A) was prepared by annealing the tungsten oxide nanoparticles at 450 °C in air for 50 h. Subsequently, oxygen vacancies were generated by annealing Sample A in a 10% H_2, 90% N_2 atmosphere at a temperature of 700 °C (Sample B) or 800 °C (Sample C) [19,20].

2.1. Analysis method

The crystallinity of tungsten oxide was measured using an X-ray diffraction measurement apparatus (D8 Advance, Bruker). The reflectance of the tungsten oxide sample was measured using an absorption spectrometer (UV-2550, Shimadzu). The specific surface area of tungsten oxide was measured by the Brunauer–Emmett–Teller (BET) method with one-point measurement.

2.2. Photocatalytic activity

The photocatalytic activity was measured by a chamber method using the apparatus shown in Fig. 1. 0.05 g of photocatalyst was placed in a 3 L stainless steel (SUS) chamber with a quartz lid. Furthermore, an acrylic plate to cut light with wavelengths of 380 nm or less was placed on the quartz lid. 1.3 μmol of acetaldehyde gas was added to the chamber, and the concentration of acetaldehyde was measured with a multigas monitor (Innova) under irradiation of 6000 lx light. From the change in the concentration of acetaldehyde, the decomposition rate, which was regarded as the photocatalytic activity, was calculated.

3. Result and discussion

Fig. 2 shows the X-ray diffraction patterns of the nanoparticles of tungsten oxides. Three sharp peaks were observed between 22 and 25°, indicating the formation of monoclinic WO_3 (Sample A) with high crystallinity [21]. The peaks of WO_3 are marked with triangles. When Sample A was heated in 10% H_2, 90% N_2 atmosphere at 700 °C, broad peaks were observed at 23.5, 33.4, 41.2, and 48.1°, which can be indexed as monoclinic $WO_{2.83}$ (Sample B, PDF 00-036-0103). The peaks of $WO_{2.83}$ are marked with squares. After annealing at 800 °C, Sample A was converted into $WO_{2.72}$ with a monoclinic structure (Sample C, PDF 00-036-0101). The peaks of $WO_{2.72}$ are marked with circles. These XRD peaks suggest that WO_3 is reduced by annealing in 10% N_2, 90% H_2 atmosphere, with causes a change in the stoichiometry [19,20].

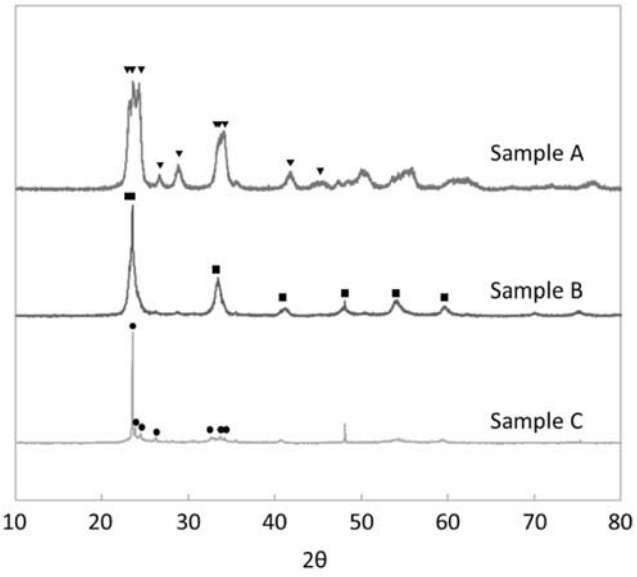

Fig. 2. XRD patterns of tungsten oxides. Sample A: prepared by annealing the tungsten oxide nanoparticles at 450 °C in air for 50 h. Sample B: prepared by annealing Sample A in a 10% H_2, 90% N_2 atmosphere at a temperature of 700 °C. Sample C: prepared by annealing Sample A in a 10% H_2, 90% N_2 atmosphere at a temperature of 800 °C.

Fig. 3 shows the UV–visible diffuse reflectance spectra of the fabricated Samples A, B, and C. Sample A has a high reflectance at 490 nm, which is attributed to the bandgap absorption characteristic of tungsten oxide (2.5 eV). In comparison, the reflectance of Samples B and C for wavelengths above 490 nm significantly decreased, indicating that a large number of oxygen vacancies were formed in Samples B and C [12,22]. According to previous reports of XPS and Raman analyses by, electrons generated by the oxygen vacancies are trapped in W ions and change W^{6+} ion to W^{4+} or W^{5+} ions, resulting in intervalence charge transfer (IVCT) [23–26]. Such a charge bias results in an enhancement of the polaron effect; therefore, the reflectance of 390 nm greatly decreased with increasing polaron absorbance. This polaron absorbance is considered to affect the decomposition of organic materials.

The specific surface areas of the tungsten oxides measured by the BET method were 49 m^2/g for Sample A, 37 m^2/g for Sample B, and

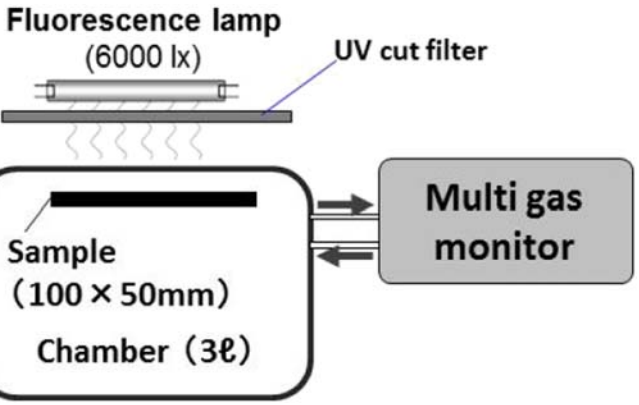

Fig. 1. Apparatus used to measure the photocatalytic activity.

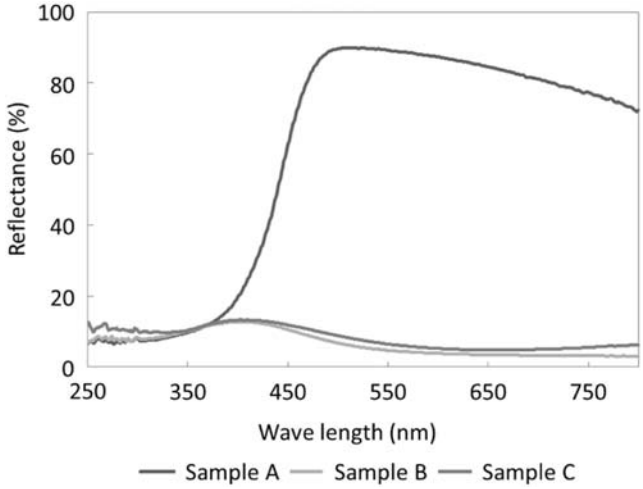

Fig. 3. Diffuse reflectance spectra of tungsten oxides.

Download English Version:

https://daneshyari.com/en/article/4971357

Download Persian Version:

https://daneshyari.com/article/4971357

Daneshyari.com