Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 483 (2005) 276–282

thin solid films

www.elsevier.com/locate/tsf

Dispersion of nanosized noble metals in TiO_2 matrix and their photoelectrode properties

Jong-Won Yoon[1], Takeshi Sasaki, Naoto Koshizaki*

Nanoarchitectonics Research Center (NARC), National Institute of Advanced Industrial Science and Technology (AIST), Central 5 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received 26 July 2004; accepted in revised form 6 January 2005
Available online 1 February 2005

Abstract

The M/TiO_2 (M=Pt, Au) nanocomposite thin films were deposited on quartz and indium tin oxide (ITO) glass substrates using a co-sputtering method. TiO_2 in rutile form is the dominant crystalline phase for as-deposited nanocomposite films. Along with heat treatment up to 600 °C, X-ray diffraction (XRD) peaks of the rutile phase as well as those of noble metal increased in intensity and decreased in width, indicating the growth of crystallites. X-ray photoelectron spectroscopy (XPS) revealed that Au and Pt existed as metallic phases in the TiO_2 matrix. The anodic photocurrents of M/TiO_2 (M=Au, Pt) thin films were observed not only in the ultraviolet (UV) range but also in the visible light range. This is due to the dispersion of nanosized noble metal in the TiO_2 matrix.

PACS: 81.15.C; 81.20
Keywords: Composite; Sputtering; Titanium oxide; Photoconduction

1. Introduction

The investigation of nanometer-scale materials has attracted the attention of many researchers [1–3]. Research has been stimulated by the envisaged applications for this new class of materials in electronics, optics, catalysis, and magnetic storage because these properties derived from nanometer-scale materials are not present in either isolated molecules or micrometer-scale solids. A major goal in material science is the preparation of an artificially designed structure of nanoparticles with new properties [4]. Well-defined, ordered solids prepared from tailored nanoparticles provide opportunities for optimizing properties of materials and offer possibilities for observing new collective physical phenomena that would be interesting and useful for applications.

To enhance the properties of nanometer-scale materials, the preparation of composite particles has attracted the attention of many researchers for enhancing the properties of nanometer-scale materials. Nanocomposites doped with semiconductors or metals have been extensively studied because of their unique optical properties such as third-order nonlinear optical effects, photoluminescence, and photocatalytic effects [5,6]. Such unique properties are also derived from phenomena occurring at the nanoparticle–matrix interface. One of the major goals behind designing the nanocomposite is to improve the catalytic properties. For example, single-component semiconductor nanoparticles exhibit relatively poor photocatalytic efficiency since the majority of photogenerated charge carriers undergo recombination [7]. Semiconductor–semiconductor or semiconductor–metal composite nanoparticles facilitate charge rectification in these systems. The deposition of a noble metal on semiconductor nanoparticles is an essential factor for maximizing the efficiency of photocatalytic reactions [8]. Despite several efforts to synthesize semiconductor–metal composite nanoparticles, little information is avail-

---

* Corresponding author. Tel.: +81 29 858 6333; fax: +81 29 861 6355.
E-mail address: koshizaki.naoto@aist.go.jp (N. Koshizaki).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.01.006

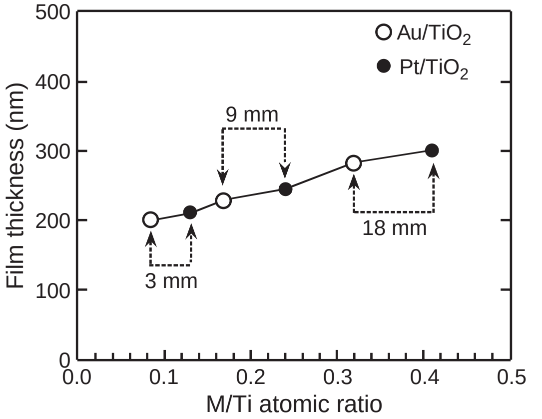

Fig. 1. Thickness of M/TiO_2 (M=Au, Pt) nanocomposite films plotted as a function of M/Ti ratios. Metal wire lengths were 3 mm, 9 mm, and 18 mm.

able on the photodynamics of these materials [9,10]. The use of a functionally active matrix can create a new type of functional nanocomposite [11,12]. In the field of photocatalysis, the polycrystalline system formed by metal-ion-doped TiO_2 has been the objective of several studies [13,14]. Also, the transition metal ion doping of a TiO_2 electrode prepared by a hydrothermal method has been studied to improve conversion efficiency of pure TiO_2 [15,16]. However, the improved photoresponse was limited in the UV range. Recently, the origin of photoresponse in the visible light range in the combined system of TiO_2 and noble metal like gold or platinum was studied experimentally for samples prepared by chemical method [17–19] and theoretically [20]. However, the photoresponse mechanism in the visible light range is not still fully understood.

In this study, we report on the formation of M/TiO_2 (M=Au, Pt) nanocomposite thin films using the RF magnetron co-sputtering method and their photoresponse. This fabrication technique can introduce a large amount of noble metal nanoparticles in the TiO_2 matrix, leading to much higher interface density, compared to the chemical method. Furthermore, noble metal nanoparticles in the nanocomposite system are more stable than those deposited on TiO_2 surface due to less chance of coagulation. Therefore, we might be able to extract the effect of interface on the photoresponse in the visible light range more clearly.

2. Experimental procedure

The M/TiO_2 (M=Au, Pt) nanocomposite thin films were deposited by co-sputtering on quartz glass or indium tin oxide (ITO) glass substrates [21]. Metal wires of 0.5 mm in diameter with various lengths were placed symmetrically on a 100 mm diameter TiO_2 target. The deposition was performed by RF sputtering at a gas pressure of 0.53 Pa using Ar gas with an RF power of 100 W. The deposition time was 2 h. After the deposition, the films were heat-treated in air at various temperatures for 1 h. Phase identification for the nanocomposite thin films was conducted by an X-ray diffractometer (XRD) using Cu K_α radiation (Rigaku, RAD-C). The surface composition and chemical states of the nanocomposite thin films were examined by X-ray photoelectron spectroscopy (XPS) (PHI, 5600ci). Depth profile analysis was performed in every 5 min on a Pt/TiO_2 sample (Pt/Ti=0.41) using Ar sputtering with 3 kV of accelerated voltage for 2 h. An Ar ion beam was rastered on the sample in a 5×5 mm area. The analyzing area was 0.8 mm in diameter at the center of the sputtered area. The binding energies (BEs) were calibrated with the C1s line of adventitious carbon at 284.5 eV. The optical absorption spectra for the nanocomposite films were measured by a spectrometer (Shimadzu, UV-2100PC). The anodic currents were measured with a potentiostat (Solartron, SI1280B) in a cell consisting of the nanocomposite as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode with a 0.1 M Na_2SO_4 aqueous solution. A xenon lamp and a monochromater (Shimadzu, SPG-120S) were used to illuminate the working electrode

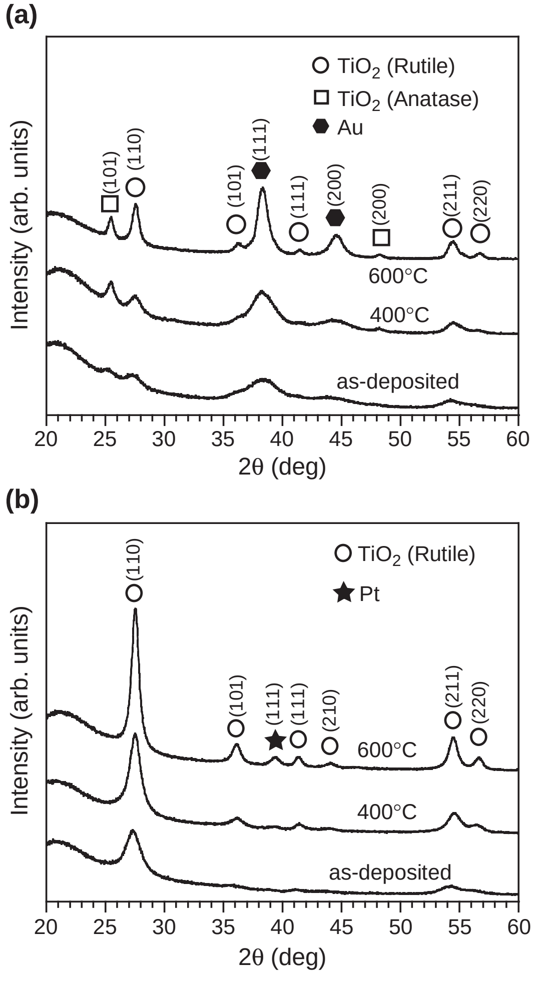

Fig. 2. XRD patterns of (a) Au/TiO_2 (Au/Ti=0.08) and (b) Pt/TiO_2 (Pt/Ti=0.13) nanocomposite films heated at different temperatures.