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Thin Solid Films 494 (2006) 228 – 233
thin solid films
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Preparation and characterization of nanocrystalline porous TiO_2/WO_3 composite thin films

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Available online 13 September 2005

Abstract

TiO_2 materials possessing not only photocatalytic but also electrochromic properties have attracted many research and development interests. Though WO_3 exhibits excellent electrochromic properties, the much higher cost and water-sensitivity of WO_3 as compared with the TiO_2 may restrict the practical application of WO_3 materials. In the present study, the feasibility of preparing nanocrystalline porous TiO_2/WO_3 composite thin films was investigated.

Precursors of sols TiO_2 and/or WO_3 and polystyrene microspheres were used to prepare nanocrystalline pure TiO_2, WO_3, and composite TiO_2/WO_3 thin films by spin coating. The spin-coated thin films were amorphous and, after heat treating at a temperature of 500 °C, nanocrystalline TiO_2, TiO_2/WO_3, and WO_3 thin films with or without pores were prepared successfully. The heat-treated thin films were colorless and coloration-bleaching phenomena can be observed during cyclic voltammetry tests. The heat-treated thin films exhibited good reversible electrochromic behavior while the porous TiO_2/WO_3 composite film exhibited improved electrochromic properties.
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Keywords: Electrochromic properties; TiO_2; WO_3; Sol–gel technique; Spin coating; Porous thin films

1. Introduction

Electrochromism have attracted many Research and Development (R&D) interests due to potential applications such as automobile and building glazings, energy saving, etc. [1,2]. Among the transition metal oxides possessing electrochromic properties, tungsten trioxide (WO_3) exhibits the best properties and is being studied by many researchers [3–5]. Titanium dioxide (TiO_2), better known by its photocatalytic properties, also exhibits electrochromic behavior, but do not appear to be a promising electrochromic material due to its relative long coloration time and low efficiency [6–8]. TiO_2, however, is much cost-effective in comparison with WO_3 material prepared by the same technique.

Many processing techniques including physical vapor depositions [6,9,10], chemical vapor depositions [11–13], and various wet chemistry methods [14,15] have been used successfully to prepare electrochromic materials. Among these techniques, sol–gel processing has become a popular means to prepare homogeneous films from a various choice of precursors in a relatively large scale. For instance, Livage and Ganguli [16] have reviewed recently sol–gel-derived electrochromic films. Numerous references concerning sol–gel synthesized electrochromic metal oxide films and devices are available.

The coloration of electrochromic material for transition metal oxides results from the electron delocalization between the multi-valence states. Diffusion of counter-ions through the materials influences its electrochromic performance. It has been reported that low-density porous WO_3 films may enhance the electrochromic properties. For instance, mesoporous tungsten oxide films have been investigated [17,18]. Cheng et al. [17] reported that mesoporous tungsten oxide

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0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.08.124

films, prepared with a copolymer template, exhibited high coloration/bleaching rates. Badilescu and Ashrit [19] prepared successfully the porous nanostructured WO_3 thin films with the aid of polystyrene microspheres.

In the present study, the feasibility of preparing nanocrystalline TiO_2/WO_3 composite thin films with or without mesoscopic pores by sol–gel technique was investigated. Pure TiO_2 and WO_3 films were also prepared for comparisons. The electrochromic properties of these films were evaluated.

2. Experimental procedures

Fig. 1 shows the flowchart for the preparation of TiO_2, TiO_2/WO_3 (at an atomic ratio of 1/1), and WO_3 thin films with or without pores. The precursor sols for TiO_2 and WO_3 were prepared from titanium tetrachloride ($TiCl_4$) and tungsten hexachloride (WCl_6), respectively, in 95% ethanol mixed hydrogen peroxide. ITO predeposited glass substrates (15 Ω/□, RITEK Corp., Taiwan, R.O.C.) with a dimension of $5 \times 2.5 \times 0.12$ cm^3 were spin coated with the corresponding precursor sols at a speed of 6000 rpm for 20 s. The as-prepared films (film thickness ~140 nm measured by SEM) were dried at 80 °C for 1 h and then annealed at 500 °C for 2 h resulting in pure TiO_2, WO_3, and composite TiO_2/WO_3 films. Porous thin films (denoted as PS-TiO_2, PS-TiO_2/WO_3, and PS-WO_3) were prepared with similar procedures. Precursor sols of TiO_2 and/or WO_3, however, were mixed with 10% (wt/vol) polystyrene (PS) microspheres (diameter ~200 nm) before spin coating.

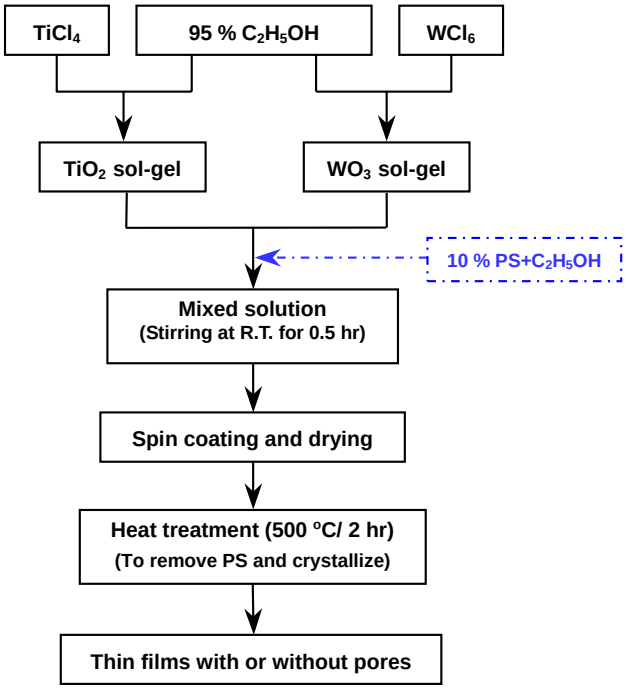

Fig. 1. The flowchart for the preparation of TiO_2, TiO_2/WO_3, and WO_3 thin films with or without pores.

The surface morphology of the heat-treated TiO_2, TiO_2/WO_3, and WO_3 thin films with or without pores was examined by scanning electron microscopy (SEM, S-4800 HITACHI, Japan). X-ray diffraction, for phase identification, was performed by a Sumadzu XRD-6000 diffractometer with a Cu Kα radiation. Electrochromic properties of these thin films were evaluated by cyclic voltammetry (CV, PARSTAT 2263, Perkin Elmer Instruments, Inc., USA), using a standard three-electrode cell system where the sample served as the working electrode, Hg/Hg_2Cl_2 as the reference electrode, and platinum as the counter electrode. A 1 M $LiClO_4$ solution in propylene carbonate was used as the electrolyte. All CV measurements were performed from −1 to 1 V at a scan rate of 30 mV/s at room temperature. Transmittance spectra of the films were examined by a spectrophotometer (Mini-D2T, Ocean Optics, Inc., USA).

3. Results and discussion

3.1. Structural characterization

All spin-coated films were amorphous and exhibited smooth surface without obvious contrast. After heat treating at a temperature of 500 °C for 2 h, amorphous to crystalline phase transition can be noticed. However, it is very important to examine the surface morphology of the heat-treated films. Fig. 2a and c show the TiO_2/WO_3 and WO_3 thin films, respectively. That heat-treated TiO_2 film possessed a grain size much finer than that of WO_3 film (Fig. 2c), while that the grain size of TiO_2/WO_3 composite thin film (Fig. 2a) in between. Meanwhile, it can be noted that the porosity (though not measured in the present study) increased from TiO_2, TiO_2/WO_3, to WO_3 thin films. After introducing PS microspheres, distinct porous thin films can be prepared. Corresponding porous PS-TiO_2/WO_3 and -WO_3 thin films are shown in Fig. 2b and d, respectively. It is interesting to note that PS-TiO_2 (not shown here) and PS-TiO_2/WO_3 composite thin films exhibited a similar surface morphology but differed significantly from that of PS-WO_3 film. This may be due to differences on the grain sizes of TiO_2 and WO_3 particles.

The grain size of TiO_2 after heat treatment at 500 °C (~20 nm measured by TEM, but not shown here) was obvious smaller than that of PS microspheres (~200 nm). The grain growth of nanocrystalline TiO_2 was slow during heat treatment and the shape of microspheres remained. As compared to TiO_2, heat-treated WO_3 film (Fig. 2c) exhibited a relatively large grain size (in the same order as the PS microspheres) and necking between WO_3 particles can be observed. For fast-growing WO_3, necking between particles induced a chain-like microstructure with numerous pores due to the addition of PS microspheres. For the porous PS-TiO_2, -TiO_2/WO_3, and -WO_3 films investigated in the present study, the additions of PS microspheres induced a continuous network of pores creating an excellent passage

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