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Gasochromic tungsten oxide films with $PdCl_2$ solution as an aqueous Hydrogen catalyst

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ABSTRACT

In this study, WO_3 nanostructured films were prepared by sol–gel spin coating process on glass substrates and drops of $PdCl_2$ solution were used as an aqueous hydrogen catalyst for gasochromic investigations. As deposited WO_3 films were annealed at different temperatures of 100, 200, 300 and 400 °C in air. The effect of annealing temperature on crystalline structure and surface morphology of WO_3 films was studied by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) and/or Atomic Force Microscope (AFM). Fourier Transform Infrared (FTIR) spectroscopy revealed the variation of chemical bonds with annealing temperature. Because of the aqueous nature of hydrogen catalyst, hydrophilicity of samples was measured by means of contact angle and it was found to increase with annealing temperature. We found a correlation between annealing temperature, hydrophilicity, palladium growth and coloring of tungsten oxide films when an aqueous hydrogen catalyst is used. The effect of catalyst concentration on colored state optical density was also studied for films annealed at 400 °C.

1. Introduction

Tungsten oxide is an *n*-type semiconductor with band gap energy about 3 eV and in the bulk form has a yellow–green appearance. This metal oxide has many applications such as catalytic [1], optical memory [2], hydrogen sensors [3–5] and smart windows based on electrochromic [6] and gasochromic properties [7–10]. Among the gasochromic materials, WO_3 is the most promising one. A gasochromic coating normally consists of an electrochromic layer such as WO_3 and a very thin catalyst top layer such as Pt or Pd. In the gasochromic process of tungsten oxide thin films, the color of layer converts from a transparent to an absorbing blue state when atomic hydrogen incorporates into the material lattice. The atomic hydrogen, H^+, and extra electrons are first produced by catalytical dissociation of H_2 through the reaction with Pd. Then these ion–electron pairs diffuse through the grain boundaries and transfer into the lattice sites and small polarons are subsequently produced. The small polaron transitions are responsible for the optical absorption of colored tungsten oxide films [11]. This process is often reversible, i.e. whenever the colored film is flushed with O_2 gas, the small polarons are recovered and finally the layer becomes bleached. This mechanism is similar to the electrochromic reaction. Many methods can be used to prepare WO_3 films, including sputtering [8], evaporation [12], spray [13], chemical vapor deposition [14], pulsed laser deposition (PLD) [15–21] and sol–gel [10]. Among these, the sol–gel technique is one of the most promising methods to prepare large surface area films, and it has many advantages such as simple equipment and low costs [21–24].

As it was mentioned, to have an optical conversion of WO_3 thin films, it is necessary to deposit a very thin layer of metallic Pd or Pt as hydrogen catalyst over it. Pd is a well-known catalyst for hydrogen. Therefore, the characteristics of Pd layer can determine the dissociation rate of absorbed gases and hence the coloring–bleaching velocity. There are different ways to deposit a thin Pd film such as sputtering [25], e-beam evaporation [26], electroless [18] and hydrogen reduction [21]. Electroless deposition of palladium has a well established mechanism that is based on the reduction of a meta-stable metallic salt complex on an activated substrate in which metal ions undergo normally a reducing mechanism from the liquid environment to a metallic phase over the whole substrate or some selective positions [27]. In hydrogen reduction method, hydrogen gas acts as a common reducing agent with no residual chemical impact on the system. Synthesis of metal nanoparticles with unique optical and chemical properties by hydrogen reduction of the metal chlorides or oxides was reported previously [28–30]. Koo et al. [31] have obtained palladium thin films on alumina or polymer substrate using atmospheric pressure hydrogen plasma that reacts with deep coated $PdCl_2$ layer. Therefore, application of hydrogen as a

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reduction agent in the creation of nanostructured Pd catalyst layer on WO_3 supports will have interesting aspects for gasochromic applications.

We previously showed the successful gasochromic coloring of tungsten oxide in which top layer of palladium nanoparticles are produced by hydrogen reduction of a pre-deposited $PdCl_2$ layer [21]. In this method, drop-dried $PdCl_2$ upon the WO_3 surface are exposed to the hydrogen steam and metallic palladium are formed over the surface by hydrogen reduction. However, the droplets of $PdCl_2$ without drying stage can also be used in gasochromic coloring of WO_3 films as an aqueous hydrogen catalyst. In this work, we examined this idea and studied the relation between post annealing temperature, palladium growth and coloring of sol–gel derived WO_3 films. The surface chemistry of metal oxide usually changes with annealing process. We observed that the hydrophilicity of layers increases dramatically with annealing temperature and this change in the surface properties affects the quality of palladium growth as well as the gasochromic behavior.

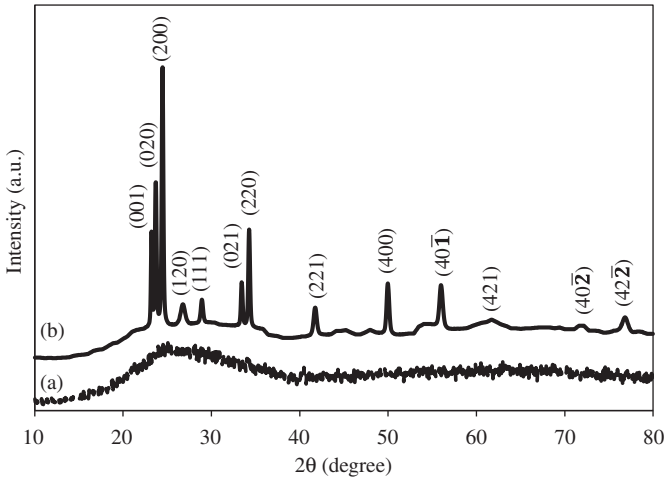

Fig. 1. XRD patterns of WO_3/glass films annealed at (a) 300 and (b) 400 °C for 1 hin air.

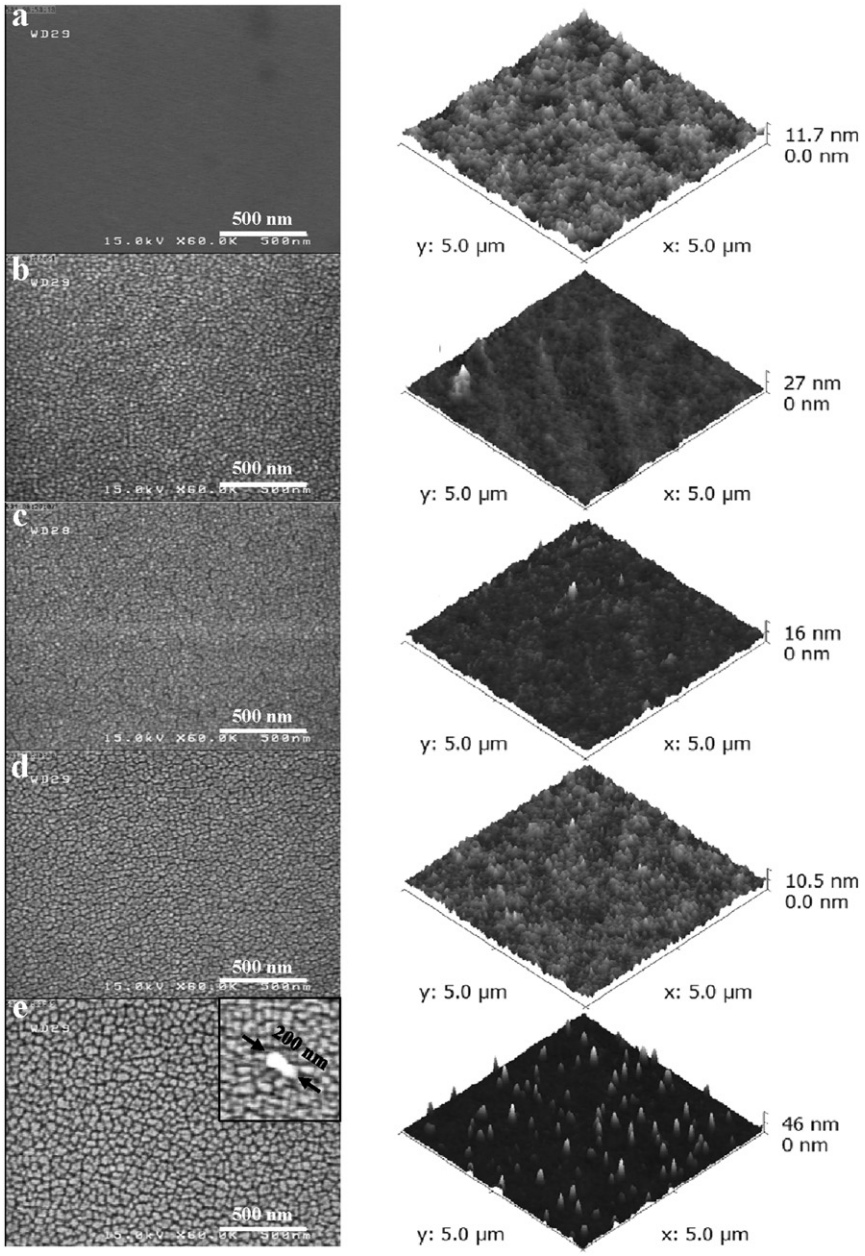

Fig. 2. FE-SEM and AFM images of WO_3/glass films before annealing (a) and after annealing at (b) 100, (c) 200, (d) 300 and (e) 400 °C for 1 h in air.