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Improved electrochromical properties of sol–gel WO_3 thin films by doping gold nanocrystals

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ABSTRACT

In this investigation, the effect of gold nanocrystals on the electrochromical properties of sol–gel Au doped WO_3 thin films has been studied. The Au–WO_3 thin films were dip-coated on both glass and indium tin oxide coated conducting glass substrates with various gold concentrations of 0, 3.2 and 6.4 mol%. Optical properties of the samples were studied by UV–visible spectrophotometry in a range of 300–1100 nm. The optical density spectra of the films showed the formation of gold nanoparticles in the films. The optical bandgap energy of Au–WO_3 films decreased with increasing the Au concentration. Crystalline structure of the doped films was investigated by X-ray diffractometry, which indicated formation of gold nanocrystals in amorphous WO_3 thin films. X-ray photoelectron spectroscopy (XPS) was used to study the surface chemical composition of the samples. XPS analysis indicated the presence of gold in metallic state and the formation of stoichiometric WO_3. The electrochromic properties of the Au–WO_3 samples were also characterized using lithium-based electrolyte. It was found that doping of Au nanocrystals in WO_3 thin films improved the coloration time of the layer. In addition, it was shown that variation of Au concentration led to color change in the colored state of the Au–WO_3 thin films.

1. Introduction

Research in the field of electrochromic transition metal oxide films has gained a lot of attention in the past several decades. In an electrochromic device, its transmittance and reflectance change in a reversible manner under the application of an external voltage [1,2]. Since an electrochromic reaction involves electron conduction and ion diffusion, the electronic conductivity and ionic diffusivity in electrochromic materials are clearly critical factors [3].

Among the transition metal oxides that exhibit electrochromic properties, WO_3 has been investigated most extensively [1–6]. This was due integrally to its fast response times, coloration efficiencies, long life times, etc. These properties tendered WO_3 desirable for use in information displays [7], anti-glare rear view mirrors of automobiles [8,9] and the so-called “smart windows” [10]. However, there are many efforts to improve its coloration performance (lower coloration time, higher color intensity and reversibility) for practical applications. For this purpose, Haranahalli and Holloway have found that the coloration and bleaching rates of WO_3 film increase with the addition of the porous conducting metallic over layer in a liquid electrolyte cell [11]. Moreover, electrochromic operation of WO_3 films doped with Co, Cr and Ni has been reported [12,13].

It has been known that gold nanoparticles have excellent inertness as well as excellent stability, and increase metallic properties and also conductivity of a layer resulting in the enhancement of electrochromic performance [12,14]. Concerning these advantages, gold nanoparticles have been recently used to modify electrochromic properties of WO_3 thin films [15–17]. He et al. has reported addition of gold over layer on WO_3 thin film formed by physical vapor deposition resulted in a better change of optical density in electrochromic process [15]. In the other works [16,17], some researchers have studied electrochromic properties of co-sputtered Au–WO_3 nanocomposite thin films containing high gold concentration (60 mol% Au) and obtained a shorter response time relative to the pure WO_3 thin film. However, in their films containing high Au concentrations, the transfer of positive ions occurs competitively between gold and tungsten trioxide resulting in the formation of ion-metal compounds which are inactive in the coloration process. In these conditions, they have observed reduction of optical density change in the Au–WO_3 nanocomposite thin films as compared to the pure thin films. Therefore, it is expected that an optimum doping of gold metallic nanophases can increase conductivity and improve electrochromic performance of WO_3 thin film.

In this paper, we present data on optical properties, crystalline structure and surface chemical state of Au doped WO_3 thin films synthesized by easy and low cost sol–gel method. In addition,

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electrochromic behavior of Au–WO_3 thin films under various applied voltages has been also studied.

2. Experimental details

Sol–gel Au doped WO_3 thin films were prepared using the following procedure. At first, 6 g of sodium tungsten dehydrate ($Na_2WO_4 \cdot 2H_2O$, 99% Merck) was immersed in 30 ml of nitric acid solution (HNO_3, 65% Merck) for 15 min to exchange the Na^+ ions with H^+. After washing three times with distilled water, the obtained yellow–greenish precipitate was dissolved in 10 ml of H_2O_2 (30% Merck), and then 1 ml of ethanol was added to the solution. After 24 h, it was exposed to light using a commercial 100 W lamp for 2 h in order to concentrate the solution. The color of the solution changed from colorless to light yellow, and it was stable for a long time. Then, after another 24 h aging, the prepared WO_3 sol was mixed with various amounts of 0.14 molar aqueous solution of $HAuCl_4$ (99.5% Merck). The molar concentration of Au in the final sols was varied by the amounts of 0, 3.2 and 6.4 mol%. The blended sols were stirred magnetically for 2 h, and subsequently the deposition process was performed by dipping the cleaned microscope slide glass and indium tin oxide (ITO) coated glass (commercial ITO; ~1 µm thickness and electrical sheet resistance ~100 Ω/□) into the solution for 60 s and pulling them out at a rate of 1 mm/s. All films, at first, were dried at 100 °C and then annealed at 200 °C in air for 1 h. Using the optical method [18], the thickness of the dried films measured about 200–300 nm.

A UV–visible spectrophotometer (Jasco-V530) was used to investigate the optical properties of the films (without eliminating the substrate effect) in the wavelength range of 300–1100 nm with 1 nm resolution. Philips PW 3710 profile X-ray diffractometry (XRD) with Cu–K_α radiation source (conventional θ–2θ diffractometer) and step size of 0.05° was used to determine phase formation, average crystalline size and structure of the layers. X-ray photoelectron spectroscopy (XPS) equipped with an Al–K_α X-ray source at an energy of 1486.6 eV was employed to investigate the surface chemical composition of the films. The hemispherical energy analyzer (Specs EA 10 Plus) operating in a vacuum better than 10^{-7} Pa was used. All binding energy values were calibrated by fixing the C(1s) core level to the 285.0 eV. All of the peaks were deconvoluted using SDP software (version 4.1) with 80% Gaussian–20% Lorentzian peak fitting.

The electrochromic properties of the Au doped WO_3 thin films were investigated on ITO/glass substrates in a 50 ml glassy cell containing two electrodes. The Au–WO_3 films, as working electrodes, were electrochemically cycled in a 1 M $LiClO_4$ in propylene carbonate (PC) electrolyte in a glass test vessel, using pure graphite as the counter electrode. All measurements have been performed at room temperature (~25 °C) and in air. Experimental details of the electrochromic test have been reported elsewhere [19]. The coloration transmittance of the Au–WO_3 thin films was studied in two states. In the first state, it was measured as a function of time at a fixed wavelength of 500 nm (in which eye has a high sensitivity) at different coloring voltages, and then negative voltages applied for bleaching the films. Furthermore, during the electrochromic process, the magnitude of the current between the two electrodes was recorded. In the second state, the transmittance was measured by the spectrophotometer in a range of 300–1100 nm wavelength for the films colored after a constant time (500 s) at different coloring voltages.

3. Results and discussion

3.1. Optical measurements

Optical transmission (T) and reflection (R) spectra of the Au–WO_3 thin films, deposited on glass substrates, have been shown in Fig. 1a. It can be seen that the transmittance of the pure WO_3 film is about 80% in the visible range and decreased slightly to less than 70% with increasing the Au concentration. A similar behavior has been also reported for Au–Al_2O_3 films [20]. It is evident that the transmittance of the doped thin films is still high enough over the visible range for optical applications. The sharp reduction of the transmittance spectra at the wavelength of ~370 nm is due to the fundamental WO_3 absorption edge [21,22]. The optical transmission of the WO_3 films strongly depends on the oxygen content in the films. In fact, nonstoichiometric films with composition of WO_{3-x} show a blue tinge color for $x > 0.03$ [23]. As it is obvious from Fig. 1a, all the prepared samples were highly transparent with no observable blue coloration indicating stoichiometric formation of tungsten trioxide in the films. Also, it is clear from the figure that the reflection of pure WO_3 thin film is about 10% in the visible range while it increases to about 25% for the Au doped films.

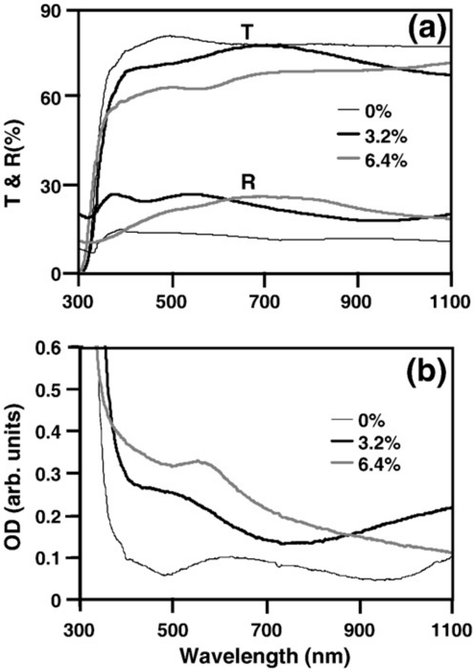

Fig. 1. (a) Optical transmittance (T) as well as reflectance (R) and (b) absorption spectra of the Au doped WO_3 thin films, grown on glass substrate, with different Au concentrations.

The optical density (OD) spectra of the glass-supported thin films have been also obtained using the following well known relation [24]:

$$OD = \alpha d = \ln(T_0 / T) \quad (1)$$

where, α, d, T_0 and T are optical absorption coefficient, thickness, transmittance of the substrate and transmittance of the film, respectively. Fig. 1b shows the optical density spectra for the Au doped films as compared to the pure WO_3 thin film. It can be seen from the absorption curves that a weak broad peak was formed for the film containing 3.2 mol% Au. This peak becomes more intense for the film with higher concentration of Au (6.4 mol%). It is known that for a metal nanoparticle with dimension much smaller than the wavelength of light, an electromagnetic wave with certain wavelength induces a resonant coherent oscillation of the free electrons across the nanoparticle. This oscillation is known as surface plasmon resonance (SPR) which results in a strong absorption of electromagnetic irradiation at corresponding wavelength [25,26]. This wavelength depends on the metal composition [27], nanoparticle size and shape [28,29] and the dielectric properties of the surrounding media [30]. According to Fig. 1b, the SPR peaks are in the range of 510–550 nm wavelengths indicating partial formation of gold nanoparticles [31,32] in the WO_3 films with a broad size distribution at 200 °C. Moreover, the presence of a single peak in the optical density spectra indicates that the shape of Au nanoparticle is sphere like [26].