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Electrochromic performance, wettability and optical study of copper manganese oxide thin films: Effect of annealing temperature

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ABSTRACT

In the present work, the nanostructured copper manganese oxide (CMO) thin films were prepared from acetate based sol–gel precursors and deposited on glass and indium tin oxide (ITO) substrates by dip-coating technique. The films were annealed at 300, 400 and 500 °C in ambient atmosphere. The effects of annealing temperature on structural, morphological, wettability, electrochromic and optical properties of CMO thin films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDX), water contact angle measurement (WCA), cyclic voltammetry (CV) measurements and ultraviolet–visible (UV–vis) spectrophotometery. The presence of mixed oxide phases comprising of copper manganese oxide ($CuMn_2O_4$) and manganese oxide at different annealing temperature was confirmed by XRD patterns. The results showed that the Mn_3O_4 phase has been changed to Mn_2O_3 when the annealing temperature is increased from 300 to 500 °C. The FESEM images indicated that the granular surface morphology was sensitive to annealing temperature. EDX studies indicated that the thin films contained O, Mn and Cu species. Wettability studies showed that the water contact angle of the nanostructured CMO thin films coated on glass substrates was influenced by the variation of annealing temperature and the surface nature of thin films was changed from hydrophilic to hydrophobic. The results of CVs measurement indicated that the anodic and cathodic charge density and capacitance of all CMO samples decreased with increasing scan rate in potential range of −1–1 eV. Also, the annealed CMO thin film at 500 °C showed better electrochromic performance with respect to other samples at lower scan rate. The thickness, refractive index, extinction coefficient and optical band gap of thin films coated on glass substrates were calculated from reflectance and transmittance spectra using an iterative numerical method. The optical band gap of nanostructured CMO thin films increased with increasing annealing temperature.

1. Introduction

The development of nanostructured materials open up a new era in basic research and solid state technology. The nanostructured materials with notable increased surface area are expected to show novel physical and chemical properties. Among the nanostructured metal oxide materials, manganese oxides occupy a prominent place due to various valence states and crystalline structures such as MnO, Mn_2O_3, MnO_2, and Mn_3O_4 [1]. Manganese oxides have attracted great research interest in the diverse field such as electrodes in batteries [3,4] catalysts [5,6], magnetic properties for removal of harmful inorganic contaminants from water [7] and biosensor [8]. Also, literature reports indicate that there have been considerable researches on the preparation of the manganese oxides in the form of thin films due to their applications in the electrochromic materials [9,10], electrochemical supercapacitors and energy storage layers [2,11]. Manganese oxide thin films have been prepared using various physical and chemical methods such as electron beam deposition [10], atomic layer deposition (ALD) [12], molecular beam epitaxy (MBE) [13], electrochemical deposition [14], potentiostatic anodic electrolysis [15], chemical spray pyrolysis technique [16], chemical bath deposition [17], sol–gel method [18,19] and so on. The results indicated that the physical properties of manganese oxide thin films are very sensitive to the preparation method and conditions. Among the mentioned methods, sol–gel dip coating is a useful coating technique due to the low cost of preparation and homogeneity of the final products. Formation of a thin film with homogeneous surface is an important parameter for improvement of surface properties such as adhesion, wettability, surface reactivity and catalytic activity. In recent years, significant efforts have been made to develop nanostructured manganese oxides by doping or mixing with other materials. A number of experiments have investigated manganese oxides doped with Pd [20], V [21], Co

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[22], Ag [23] and Zn [24] to provide more sophisticated control over the catalytic, supercapacitor and magnetic applications. Also, there are experimental results of the mixed manganese oxides such as Mn_3O_4/MWCNT composite for lithium-ion batteries [25], Mn_3O_4/graphene (GM) composites and MnO_2:La/MWCNTs composite for supercapacitors [26–28], Mn_2O_3/TiO_2 and MnO_2/TiO_2 nanocomposites for photocatalytic activity and Ni and Co doped $CuMn_2O_4$ for magnetic application [29–31]. Copper manganese oxides (CMOs) compounds are also a kind of mixed manganese oxides that are widely studied for catalytic application. In recent decade, $Cu_xMn_{3-x}O_4$/polypyrrole(PPy) composite, Au supported on Al_2O_3–CuO–Mn_2O_3 composite, Co/$CuMnO_x$, $Cu_xMn_{3-x}O_4$ compounds [32–39] have been proposed for this application. To the author's knowledge, there is little information available in the literature on the optical properties of copper manganese oxides (CMOs) thin films [18,40] and there have been no reports on the study of electrochromic performance and wettability of CMO thin films. Therefore, the preparation of CMO thin films for different applications such as unwettable layers and electrochromic electrode is worthwhile.

In the present work, the copper manganese oxide (CMO) thin films were prepared by a simple sol–gel process from metal acetates and organic solvent and deposited on glass and indium tin oxide (ITO) substrates by dip-coating technique. In this study, for the first time, the effects of heat treatment on electrochromic, wettability, optical, structural and morphological properties of CMO thin films were investigated. The mentioned properties were examined by cycling voltammetry, contact angle measurement (CA) and UV–vis spectrophotometry, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy analyses, respectively. Furthermore, the anodic and cathodic charge density was determined by CV measurements at different scan rate. The optical band gap and optical constants of the CMO thin films were calculated by transmittance and reflectance spectra.

2. Experimental methods

2.1. Film preparation

The nanocomposite CMO thin films were prepared on glass and ITO substrates using the sol–gel dip-coating technique. In the preparation of the binary solution (0.4 M), manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$, Merck) and copper acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$, Merck) were used as procurers with a $Cu(ac)_2/Mn(ac)_2$ molar ratio of 20/80. Firstly, $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Cu(CH_3COO)_2{\cdot}H_2O$ were simultaneously dissolved into moderate amount absolute ethanol at room temperature under continuous stirring. The monoethanolamine (MEA, C_2H_7NO, Merck) as stabilizer was slowly added to manganese-containing solution and copper-containing solution after 7 and 15 min, respectively. In each solution, the molar ratio of MEA to manganese acetate and copper acetate was 1:1. Also, after 5 min stirring, copper-containing solution (clear and blue color) was added to manganese-containing solution (clear and brown color). Then, the mixed solution was stirred for 1.5 h at room temperature until a homogeneous and stable solution was obtained. After aging of solution for 24 h, deposition of thin films on glass and ITO substrates was performed by dip-coating technique at room temperature. The substrates were coated by dipping with withdrawal speed of 8.5 cm/min and the obtained wet films were dried in an oven at 160 °C for 20 min. The deposition process was repeated for six times. Eventually, the CMO thin films were heat treated in a furnace at three different temperatures (300, 400 and 500 °C) for 1 h in air ambient. The prepared thin films (annealed at 300, 400 and 500 °C in the air) were named as CMO_3, CMO_4 and CMO_5, respectively.

2.2. Film characterization

The phase identification was performed using X-ray diffractometry (XRD, Philips PW-1800) with Cu-Kα radiation (λCu-Kα = 0.15406 nm). The surface morphology of the deposited thin films was observed using a field emission scanning electron microscope (FESEM, Hitachi S4160, Japan). The identification of element in final products was studied by the Energy Dispersive X-ray spectroscopy (EDS, Oxford Instrument, England). The wettability test was performed by water contact angle (WCA) measurement using Dataphysics OCA 15 Plus instrument equipment with CCD camera in ambient condition at room temperature. Electrochemical properties were evaluated by a high power Wenking potentiostat (Model Hp 88, Bank Electronic) using a standard three-electrode cell system with Ag rod electrode in the 1 M LiClO4/PC electrolyte at room temperature. Cyclic voltammetry (CV) analysis was carried out at voltage range of −1–1 V at the scan rate from 10 to 100 mV/s. Optical transmittance (T) and reflectance (R) spectra were recorded by UV–vis spectrophotometer (Perkin-Elmer Lambda 25) in the wavelength range 200–1100 nm with unpolarized light, at room temperature. The transmission and reflection spectra were used to determine the thicknesses of thin films, optical constants and optical band gap.

3. Results and discussion

3.1. Structural studies

The XRD analyses indicated that the prepared CMO thin films are amorphous. Hence, in order to identify crystalline phases of CMOs at different annealing temperatures, the thicker copper manganese oxide (CMO) and manganese oxide (MO) samples were prepared and scratched. Then, X-ray diffractions were taken of the CMO and MO scratched films. The XRD patterns of the pure manganese oxide (MO) films, without additional dopant, were used to determine and identify the crystalline phases of the MO films at different annealing temperatures. From XRD patterns of MO_300 coatings revealed the Mn_3O_4 phase peaks, which were close to those reported in the ICDD card (No. 18-0803). XRD patterns of MO_400 sample (Fig. 1(b)) indicate that, the intensity of the Mn_3O_4 main peak decreased and the minor peaks disappeared. By increasing the temperature up to 500 °C, the XRD pattern of the sol–gel manganese oxide (MO) coatings exhibited peaks for cubic Mn_2O_3 without any other phase. The appeared peaks of Mn_2O_3 (MO_500 pattern in Fig. 1(c)) were in excellent agreement with the data of ICDD card (No. 41-1442). The comparison of XRD patterns of MO coating (MO_300, MO_400 and MO_500) indicated that the rise in annealing temperature with an increase in oxidation state was caused transformation of Mn ion in Mn_3O_4 ($Mn^{2+}Mn_2^{3+}O_4^{2-}$) from Mn^{2+} to Mn^{3+} ions. Therefore, the tetragonal Mn_3O_4 was transformed into cubic Mn_2O_3 structure with increasing temperature and this shows a same trend as reported in literature [41–44]. When the XRD patterns of MO films are compared with the patterns of CMO films, phase separation of manganese oxide from copper manganese oxide is easily possible for each annealing temperature.

The X-ray diffraction patterns for the copper manganese oxides (CMOs) at different temperatures are also shown in Fig. 1. The comparison of XRD patterns of the CMOs with MOs samples in Fig. 1(a)–(c) was used to investigate the emergence and transformation of crystalline phases with increasing of annealing temperature. The XRD pattern of Fig. 1(a) shows polycrystalline nature of CMO_300 sample with the mixed phases comprising of Mn_3O_4