

Microstructural, photocatalysis and electrochemical investigations on CeTi_2O_6 thin films

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Abstract

The properties of sol–gel derived CeTi_2O_6 thin films deposited using a solution of cerium chloride heptahydrate and titanium propoxide in ethanol are discussed. The effect of annealing temperature on structural, optical, photoluminescence, photocatalysis and electrochemical characteristics has been examined. Lowest annealing temperature for the formation of crystalline CeTi_2O_6 phase in these samples is identified as 580 °C. The optical transmittance of the films is observed to be independent of the annealing temperature. The optical energy bandgap of the 600 °C annealed film for indirect transition is influenced by the presence of anatase phase of TiO_2 in its structure. Fourier transform infrared spectroscopy investigations have evidenced increased bond strength of the Ti–O–Ti network in the films as a function of annealing temperature. The photoluminescence intensity of the films has shown dependence on the annealing temperature with the films fired at 450 °C exhibiting the maximum photoluminescence activity. The decomposition of methyl orange and eosin (yellow) under UV–visible light irradiation in the presence of crystalline CeTi_2O_6 films shows the presence of photoactivity in these films. The photocatalytic response of CeTi_2O_6 films is found to be superior to the TiO_2 films. In comparison to crystalline films, the amorphous films have shown superior electrochemical characteristics. The 500 °C annealed amorphous films have exhibited the most appropriate properties for incorporation in electrochromic devices comprising tungsten oxide as the primary electrochromic electrode.

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1. Introduction

Counter electrodes in transmissive electrochromic devices (ECDs) are differentiated under two categories. The first category involves an electrochromic (EC) layer, which is complementary with the chosen electrochromic material. The combination of WO_3 with NiO_xH_y is such typical example. The second possibility is an optically passive counter electrode, which remains colorless in both oxidized and reduced states. High transmittance, high ion storage capacity (ISC), and good cycling stability within the operational voltage and temperature range of the ECDs are some of the important requirements of a counter electrode. Mixed CeO_2 – TiO_2 films are one of the promising passive counter electrode materials. CeO_2 films

appear to lead as passive counter electrodes due to the absence of drawbacks existent in the other electrodes such as SnO_2 : X (Mo, Sb), which is known for instability of SnO_2 towards Li ion intercalation and V_2O_5 , which exhibits reduced transmission in the bleached state. Although, CeO_2 films are shown to have good ion storage capacity, the slower rate of Li ion intercalation and deintercalation reactions in these films limits their application in the ECDs. The addition of elements with ionic radius smaller than that of Ce such as Ti, Zr, V, Sn, Mo and Si etc. have yielded films, which are better as passive counter electrodes. The partial substitution of Ce atoms by Ti offsets the limitations in the CeO_2 films. In these mixed CeO_2 – TiO_2 films, CeO_2 acts as the site of electron injection and TiO_2 contributes to facile diffusion of the Li^+ ions as it reduces the size of insertion site for Li^+ ion. Films of pure and doped CeO_2 have been deposited by different techniques. Sputtering technique has been adopted by Granqvist et al. [1] and the films thus obtained have been extensively studied. The potential of such

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films as passive counter electrodes has been reported. The widely used sol–gel process offers numerous advantages over the other conventional deposition techniques, which include tailor making of the film's properties, introduction of porosity in the films, low process cost and possible processing at low temperature. Preparation of CeO₂ based films by sol–gel technique has been attempted following various routes. The use of alkoxides, the most popular precursor material in sol–gel processing has been reported by Deroo et al. [2]. Cerium salts like CeCl₃·7H₂O and [(NH₄)₂{Ce(NO₃)₆}] in combination with Ti alkoxides have been shown [3] as one of the routes to obtain CeO₂–TiO₂ films. Makishima et al. [3] varied the type of alkoxy group of titanium alkoxide in order to study its influence on the properties of the films. The films deposited by these authors have been sintered at 500 °C and their X-ray diffraction (XRD) patterns are characterized by the appearance of diffraction peaks of the CeO₂ phase alone. Photocatalytic reaction sensitized by TiO₂ and other semiconducting materials has attracted extensive interest as a potential way of solving energy and environmental issues. Several cerium titanates have been investigated for photocatalytic activity. Cerium titanate, CeTi₂O₆ with mainly Ce⁴⁺ state is known to cause photo-bleaching of methylene blue aqueous solution with irradiation of Xe discharge light [4]. Mixed CeO₂–TiO₂ films are also reported [5] to decolorize methyl orange solutions upon irradiation of the UV light. The potential of CeO₂–TiO₂ thin film electrodes as an amperometric sensor in flow injection to monitor electroinactive monovalent cations [Li⁺, Na⁺, K⁺, NH₄⁺, N(C₂H₅)₄⁺] has been shown by Tavcar et al. [6].

Brannerite, UTi₂O₆ is an accessory phase in the titanate-based crystalline ceramics of synroc [7]. The high U-content of brannerite (up to 62.8 wt.%) and its potential as a nuclear waste form for the immobilization of actinides has been shown earlier. The ideal formula of natural brannerite is (U,Th)_{1-x}Ti_{2+x}O₆ with a deficiency in uranium and excess titanium. Many cation substitutions have been identified for both uranium (Pb,Ca,Th, Y and Ce) and titanium (Si, Al, Fe) in natural brannerite. The compound CeTi₂O₆ is isostructural with PuTi₂O₆ and is used to estimate the properties of PuTi₂O₆ [8]. Ce is commonly used to estimate the properties of solids containing plutonium owing to their similar ionic radii (Ce(IV)=0.087 nm; Pu(IV)=0.086 nm). CeTi₂O₆ in the powdered form has been prepared earlier by sintering in air a pellet containing stoichiometric portions of CeO₂ and TiO₂ at 1350 °C for >100 h.

In the present work, the CeTi₂O₆ phase has been prepared in thin film form using a sol–gel process. In comparison to the powdered CeTi₂O₆ material prepared by other research groups by ball milling stoichiometric portions of CeO₂ and TiO₂, the CeTi₂O₆ compound in the present study is prepared in thin film form using a simple sol–gel process wherein homogeneous solution containing Ce and Ti in desired atom ratio is prepared at relative ease and greater precision. The films have been characterized using X-ray diffraction, transmission electron microscopy (TEM), Fourier Transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), UV–visible spectrophotometry, fluorescence spectrometry, photocatalysis, and electrochemical techniques.

2. Experimental details

2.1. Preparation of deposition solutions and films

To CeCl₃·7H₂O (Merck) dissolved in ethanol, titanium propoxide (Aldrich) was added to obtain the deposition solution. This “deposition solution” was stored at room temperature in a closed glass vessel to prevent rapid precipitation of the alkoxide due to hydrolysis. During the experimental process, the room temperature was (20±5) °C and the humidity remained at (60±10)%. Addition of the alkoxide to the ethanolic solution of the cerium salt induces a color change so that the color of the deposition solution is bright yellow. The gelation period of the sol is about a week and it has shown a strong dependence upon the ambient temperature and humidity.

Transparent electrically conducting (SnO₂:F coated) glass and the micro slide glass substrates were spin coated at 3000 rpm for 35 s by the deposition solution to achieve the as-deposited films. The as-deposited films thus obtained were dried at room temperature for 15 min., and subsequently densified for 5 min. in air at 450, 500, 560, 580 and 600 °C. For each annealing temperature, four samples were prepared. Pale yellow homogeneous films with high adherence to the substrates and excellent chemical as well as mechanical stability were obtained. The stability of the films in acidic and alkaline media shows their high chemical inertness.

2.2. Characterization of films

X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 5° to 70° with a D8 Advanced Bruker Diffractometer. Fourier transform infrared (FTIR) spectra of the films in the transmission mode were recorded in the wavenumber range of 400–4000 cm⁻¹ on a Perkin–Elmer Model BX2 spectrophotometer. The microstructural studies were performed on a JEOL JEM 200 CX transmission electron microscope (TEM) operated at electron accelerating voltage of 200 kV. The TEM sample preparation was done by placing the scraped off film over a carbon coated nickel grid. The surface morphology of the films was observed using scanning electron microscopy (SEM) on a JEOL JSM 840 scanning electron microscope operated at electron accelerating voltage of 15 kV. Hardness of the films was measured with a digital micro hardness tester model FM7e (Future Tech. Corp., Japan) and the calculation of hardness values were made through a computer controlled hardness reading software system, employing a CCD camera for receiving data signals. Optical transmittance and absorbance data of the films and solutions was measured in the range of 300–2000 nm using a UV 3101 PC Shimadzu spectrophotometer. The photocatalytic activity of the samples was evaluated by methyl orange and eosin (yellow) decomposition under UV–visible light irradiation. The irradiation was provided by 80 W mercury vapor light centered at 365 nm wavelength. The initial concentration of methyl orange and eosin (yellow) in water was fixed at 4×10⁻⁵ M. The extent of methyl orange and eosin decomposition was determined by measuring their absorbance after different durations. Photoluminescence (PL) measurements were carried out at room temperature in the

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