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Preparation of electrochromic thin films by transformation of manganese(II) carbonate

Sasho Stojkovikj [a], Metodija Najdoski [a], Violeta Koleva [b], Sani Demiri [a]

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Highlights

- A new chemical bath method for deposition of $MnCO_3$ thin film is designed.
- The deposition has been performed from aqueous solution containing urea and $MnCl_2$.
- The thin films with thickness in the range of 70–500 nm are deposited.
- The as-deposited films were electrochemically transformed into electrochromic films.
- These films exhibit electrochromism changing the color from brown to pale yellow.

Abstract

A new chemical bath method for deposition of manganese(II) carbonate thin film on electroconductive FTO glass substrates is designed. The homogeneous thin films with thickness in the range of 70 to 500 nm are deposited at about 98 °C from aqueous solution containing urea and $MnCl_2$. The chemical process is based on a low temperature hydrolysis of the manganese complexes with urea. Three types of films are under consideration: as-deposited, annealed and electrochemically transformed thin films. The structure of the films is studied by XRD, IR and Raman spectroscopy. Electrochemical and optical properties are examined in eight different electrolytes (neutral and alkaline) and the best results are achieved in two component aqueous solution of 0.1 M KNO_3 and 0.01 M KOH. It is established that the as-deposited $MnCO_3$ film undergoes electrochemically transformation into birnessite-type manganese(IV) oxide films, which exhibit electrochromic color changes (from bright brown to pale yellow and vice versa) with 30% difference in the transmittance of the colored and bleached state at 400 nm.

Introduction

One of the most important properties of the materials used in various fields of high technology is electrochromism. A material is electrochromic if it has the capability to maintain reversible and persistent change in the optical properties (color change) when an electrical potential is applied to it. The reversible change in the color is induced by the change in the oxidation state of the metal ions which is associated with relevant insertion/extraction of ions from the electrolyte into/from the material. WO_3 is one of the most extensively studied electrochromic material [1]. In comparison to this material, the electrochromism of manganese based compounds is less explored. Among them the most promising compound is MnO_2, which is an anodically coloring electrochromic oxide. The Mn^{4+} state has an optical absorbance due to the *d–d* transition in the visible light range, giving a brownish color and the reduction to Mn^{3+} state changes the color to pale yellow [2].

The electrochromic properties of manganese oxide thin films with different structures (γ-Mn_2O_3/Mn_3O_4 and layered $Mn_7O_{13}{\cdot}5H_2O$) prepared by electrodeposition at different potentials have been reported by Chigane et. al. [3]. Long et al. [4] have found that sol–gel derived thin films of Na-birnessite show relatively high electrochromic efficiency. The influence of the number of layers of MnO_2 nanosheets prepared by layer-by layer assembly on the electrochromic properties has been examined by Sakai et al. [2]. It is established that appropriate change in the optical density can be achieved by controlling the number of deposition cycles. This result can be used for tailoring the optical properties.

Generally, manganese based thin films are prepared using various methods such as: dip coating [5], electrodeposition [6], potentiostatic electrolyses [2], chemical vapor deposition [7], thermal decomposition [8], atomic layer deposition [9], aqueous precipitation (chemical bath deposition) [10] etc. Each of the coating methods has various advantages and disadvantages, though all of them are capable to produce the desired material. Among them the chemical bath deposition (CBD) is low-cost, very simple and large-area applicative technique that requires only aqueous solution of the chemical precursors. The reaction mechanism usually engages two stages: nucleation and particle growth, based on formation of the solid phase from the solution. In addition, CBD allows fabrication of thin films at low temperature.

Most recently we have developed a chemical method for deposition of K-birnessite-type manganese oxide thin film with electrochromic properties [11]. The method is based on the successive immersion of the substrates in aqueous solutions of $MnCl_2$ and $KMnO_4$ and it allows the preparation of films with thickness from 50 nm to 250 nm for about 2–5 min. Both as-prepared and annealed films demonstrate good electrochromic characteristics with a difference in the transmittance of 40% between the reduced and oxidized state in aqueous KNO_3 electrolyte [11].

In the search for new manganese electrochromic thin films we have examined films based on manganese(II) carbonate. Manganese(II) carbonate by itself has been widely applied in solid oxide fuel cell (SOFC), inorganic–organic hybrid composite materials, pigments and is often used as solid precursor to synthesize the respective metal oxides [12]. However, to our knowledge, there are no reports in literature of electrochromic thin films based on manganese(II) carbonate. In the present paper we propose a chemical bath deposition method for preparation of manganese(II) carbonate thin films. The method is very simple and consists of heating a solution containing manganese(II) chloride and urea. Three types of films originating from the initial manganese(II) carbonate films have been considered: as-deposited, annealed and electrochemically transformed thin film. The structure, electrochemical behavior and electrochromic properties of the three types of manganese thin films have been studied and compared.

Section snippets

Preparation of the FTO glass substrates

Glass substrates coated with electroconductive fluorine doped tin(IV) oxide (FTO) having electric resistance of 10–20 Ω/mm^2 and dimensions of 5 cm×2.5 cm×0.2 cm were used for thin films deposition. The substrates were preliminary cleaned with hexane and acetone, and dried at room temperature. Then, they are washed with deionized water and dried again.…

Chemical deposition of $MnCO_3$ thin films

The chemical bath solution is prepared at room temperature by dissolving 0.5 g manganese(II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) and 2 g urea (H_2NCONH_2)…

Results and discussion

Fig. 1(a) shows the XRD pattern of the as-deposited film. As seen it is well crystalline and the observed reflections match very well with rhodochrosite phase, $MnCO_3$ (JCPDS 83–1763). Some weak reflections from the FTO layer (SnO_2, JCPDS 46–1088) are also seen.

The chemical deposition of $MnCO_3$ thin films is based on two consecutive chemical processes. The first process consists of formation of Mn^{2+} adducts with urea at room temperature and it has been already described as follows [13], [14] in…

Conclusion

Electrochromic manganese oxide films with different thickness derived from as-deposited $MnCO_3$ films have been prepared and studied by powder XRD, IR and Raman spectroscopy, cyclic voltamommetry and optical spectroscopy. The redox processes are examined in different neutral and alkaline electrolytes such as $LiClO_4$ in propylene carbonate, $LiClO_4$(aq), aqueous solution of KOH with various concentrations. The best reversibility of the redox processes is found in two component electrolyte containing…

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2023, Materials Today: Proceedings

Citation Excerpt :
…Cathodic EC materials are colored with negative potentials (WO3), while anodic EC compositions are colored with positive potentials (such as WO3) (NiO). The most well-known inorganic EC substances are metallic nanoparticles, such as tungsten, nickel, manganese, palladium, cobalt, titanium, rhodium, molybdenum, iridium, cerium, ruthenium oxides [12–19]. Tungsten oxide (WO3) is a highly effective inorganic EC material that is widely used in sunscreens (WO3) [20–26].…

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Citation Excerpt :
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