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Electrically activated thin film optical coatings as functional layers in electrochromic devices

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Abstract

This study presents results on technology and characterization of molybdenum oxide, tungsten oxide and mixed oxide films based on Mo and W. These films were deposited by low-temperature carbonyl CVD process at atmospheric pressure and by simplified sol–gel method using spinning and spraying approaches. The obtained films were structurally and optically investigated. The films show good optical quality with optical transmittance of about 70% in the visible spectral range. Cyclic voltammograms as well as the transmittance modulation at different wavelengths in the visible spectral range were measured to characterize the electrochromic behaviour of the films. The colour efficiencies of the optimized films are in the order of 110–115 cm^2/C, in case of spray deposited WO_3-sol–gel films—130 cm^2/C.

Keywords: CVD; Sol–gel; Tungsten oxide; Mixed molybdenum–tungsten oxide films; Electrochromic properties

1. Introduction

Transition metal oxides gained interest due to their numerous applications [1,2]. Thin films of WO_3 are studied as gas sensor in respect of their microstructure and film morphology [3], as photosensitive semiconductor electrodes [4] and as well as diodes. Transition metal oxides exhibit electrochromic effect described as reversible optical modulation under external voltage. So far, the tungsten oxide is the most extensively

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investigated electrochromic material [3–6], applied in the first prototypes of electrochromic smart windows. In general, tungsten oxide has a tendency to form sub-stoichiometric phases [5]. Due to this, amorphous and polycrystalline WO_3 thin films possess a high capacity for reversible Li^+ insertion and highly reversible intercalation and transport properties. It shows high colour efficiency and relatively low price, it is non-toxic material [7].

MoO_3 shows many advantages, one of which is the optical absorption band close to sensitivity of the human eye [8], but it is still not largely used as active electrochromic layer due to its instability in acid and base media [9]. Our previous studies on APCVD produced pure metal oxide films showed that WO_3 has high colour efficiency, but at low temperatures grows very slowly. MoO_3 from its side grows rapidly at low temperatures and has moderate colour efficiency. That is why WO_3 with MoO_3 system (formulae—$Mo_xW_{1-x}O_3$) is expected to improve the electrochromic properties by uniting the promising features of the individual oxides. Mixed oxide systems were proposed and reviewed as electrochromic materials by Granqvist [10] and Monk [11]. Studies on technology and characterization of sol–gel derived W and Mo based oxide films were also performed to enlarge the area of cost-effective processes for producing films as functional layers in EC devices. Two approaches were employed—spinning and spraying.

The aim of the present research is to investigate from one side the relation between CVD and sol–gel process parameters and film structure and optical properties and from the other side to relate the propertie of the films with their electrochromic performance as functional layers in electrochromic devices. The film structure study was performed by Raman and IR spectroscopy. Electrochromic properties were characterized by cyclic voltammetry on the basis of which colour efficiencies were determined.

2. Experimental details

CVD-metal oxide films were deposited by pyrolytical decomposition of $W(CO)_6$ and $Mo(CO)_6$ or their physical mixture (in ratio 1:4) in argon–oxygen at atmospheric pressure (APCVD process) in a horizontal cold wall-CVD reactor. The precursor was heated at 90 °C. Argon (99.995%) flow carries the precursor vapour to the reactor. The selected flow rate of argon through the sublimator assures constant amount of precursor vapour. The ratio of the flowing through the source chamber argon to the oxygen flow rate was 1:32. The temperature was 200 °C where the pure component films grow successfully.

The sol–gel films were obtained by simplified sol–gel method, using metal powders instead of corresponding salts. For instance, in case of WO_3, for the solution, tungsten was dissolved in hydrogen peroxide (H_2O_2) and dried until a xerogel was formed. This xerogel was finally dissolved in ethanol. Thin films were deposited by spin coating on ITO-covered conductive glass or on silicon wafers. After spin coating, the substrate was dried in air at 150 °C. To achieve a film thickness of about 200 nm, this procedure was repeated 5 times [12].

Alternatively, sol–gel films were also deposited by spraying the solution with an airbrush gun on the substrates at room temperature. With this technique, films with sufficient thickness can be produced in one-step process. The resulting films were annealed at 100, 200 and 275 °C.

Raman study was performed with SPEX 1403 Raman spectrometer with laser line—Ar^+ 488 nm, the laser power—54 mW in the spectral range 200–1200 cm^{-1}. The presented