Physical Combinatorial Deposition and Characterization Methods for Advanced Electrochromic Metal Oxides

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By

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I. Background of the research.

Cost energy consumption produced expensive bills, and extra heat absorbed from buildings is found to be one of the major problems in our modern era. Improving the thermal and optical properties of smart windows can reduce a building's energy deficiency by up to 40% [Lee **2013**]. Because the air conditioning, heating, and ventilation in buildings account for 30–40% of the world's energy consumption, therefore, it is important to develop technologies that dynamically control the transparency of windows to reduce energy consumption in buildings. The mechanism of an electrochromic (EC) device is to exhibit repeated coloration/bleaching cycles with back-and-forth charge of small voltages. Electrochromic film is one of the layers in an EC device which was placed on each side of a liquid (or solid) electrolyte layer. The EC layers have been presented as thin films of amorphous or crystalline oxides deposited on transparent conducting oxide electrodes (TCOE) coated glass. [Granqvist **2012**]. Under applied DC bias, transition metal oxides can change their color. This reversible color change is known as electrochromism.

Electrochromic features like coloration efficiency (CE), cyclic durability and kinetics of coloration cycles of metal oxide strongly depend on its structure, morphology, and composition, and therefore on the deposition methods and growth parameters.

Electrochromic phenomena are defined as color change caused by applied electric current. Electrochromic windows are among the favorable solutions to this problem, as they change their light-transmitting properties when exposed to DC bias [Granqvist **2006**]. The active components of such electrochromic window technologies are metal oxide layers or organic films [Granqvist **2006**] that exhibit electrochromism, a phenomenon where a material changes its optical properties upon charge injection or extraction. There are many types of such as Titanium Dioxide (TiO2), Chromium Oxide (CrO), Niobium Pentoxide (Nb2O5), Tin Oxide (SnO2), Nickel Oxide (NiO), Iridium Oxide (IrO2), Zinc oxide (ZnO), Tungsten Trioxide (WO3), Molybdenum Trioxide (MoO3), and Vanadium Oxide (V2O5) [Granqvist **1995,** González-Borrero **2010,** Novinrooz **2005,** Hsu **2008,** Chaichana **2018**, Colton **1978,** Wen **2015,** Llordes **2016**].

Electrochromic properties, mainly coloration efficiency, kinetics of the coloration bleaching process, and cyclic durability of metal oxides strongly depend on its compositional morphological, and structural. It is important to study the effect of deposition techniques and growth parameters

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II. Objectives

Relatively few publications have studied the possible advantages (higher CE) of the mixtures of different metal oxides as electrochromic materials. The change in light absorption for the same electric charge represents the electrochromic effectiveness, and it can be higher in mixed metal oxide layers.

Only in a few cases have the properties of mixed tungsten and molybdenum oxides been studied, despite the fact that they are the most studied material for electrochromic devices. Labadi et al. [Lábadi **2024**] fabricated a combinatorial Mo_xW_{1-x} oxide thin film sample (where $0 < x < 1$) by reactive magnetron sputtering onto ITO-coated glass and determined the optimal composition for the best EC efficiency. A continuous

composition range was deposited in an experiment on a single substrate using a combinatorial process, the sample realized the entire composition range of the MoO_3-WO_3 system.

This work focused on the electrochromic behavior of mixed metal oxide layers deposited by reactive DC magnetron sputtering instrument. Transition metal oxides such as Titanium oxide (TiO_2), Tin oxide (SnO_2), Zinc oxide (ZnO) and Molybdenum Trioxide (MoO_3) have been used in this study as promising electrochromic material. By using this combinatorial process, all the compositions (from 0 to 100%) were achieved after one sputtering preparation cycle. The objective of this work was to investigate the electrochromic effectiveness (the change of light absorption for the same electric charge) of mixed metal-oxide layers in a wide compositional range. We expected that using metal atoms with different diameters in the layers would have a positive effect.

III. Research methods

Sample preparation

During this work, reactive magnetron sputtering (in Ar-O2 plasma) has been used to produce all combinations (from 0 to 100%) of mixed metal-oxide layers on silicon wafers. The sample preparation time took 4 h in the vacuum chamber, including the vacuum-preparation time. By using the combinatorial process, all the compositions (from 0 to 100%) have been achieved in the same sputtering chamber after one sputtering.

Reactive sputtering can be defined as the sputtering of elemental targets in the presence of chemically reactive gases that react with both the ejected target material and the target surface. It has become a very popular technique in today's search for new material properties, for the deposition of a very wide range of compound and alloy thin films including oxides

Characterization

Spectroscopic ellipsometry (SE) is an optical characterization technique with high accuracy. We used the combinatorial approach to map our mixed metal

oxides in the same way as in our group's earlier paper [Fried 2022]. Different optical models, such as Effective Medium Approximation (EMA) and 2-Tauc-Lorentz Oscillator (2T–L), were used to achieve a composition map and a thickness map of the sample layers. Scanning electron microscopy (SEM) with Energy-Dispersive X-Ray Spectroscopy (EDS) has been used to check the SE results. X-ray Diffraction (XRD) measurements were performed to investigate the microstructure of the layers.

The main criterion for assessing EC device performance is the coloration efficiency (CE). Transmittance changes were measured in the straight-through direction during the coloration process, while the charge was calculated from the integral of the current vs. time data and the electrolyte-wetted area of the sample.

IV. New scientific results.

1. I developed a new method for preparing combinatorial binary oxide samples in the full composition range. The mixed oxides are deposited by reactive magnetron sputtering, and every binary composition is present on the same sample. The

composition-graded layer is prepared by moving the samples under sputtering targets in a reactive Argon-Oxygen (Ar-O_2) gas mixture. The deposition method allows the determination of the optimal compositions for electrochromic application [T2, T3]

2. Using the method described in (1) in the (TiO_2–SnO_2) binary system I proved that [T1]:
a., the optimal composition for CE is (30%) TiO_2 - (70%) SnO_2 (with ±2,5% error).

b., using an electrochemical cell combined with Spectroscopic Ellipsometry, I mapped the thickness and composition of TiO_2-SnO_2 mixed oxide samples, and I compared the application of two optical models [Bruggeman Effective Medium Approximation (BEMA) vs. 2-Tauc–Lorentz multiple oscillator model (2T–L)]. I proved that the 2T–L in the case of molecular-level mixed layers, 2T–L model is better than the BEMA since I found that the Mean Square Error (MSE) values are significantly lower in the (TiO_2-SnO_2) binary system.

3. Using the method described in (1) in the (TiO_2-MoO_3) binary system I proved that [T2, T3]

a., since the Ti-rich side was at significantly higher temperature during the deposition the Ti- rich oxide was polycrystalline while on the Mo-rich side the oxide remained amorphous or nanocrystalline. Due to the morphology difference two distinct optimal values of CE exists in this binary system:

b., the first optimal composition for CE in the (TiO_2-MoO_3) binary system exists is at ~ 60% - 40 % Ti-Mo ratio (CE value is 22.2 cm^2 C^{-1} at 600 nm) (with ±2,5% error). This optimum is in the polycrystalline domain

c., the second optimal composition for CE in the (TiO_2-MoO_3) binary system is at ~ 20% - 80 % Ti-Mo ratio (CE value is 19.8 cm^2 C^{-1} at 600 nm) (with ±2,5% error). This optimum is in the amorphous domain.

4. Using the method described in (1) in the (SnO_2-ZnO) binary system I proved that [T4]

the maximum value of the CE is between 46 and 21 cm^2 C^{-1} between wavelengths of 400 and 800 nm at ~ (71–29) % Sn-Zn ratio. (with ±2,5% error)

5. I have proved that the examined mixed metal oxides have the potential to exhibit at least 3 times better CE values than the corresponding pure materials. [T2]

V. Potential applications of the results

The mixed metal oxides showed at least 3 times better EC properties than the pure oxides, due to possible electron transitions between two sets of electrons the EC effect can be more obvious in mixed oxides because of the electrochromic Effectiveness, can be higher in mixed metal-oxide layers and mixing metal atoms with different diameters in the layers can enhance the CE.

Better comprehension and enhanced preparation of mixed-metal oxides design would provide better marketing and increase business potential for this field of study. The potential economic impact of developing more selective thin films depends on how we could present high accuracy samples. Then it will have a long-lasting work

effect on electrochromic materials with a high chance of being desirable for marketing, because of the variety of its applications.

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VII. Scientific publications related to the thesis points

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