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Abstract: Electrochromic measurements have been performed to optimize the composition of reactive magnetron-sputtered mixed layers of Zinc oxide and Tin oxide (ZnO-SnO₂). A combinatorial material synthesis approach was applied throughout the deposition experiments, and the samples represented the full composition range of the binary SnO₂-ZnO system. The Coloration Efficiency (CE) of the mixed oxide films were determined with simultaneous measurement of layer transmittance and applied electric current through the using organic propylene carbonate electrolyte cells in a conventional three-electrode configuration. Optical parameters and composition have been determined and mapped by using Spectroscopic Ellipsometry (SE). Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS) has been used to check the SE results as it was used in our earlier paper [N. T. Ismaeel et al, Materials 2023, 16(12), 4204] for (TiO₂-SnO₂). Zn and Sn targets were put separately from each other, and the Indium-Tin-Oxide (ITO) covered glass and Si-probes on a glass substrate (30 cm × 30 cm) were moved under the two separated targets (Zn and Sn) in a reactive Argon-Oxygen (Ar-O₂) gas mixture. By using this combinatorial process, all the compositions (from 0 to 100%) were achieved in the same sputtering chamber after one sputtering process. CE data evaluated from the primary data plotted against the composition displayed a characteristic maximum at around 29 % ZnO. Our combinatorial approach allows the localization of the maximum at 5% accuracy.

Keywords: combinatorial sample; Zinc-Tin oxide; reactive sputtering; electrochromic materials; coloration efficiency

1. Introduction

Metal oxides are widely studied with respect to their electrochromic behavior and properties for applications such as display devices and smart windows. To decrease the absorbed heat in buildings, electrochromic films have been used as smart windows Electrochromic materials have been applied in energy-effective glazing, automobile sunroofs, smart windows, and mirrors. The structure of a smart window contains an electrochromic material layer (usually metal oxide) sandwiched between a transparent conductive layer and some solid electrolyte. Recently, energy efficiency has been affected and focused on energy solution strategies for utilizing this important field.

The electrochromic process is based on a reversible redox process and characterized by the Coloration Efficiency (CE). The energy-saving windows (smart window), energy storage systems: such as electro-chromic (EC), photochromic and thermochromic have been designed on the same mechanism and both have sandwich device structures, and it was based on the electrochemical reaction of the electrode materials.

Transition metal (Titanium, Tungsten, Nickel, Vanadium, Molybdenum and others) oxide films are the most interesting and most widely studied materials for this purpose. Conventional thin

film preparation methods include for instance: chemical methods (spin coating, sol–gel deposition, chemical bath deposition, Langmuir–Blodgett technique, etc.), chemical and physical vapor deposition, electrochemical methods (anodization, plating), see ref. [1] and references therein.

Nevertheless, relatively few publications studied the possible advantages (higher CE) of the mixtures of different metal-oxides as electrochromic material. The electrochromic effectiveness (the change of light absorption for the same electric charge) can be higher in mixed metal-oxide layers.

Earlier, we performed experiments with mixed metal-oxides and found positive effect in electrochromic behavior. Ismaeel et al [2] determined the optimal composition of reactive magnetron-sputtered combinatorial mixed layers of Titanium oxide and Tin oxide (TiO_2-SnO_2) for electrochromic purposes. The maximum enhancement in light absorption was found at (30%) TiO_2– (70%) SnO_2 composition.

In other experiments, also combinatorial material synthesis approach has been applied for the binary MoO_3/WO_3 system. By using organic propylene carbonate electrolyte cells in a conventional three-electrode configuration, electrochromic redox reactions have been made. CE data have been evaluated from the primary data plotted against the composition that displayed a characteristic maximum at around 60% MoO_3. The localization of the maximum at 5% accuracy has been allowed in that combinatorial approach [3].

Many researchers have used SE for pure or combinatorial material investigation [4-11] Fried et al. [12] have used SE (which is a fast, cost-effective, and non-destructive method) for the investigation and mapping of WO_3-MoO_3 mixed layers after sputtering. The used optical models were useful to achieve the composition map and thickness map of the sample layers.

The objective of this work was to investigate the electrochromic effectiveness (the change of light absorption for the same electric charge) of SnO_2-ZnO mixed layers in a wide compositional range and the CE has been determined, too. Using metal atoms with different diameters in the layers would have a positive effect. According to our best knowledge, ZnO was investigated only as a dopant in other electrochromic metal-oxide [13] while SnO_2 or SnO_2-metal-oxide [14, 15] mixtures were studied only as photocatalytic materials. There is no such publication where pure SnO_2 or ZnO-SnO_2 mixtures are studied as electrochromic material.

This paper aims to assess the results of investigations of such materials showing the enhanced electrochromic behavior compared to the pure materials. One can expect that mixing metal atoms with different diameters in the layers can enhance the CE.

2. Materials and Methods

Optimal composition of reactive magnetron-sputtered combinatorial mixed layers of Tin oxide and Zinc oxide (Sn_xZn_{1-x}) have been determined where (where $0 < x < 1$) for electrochromic purposes. Metallic Sn and Zn targets were put separately from each other, and Indium-Tin-Oxide (ITO) covered glass and Si-probes on a glass substrate (30 cm × 30 cm) were moved under the two separated targets (Sn and Zn) in a reactive Argon-Oxygen (Ar-O_2) gas mixture, see Figure 1(a). The Tin-Zinc-oxide layers were deposited onto ITO covered 100x25 mm size glass surfaces. Layer depositions were made by reactive sputtering in an (Ar + O_2) gas mixture at ~2×10^{-4} Pa base pressure and at ~10^{-1} Pa process pressure. The target - substrate working distance was 6 cm. 30 sccm/s Ar and 70 sccm/s O_2 volumetric flow rates were applied in the magnetron sputtering chamber. Plasma powers of the Sn and Zn metal targets were selected as 800 and 1000 W respectively. Samples were moved back and forth at 25 cm/s of walking speed between the Sn and Zn targets and a mixed oxide film was deposited onto the ITO surface, see Figure 1(b). 5 min cooling interrupt was applied after every 50 walking cycles.
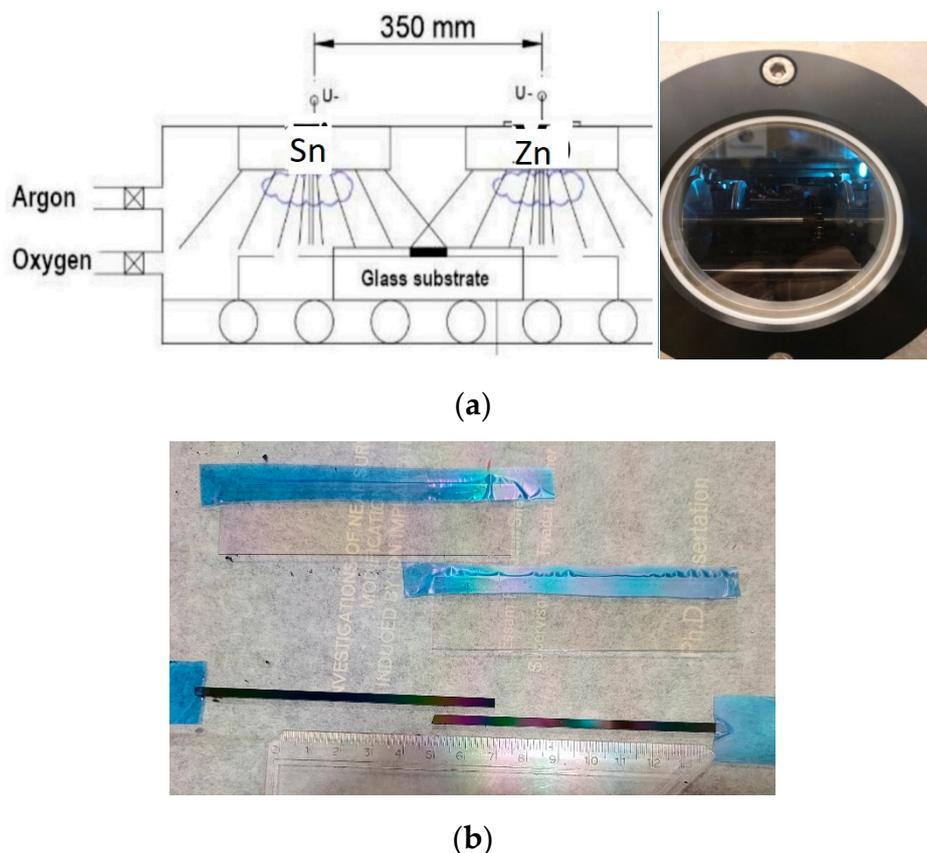
(**a**)

(**b**)

Figure 1. SnO$_2$-ZnO (a) arrangements of the two targets (at 35 cm distance from each other) and the chamber for the DC magnetron sputtering after being vacuumed, blue light is from the Ar-O$_2$ plasma. (b) ITO-covered glass and Si-probes on a glass substrate, before-electrochromic-experiments, the Sn in the left and the Zn in the right. (c) after-electrochromic-experiments.

Spectroscopic Ellipsometry (SE) is an optical characterization technique with high-accuracy [16]. We used the combinatorial approach to map our mixed metal oxides as it was established in our earlier paper [12]. Different optical models, such as Effective Medium Approximation (EMA) and 2-Tauc-Lorentz Oscillator (2T–L), have been used to achieve the composition map and thickness map of the sample layers. We used SE similar manner to determine the composition map and thickness map of our Sn-Zn combinatorial layers.

To determine the optimal composition for the best CE value, the layers were deposited onto ITO-covered glass. The composition map and thickness map were measured on the Si-probes, see Figure 1 (b). We checked the resulted compositional map on the Si-probes Figure 1 (b) by using SEM with EDS, see Figure 3.

The CE η is given by the following equation:

$$\eta(\lambda) = \frac{\Delta OD(\lambda)}{q/A} = \frac{\ln\left(\frac{T_b}{T_c}\right)}{Qi}$$

(1)

where Q$_i$ is the electrical charge inserted into the electrochromic material per unit area, ΔOD is the change of optical density, T$_b$ is the transmittance in the bleached state, and T$_c$ is the transmittance in the colored state. The unit of CE is cm^2/C.
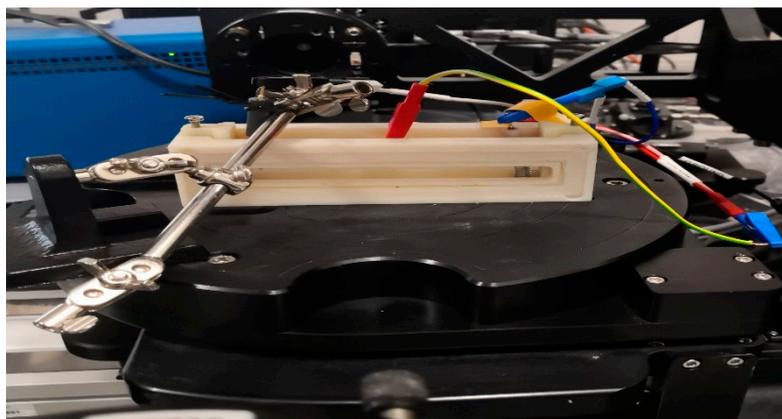
Figure 2. SnO₂-ZnO-during-electrochromic-experiments by SE.

CE has been determined in a transmission electrochemical cell, see Figure 2. The cell was filled with 1M lithium perchlorate (LiClO₄) / propylene carbonate electrolyte. A 5 mm width masked (Sn-Zn oxide-free) ITO stripe of the slides remained above the liquid level allowing direct electric contact of the cell. A Pt wire counter electrode was placed into the electrolyte alongside with a reference electrode. This arrangement was a fully functional electrochromic cell. The applied current was controlled through the cell using a Farnell U2722 Source Measurement Unit (SMU). Constant current was applied through coloration and bleaching cycles of the electrochromic layer and simultaneous spectral transmission measurements were performed by using the Woollam M2000 spectroscopic ellipsometer into transmission mode.

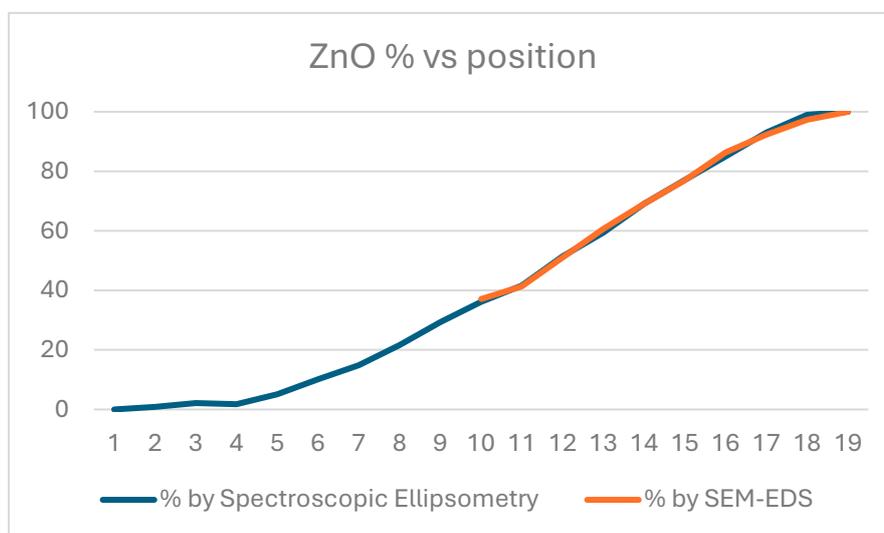The precision of the Sn/Zn ratio is 2 %, while the precision of the position is 1 mm.

Figure 3. ZnO ratio measured on the Si-probes by SE and SEM-EDS.

3. Result

The main criterion of the EC device performance is CE. Transmittance changes were directly measured 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.

Figure 4 shows the calculated CE data as a function of MoO3 fraction of the layer (individual color coded curves represent different wavelengths), while Figure 5 is a 3D representation of the data. Individual points were calculated from the average of three independent measurements. Error is estimated as 3 %, calculated on the basis of the accuracy of sample positioning in the measuring cell and the spot size of the optical beam. The calculated data are given in Table 1 according to equation (1).
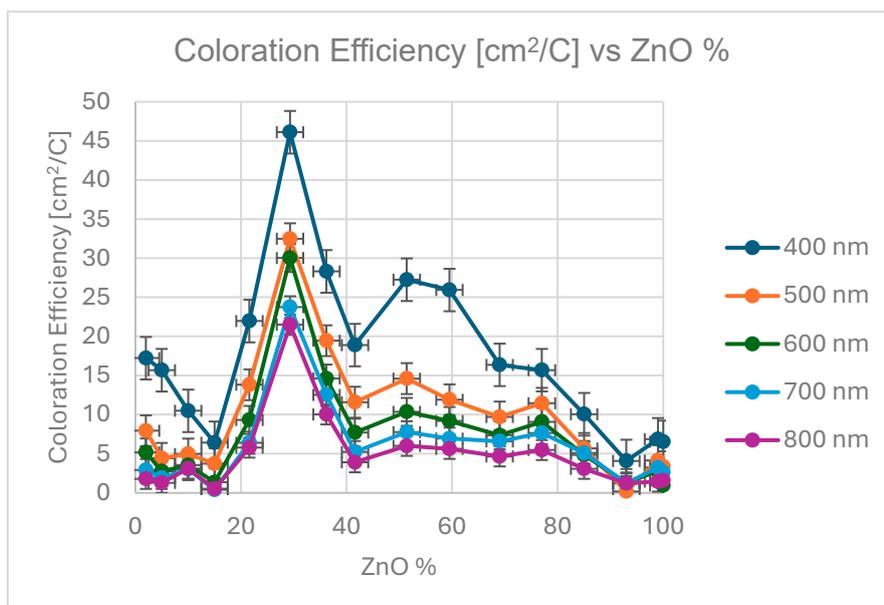
Figure 4. CE of SnO_2-ZnO vs. Zn % for wavelengths from 400-800 nm. (Individual color coded curves represent different wavelengths: 1 – 400 nm, 2 – 500 nm, 3 – 600 nm, 4 – 700 nm, 5 – 800 nm.
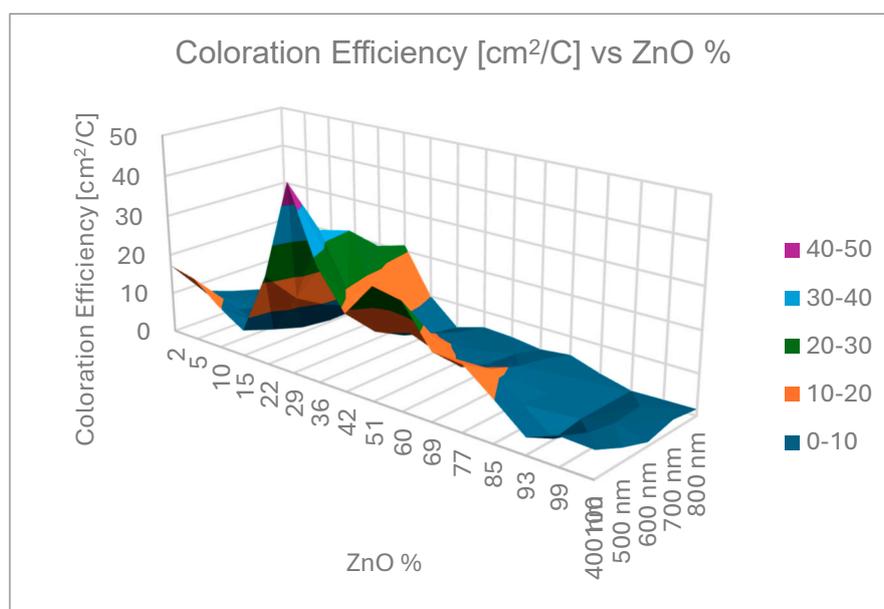

Figure 5. 3D diagram of the CE data of SnO_2-ZnO vs. Zn % vs. Mo % for wavelengths from 400-800 nm visible spectral range.

To check the position dependent composition, SEM with EDS has been used, see Figure 3.

Table 1. Calculated data for the CE according to the wavelengths 400-800 nm.

ZnO (%)	400 nm	500 nm	600 nm	700 nm	800 nm
2	17.2	7.9	5.1	2.9	1.8
5	15.7	4.4	2.7	1.9	1.3
10	10.5	5.0	3.5	3.0	3.1
15	6.4	3.7	1.3	0.4	0.5
21.6	22.0	13.8	9.3	6.4	5.8
29.3	46.1	32.5	30.0	23.7	21.5
36.2	28.3	19.5	14.6	12.5	10.1

41.6	18.9	11.6	7.7	5.2	3.9
51.4	27.3	14.6	10.3	7.8	6.0
59.5	25.9	11.9	9.2	6.9	5.6
69	16.4	9.7	7.3	6.6	4.6
77	15.7	11.5	9.1	7.6	5.5
85	10.0	5.7	4.8	5.1	3.1
93	4.1	0.2	1.3	1.2	1.2
99	6.8	4.0	2.8	3.2	1.4
100	6.5	3.3	1.0	2.6	1.6

4. Discussion

The CE maximum have been founded at 29 % Zn for each wavelength between 20-50 cm^2/C. This 29 % is very close to optimum value of 30 % in the case of TiO_2-SnO_2 mixture which was investigated in our earlier paper [2]. We expected that mixing metal atoms with different diameters in the layers can enhance the CE. This 70-30 % mixture of different metal oxides seems to be the optimum for the Li-diffusion in these sputtered materials.

5. Conclusions

We could optimize the CE of mixed Tin oxide and Zn oxide (SnO_2-ZnO) layer deposited by reactive magnetron sputtering. We prepared combinatorial samples by moving the samples under the Sn and Zn sputtering targets in a reactive Argon-Oxygen (Ar-O_2) gas mixture.

By using this combinatorial process, every compositions (from 0 to 100%) were achieved in the same chamber after one sputtering. The mixed metal oxides showed at least 3 times better CE values than the pure oxides.

CE has been considered as the important parameter in this study. The maximum value of the CE is between 46 and 21 cm^2/C between the wavelength 400 and 800 nm at ~ 71 % - 29 % Sn-Zn ratio.

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