BY Phd Student
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Combinatorial Preparation and Characterization Methods for High Through-put Study of Advanced Functional Materials

Aim of the Research

To understand and optimize the electrochromic behavior of mixed metal oxides deposited by reactive sputtering.

Research Work

We prepared thin films of mixed [Titanium Oxide and Molybdenum Trioxide (TiO_2-MoO_3) & (Titanium, Tin) Oxide (TiO_2-SnO_2) and (Tungsten, Molybdenum) Trioxide (WO_3-MoO_3)] mixed layers on glass by reactive DC magnetron sputtering and determined the optimal composition for electrochromic purposes. We mapped (composition and thickness) maps and optical parameters by using Spectroscopic Ellipsometry (SE).

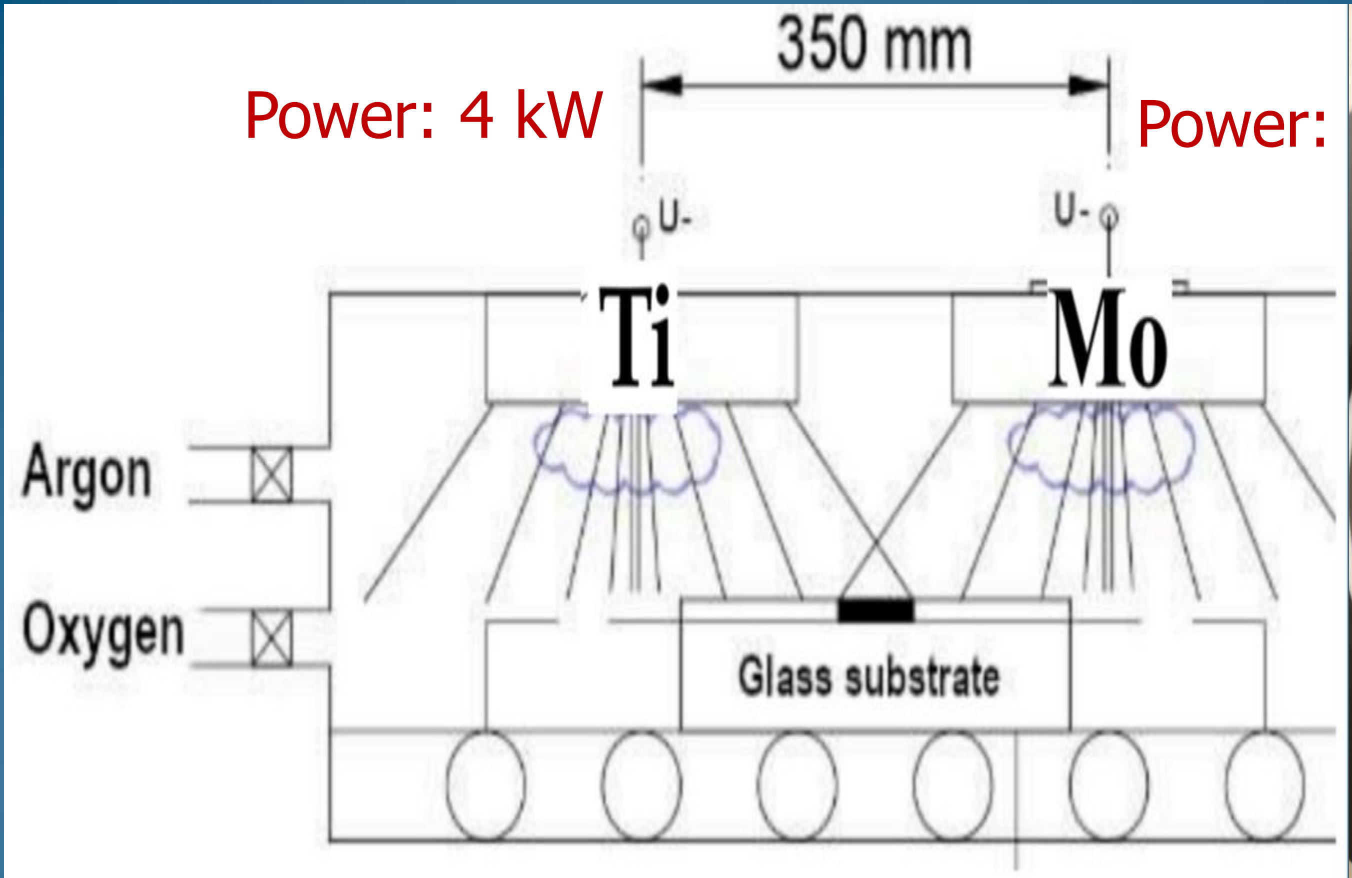
Research methods:

Preparation methods

Reactive DC magnetron sputtering

Characteri-zation methods

Spectroscopic Ellipsometry (SE), Rutherford Backscattering Spectrometry (RBS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS).



a) b)

Figure (1) a) arrangements of the two targets in closer position (35 cm from each other); b) the chamber for DC magnetron sputtering device after air vacuumed. Blue light is from the Ar-O_2 plasma gas mixture.

The main standard of the EC device performance is Coloration Efficiency η (CE, the change of light transmission for the same electric charge) of mixed metal oxides (TiO_2-MoO_3) has been determined in a transmission electrochemical cell, see Fig. 4, is given by following equation :

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

where Qi is the electronic 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 the Coloration Efficiency is cm^2/C see Fig. 8.

Figure (2) TiO_2-MoO_3, ITO- covered glass and Si-probes on a glass substrate, before-electrochromic-experiments, the Ti-rich in the left side and the Mo-rich in the right side .

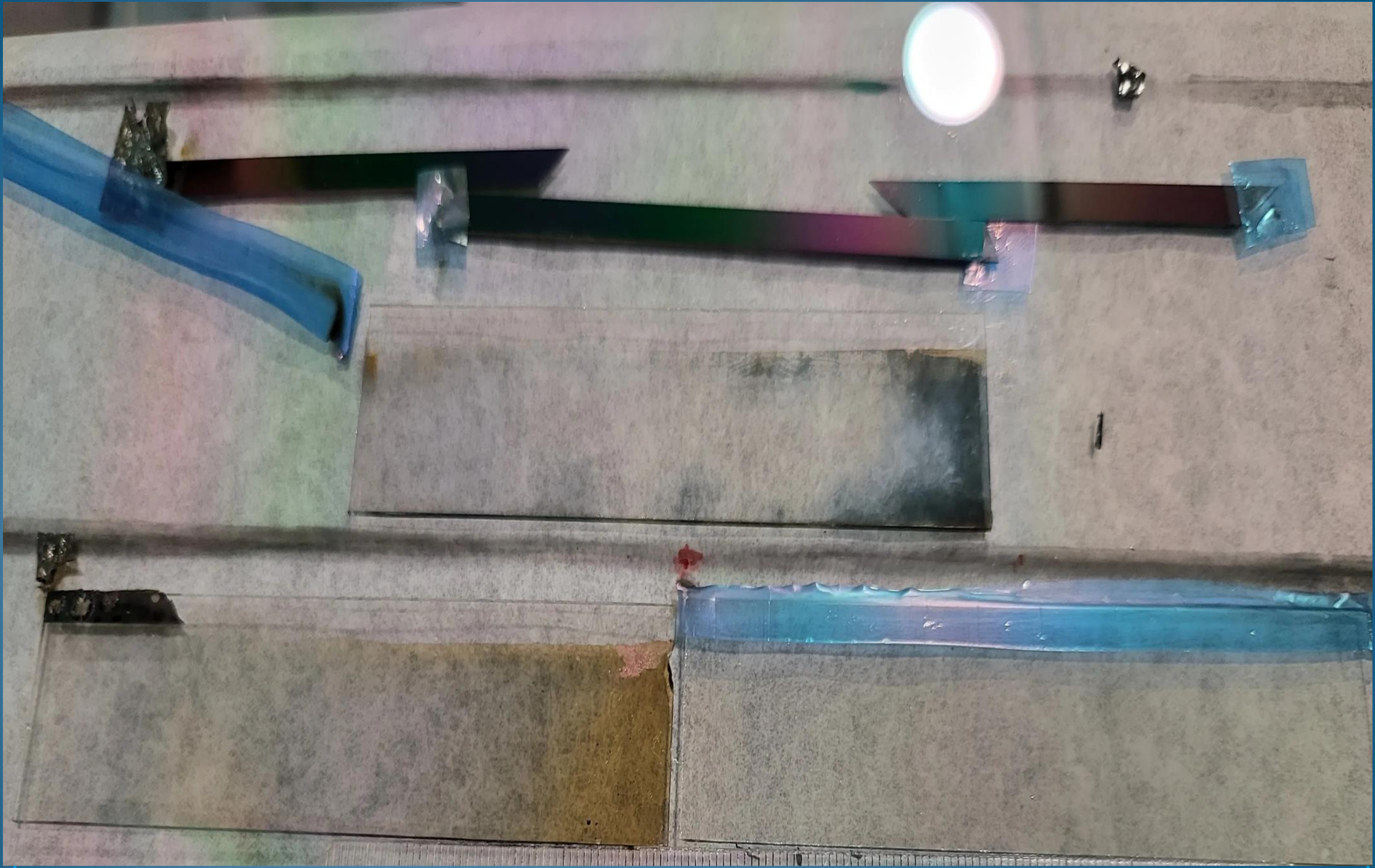


Figure (3) **TiO_2-MoO_3 after-electrochromic-experiments. Thermal shock can be seen in the Ti-rich side (see sticker)**

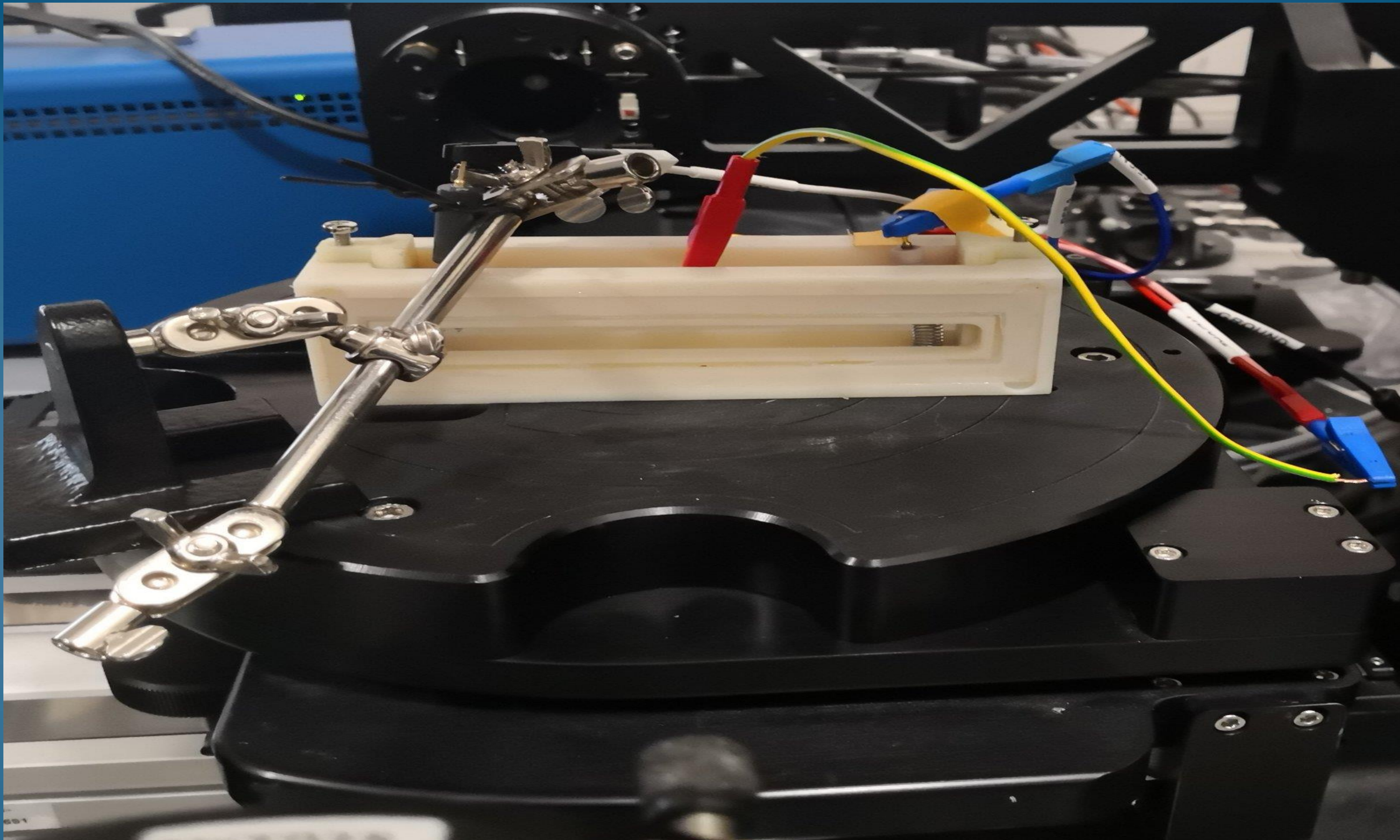


Figure (4) **TiO_2-MoO_3 during-electrochromic-experiments by SE, to determine CE in a transmission electrochemical cell.**

Electrochromic measurements have been performed to optimize the composition of (TiO_2-MoO_3) mixed layers.

The mixed oxide film was deposited onto the Indium-Tin-Oxide surface (ITO) covered glass.

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 see Fig. 7.

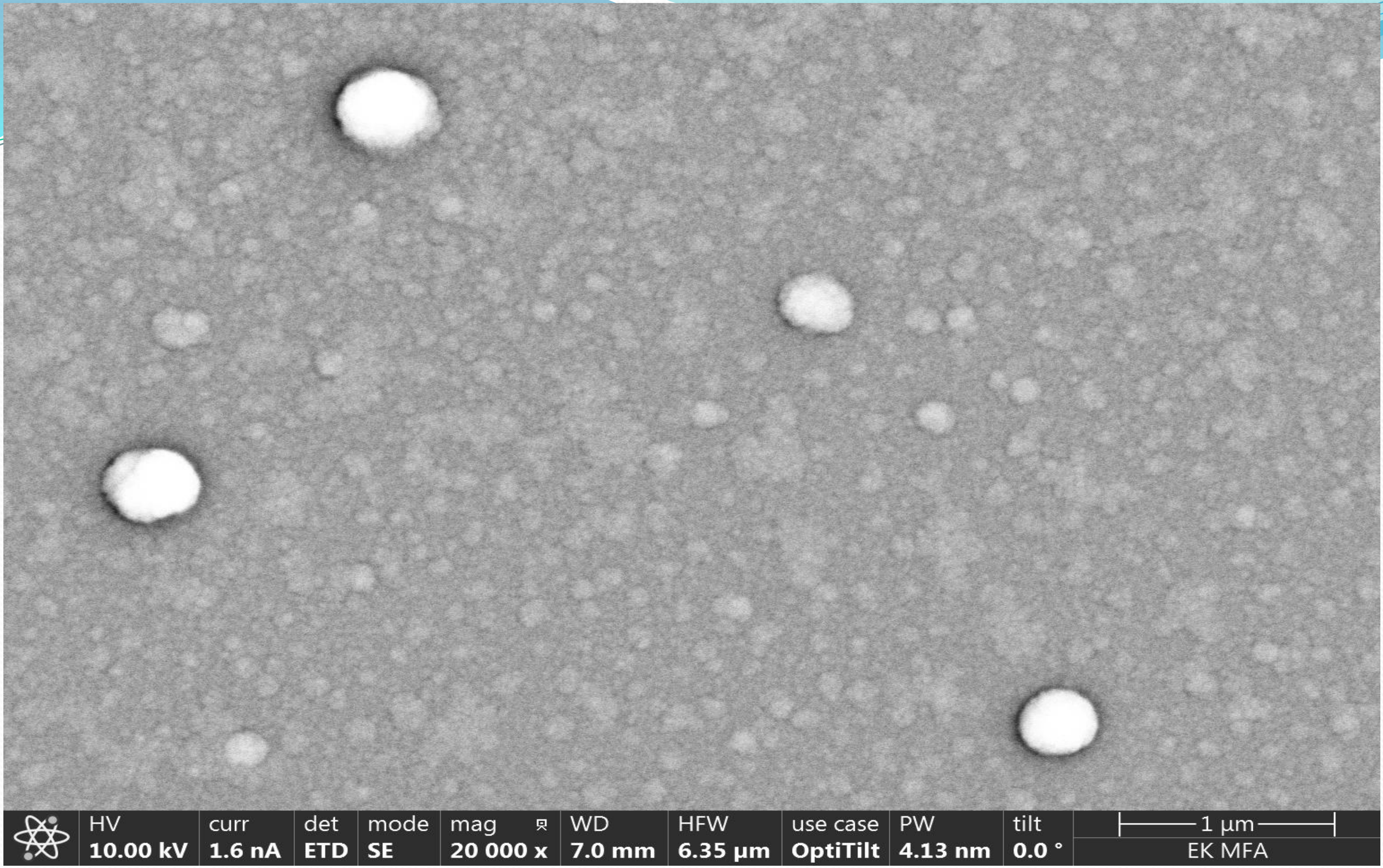


Figure (5) **SEM micrograph from the TiO_2-MoO_3 surface Ti-rich-side, Polycrystalline structure can be seen caused by thermal shock.**

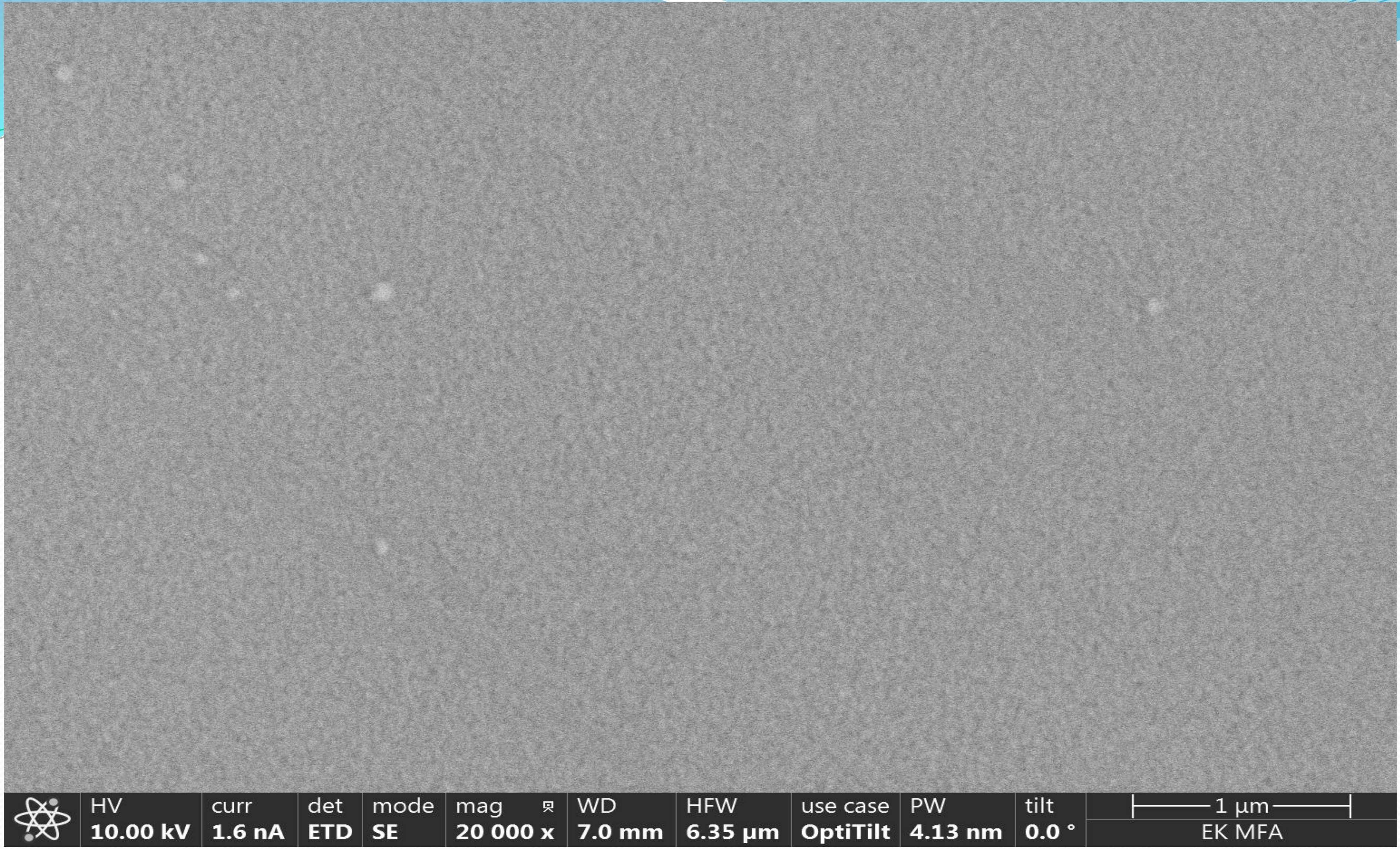


Figure (6) **SEM micrograph from the TiO_2-MoO_3 surface Mo-rich-side, it is remained amorphous (or nanocrystalline).**

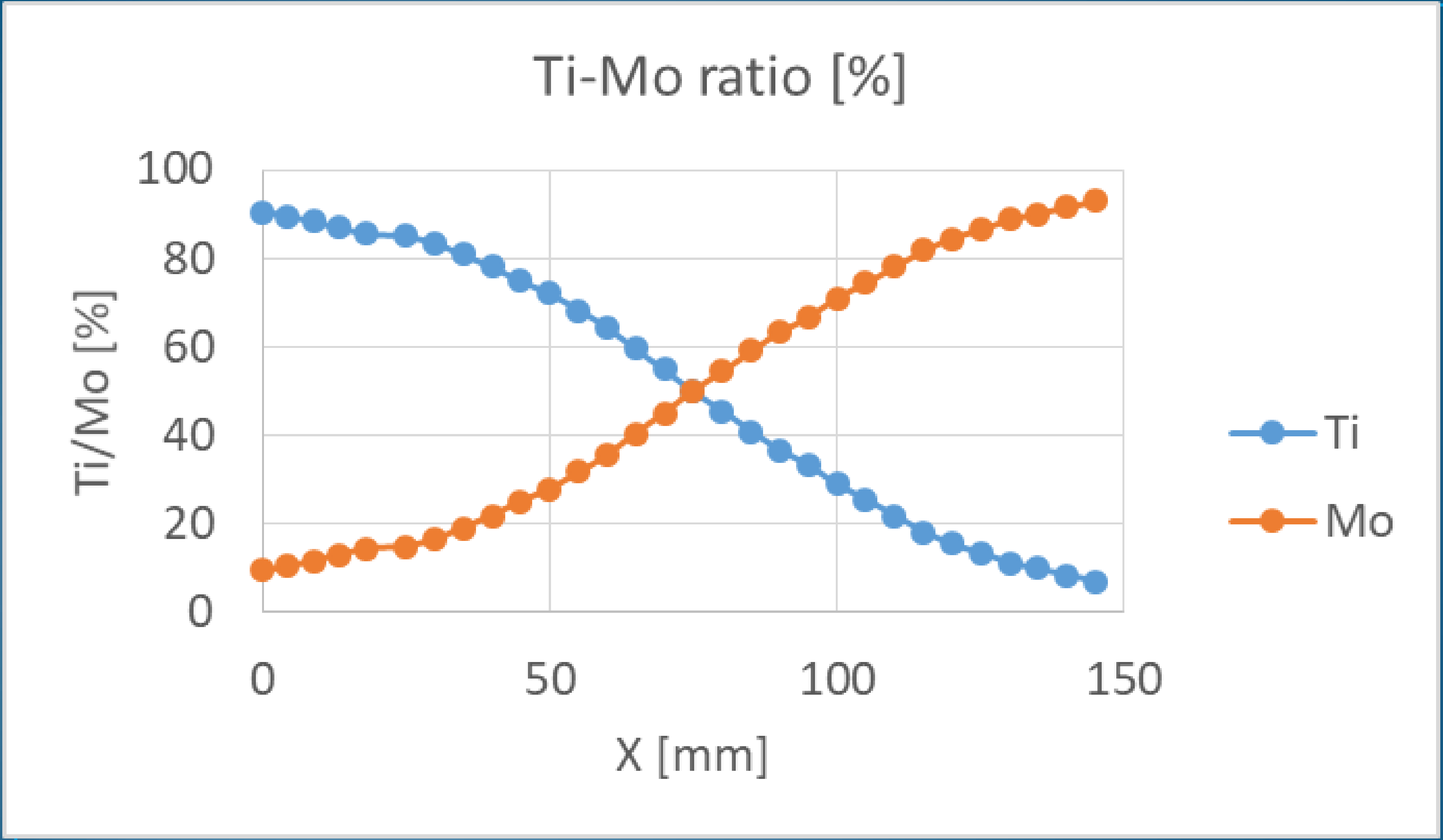


Figure (7) **Ti/Mo ratio measured on the Si-probes by SEM-EDS. The accuracy of the Ti/Mo ratio is 2 %, while the precision of the position is 1 mm.**

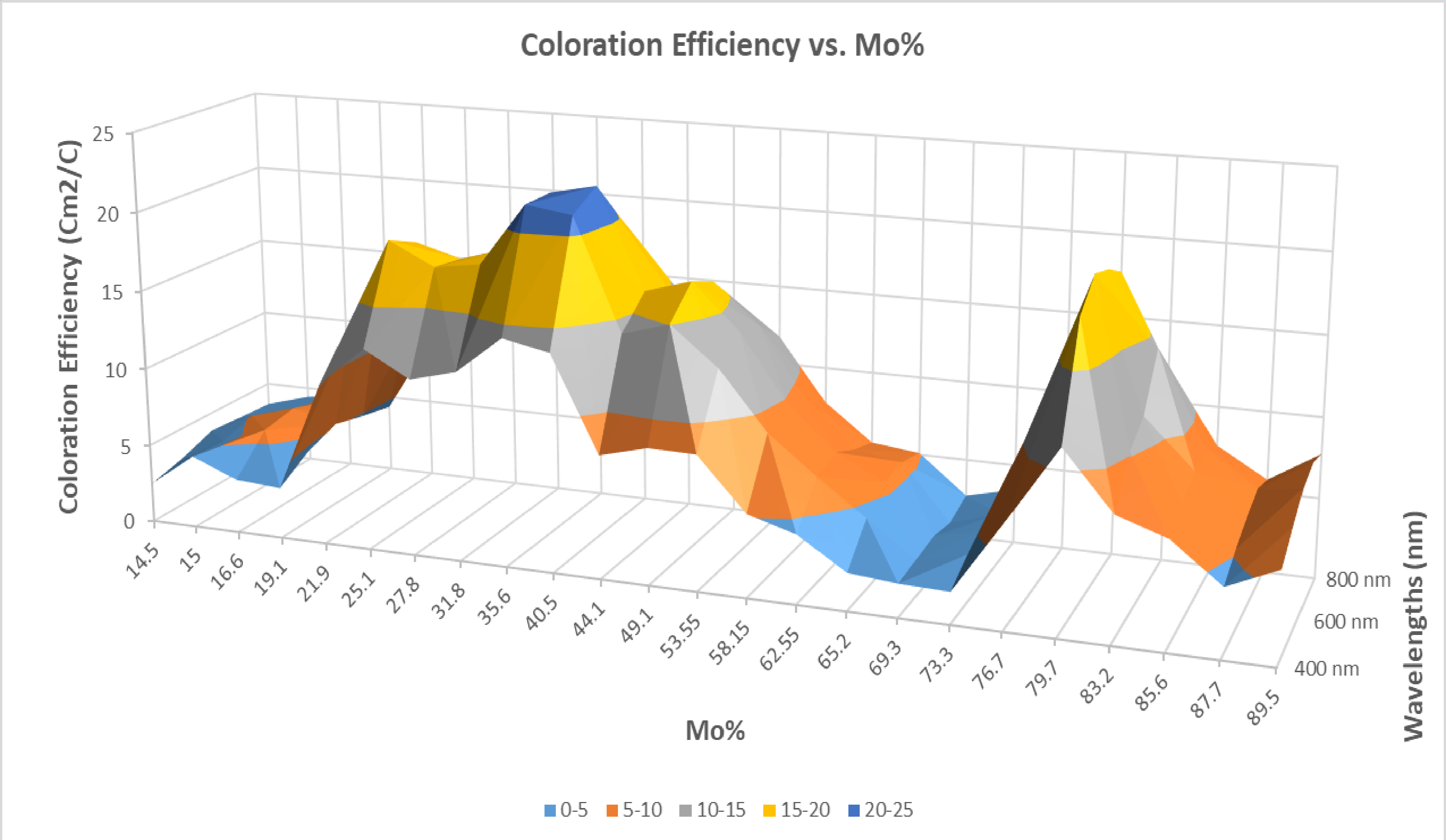
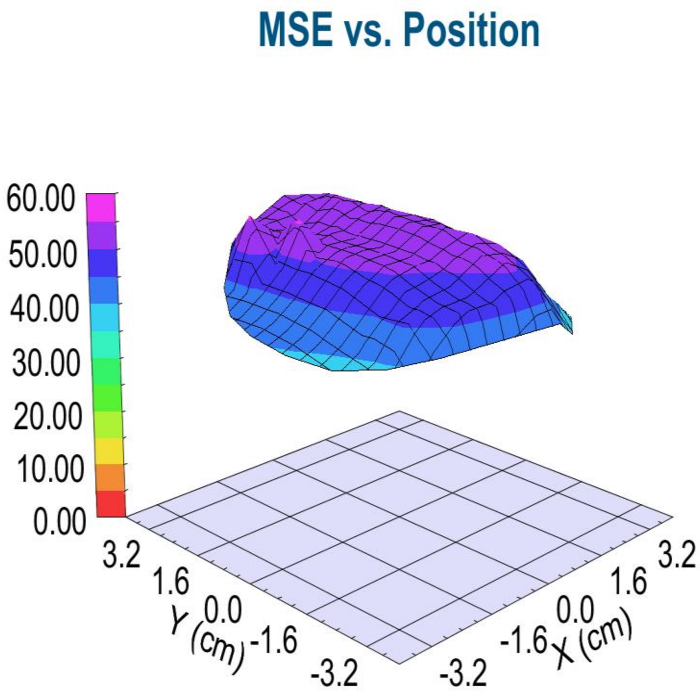
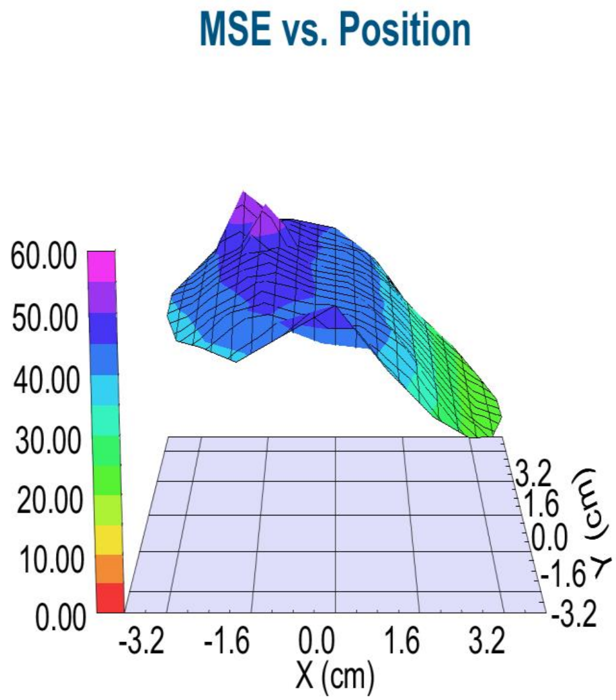


Figure (8) ***3D diagram of the Coloration Efficiency data of TiO_2-MoO_3. vs. Mo % for wavelengths from (400-800) nm visible spectral range.***

For (TiO_2-SnO_2), the selection between the suitable optical models (2-Tauc-Lorentz oscillator vs. BEMA) models depending on the process parameters, if one has more than one "Molecular layer" in the "sublayers", BEMA can be used. If one has an Atomic mixture, the Multiple oscillator model is better (more precise) for this type of layer structure. We are satisfied that we have best match between the model and the experiment, and we have a fast and non-destructive method to determine the thickness and compositions of our combinatorial samples when we measure the optimal electrochromic behavior of these samples. We have shown that the optimal composition is at [(30%)TiO_2–(70%)SnO_2].



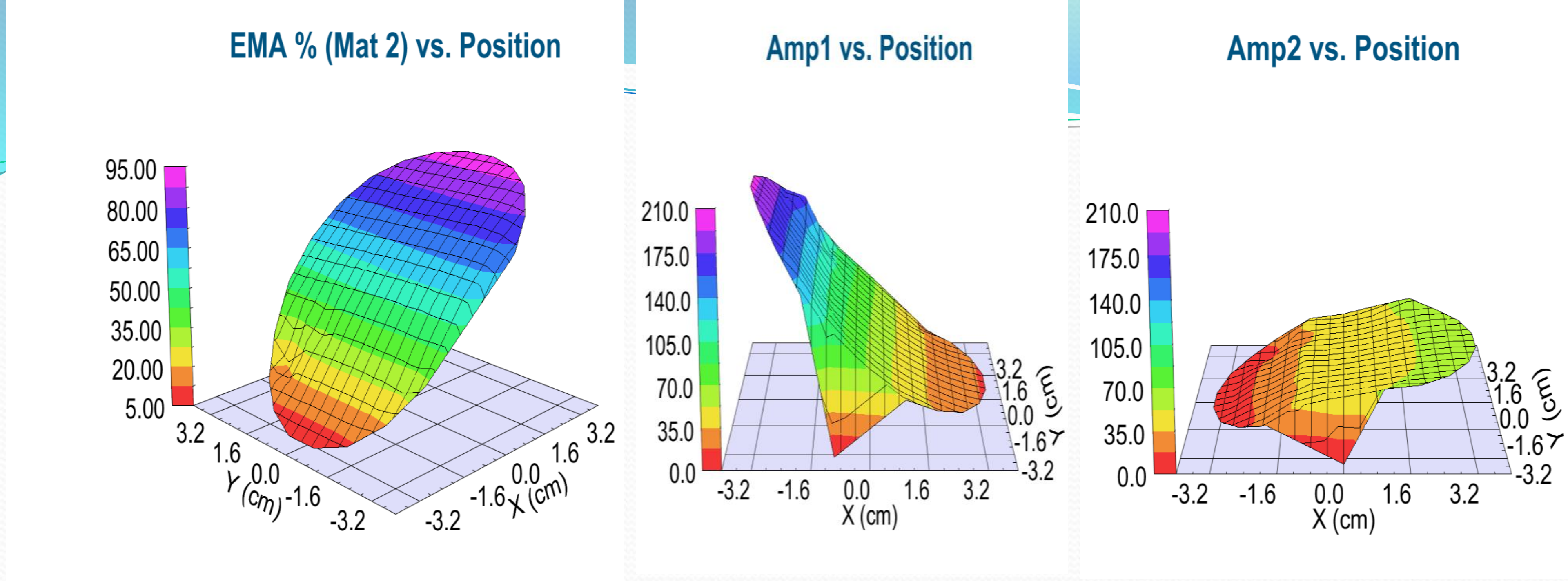
(a)



(b)

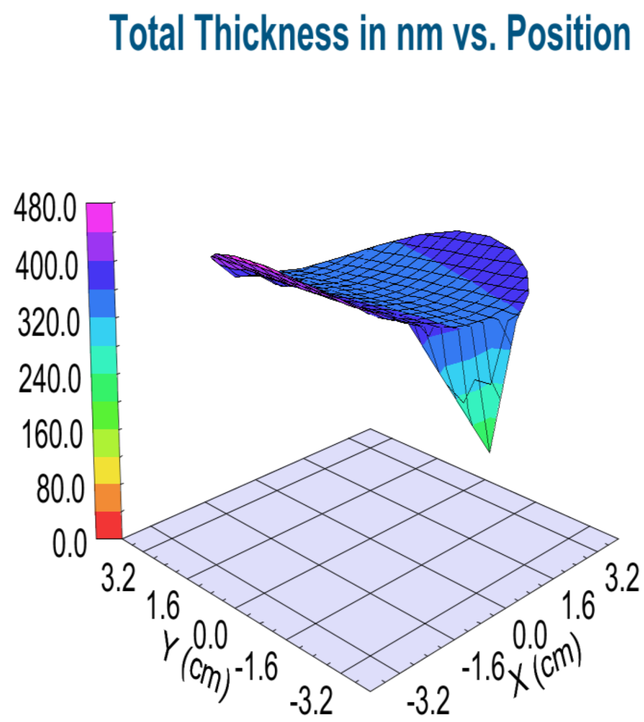
Figure (9) Comparison of MSE (a) EMA and (b) 2TL modelling TiO_2-SnO_2- 4inch-ref-Si.

MSE is the highest in the case of EMA-model, 2TL-model is better!

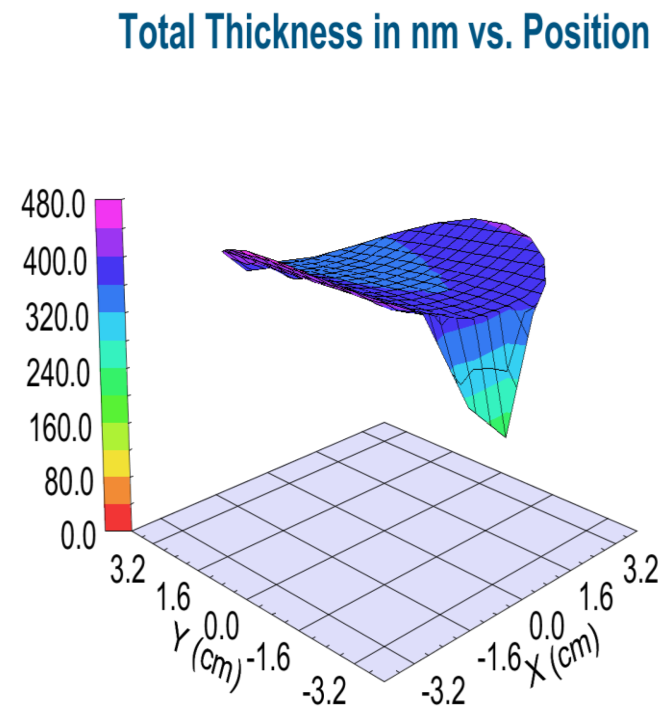


(c) **(d)**

Figure (9) Comparison of (c) Volume fraction % by EMA and (d) Amp1 and Amp2 by 2TL modelling of TiO_2-SnO_2- 4inch-ref-Si.



(e)



(f)

Figure (9) Comparison of Total Thickness by (e) EMA and (f) 2TL modelling TiO_2-SnO_2- 4inch-ref-Si.

Conclusions

By using this combinatorial process, all the compositions (from 0 to 100%) were achieved. The mixed metal oxides showed better EC properties than the pure oxides, because 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.

The Two peaks can be explained by the microstructure difference on the two sides of the CE curves, Ti-rich side was at significantly higher temperature during the deposition process, so the Ti-rich oxide is polycrystalline compared to the Mo-rich side where the oxide remains amorphous or nanocrystalline. The maximum value of the CE is 22.2 cm^2/C at the wavelength 600 nm at ~ 60% - 40 % Ti-Mo ratio on the Ti-rich polycrystalline material, while CE is 19.8 cm^2/C at the wavelength 600 nm at ~ 20% - 80 % Ti-Mo ratio on the Mo-rich amorphous (or nanocrystalline) material.

Teaching activity

1- I have a new publication, Authors: Noor Taha Ismaeel, Zoltan Labadi, Petrik Peter and Miklos Fried. Title: (Combinatorial Preparation and Electrochromic Investigation of Metal Oxide Mixtures), Symposium on Materials Science 2023 Bp, Hungary : Obuda University (2024) pp. 15-19. , 5 p., ISBN:9789634493532 https://real.mtak.hu/195797/

2- We re-submitted the article manuscript to the Acta Polytechnica Hungarica Journal after we answered all the questions and suggestions of the Referees (including changing the title) in April 2024. (First submittion was on 14 of December 2023.) Authors: Noor Taha Ismaeel, Zoltan Labadi and Miklos Fried. Title: Investigation of Combinatorial TiO2- MoO3 Mixed Layers to Enhance the Coloration Efficiency. Number: 6540. You can access it via the Acta1034 EasyChair Web page: https://easychair.org/conferences/?conf=acta1034

3- We try to submit a Review manuscript to the ACS Omega Journal. Title: Electrochromic efficiency in $A_xB_{(1-x)}O_y$ type mixed metal-oxide alloys.

4- I continued the investigations and my efforts were divided into two parts: the publications and starting to write my thesis.

Planned steps forward:-

1. Further investigation of stoichiometric and sub-stoichiometric oxides for gas sensorics purposes see Fig. 10.

Figure (10) ***Photographs (from different view-angle) of WoO_3/MoO_3 (lower) or WoO_{3-x}/MoO_{3-x} (upper) combinatorial sets on heat-able sensor chips. Inserted photograph shows Pt contacted sample.***

Publikációk listája a PhD képzés kezdetétől /

List of publications from the beginning of the training programme

No	Title	Name of journal or conference	IF, Q	Total credit	%	Credit
1-	https://www.mdpi.com/1996-1944/16/12/4204 https://real.mtak.hu/166660/ Investigation of Electrochromic, Combinatorial TiO_2-SnO_2 Mixed Layers by Spectroscopic Ellipsometry Using Different Optical Models	MATERIALS **2023**	3.4 Q2	36	100	36
2-	https://ellipsometry.hu/Anyagtudomany-Symp-Matrahaza-2022-10-5-7-ISBN-978-963-449-320-4-2023.pdf ISBN: 9789634493204 https://real.mtak.hu/163841/ Combinatorial Preparation and Characterization Methods for High Throughput Study of WO_3-MoO_3 Mixtures	Symposium on Materials Science Conference Journal **2022**		24	100	24

3-	https://konf2022.kvk.uni-obuda.hu/program ISBN 978-963-449-299-3 https://m2.mtmt.hu/gui2/?mode=browse&params=publication;33299496 Combinatorial Preparation and Characterization Methods for High Throughput Study of Advanced Functional Materials	XXXVIII. Kandó Conference **2022**		100	24
4-	https://doi.org/10.32802/asmscj.2022.1263 https://m2.mtmt.hu/gui2/?mode=browse&params=publication;33991503 The Effectiveness of a 980-nm Diode Laser to Treat Face Haemangioma: A Randomised within-Patient Trial	ASM Science Journal **2022**	Scopus	100	
5-	https://doi.org/10.32802/asmscj.2022.1215 https://m2.mtmt.hu/gui2/?mode=browse&params=publication;33991556 The Combination Effect of Co2 Laser and Topical Growth Factor Solution for Treatment of Atrophic Post-Burn Scar	ASM Science Journal **2022**	Scopus	100	

6-	https://www.iasj.net/iasj/download/bd56f1e825a3bfa5 https://m2.mtmt.hu/gui2/?mode=browse&params=publication;33991701 Study the Effect of Nano Aluminum Oxide Coating on PMMA as Thermal Insulator	Iraqi Journal of Laser **2022**			100	
7-	https://konf2023.kvk.uni-obuda.hu/program	XXXIX. Kandó Conference **2023**		24	100	24
8-	https://www.transfernow.net/dl/20240527e9HdX4Ik/Guhpemi8 ISBN 978-963-449-353-2 https://real.mtak.hu/195797/ Combinatorial Preparation and Electrochromic Investigation of Metal Oxide Mixtures	Symposium on Materials Science Conference Journal **2023**		24	100	24


Thanks for your attention
Köszönöm a figyelmet