BY Phd Student

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superviso

supervisor

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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 have prepared thin films of mixed Titanium, Tin Oxide and WO_3-MoO_3 mixed layers on glass- (for electrochromic measurements) and Si-substrates (for spectroscopic ellipsometry and RBS control measurements), by reactive DC magnetron sputtering. The deposited $A_xB_{1-x}O_n$ type films will be Characterized by a variety of methods.

Research methods:

Preparation methods

Pulsed mode reactive DC magnetron , Biased RF sputtering systems (see Fig. 1) and Laser ablation deposition system

Characteri-zation methods

Spectroscopic Ellipsometry, Rutherford Backscattering Spectrometry, Transmission Electron Microscopy, Scanning Electron Microscopy and Atomic Force Microscopy

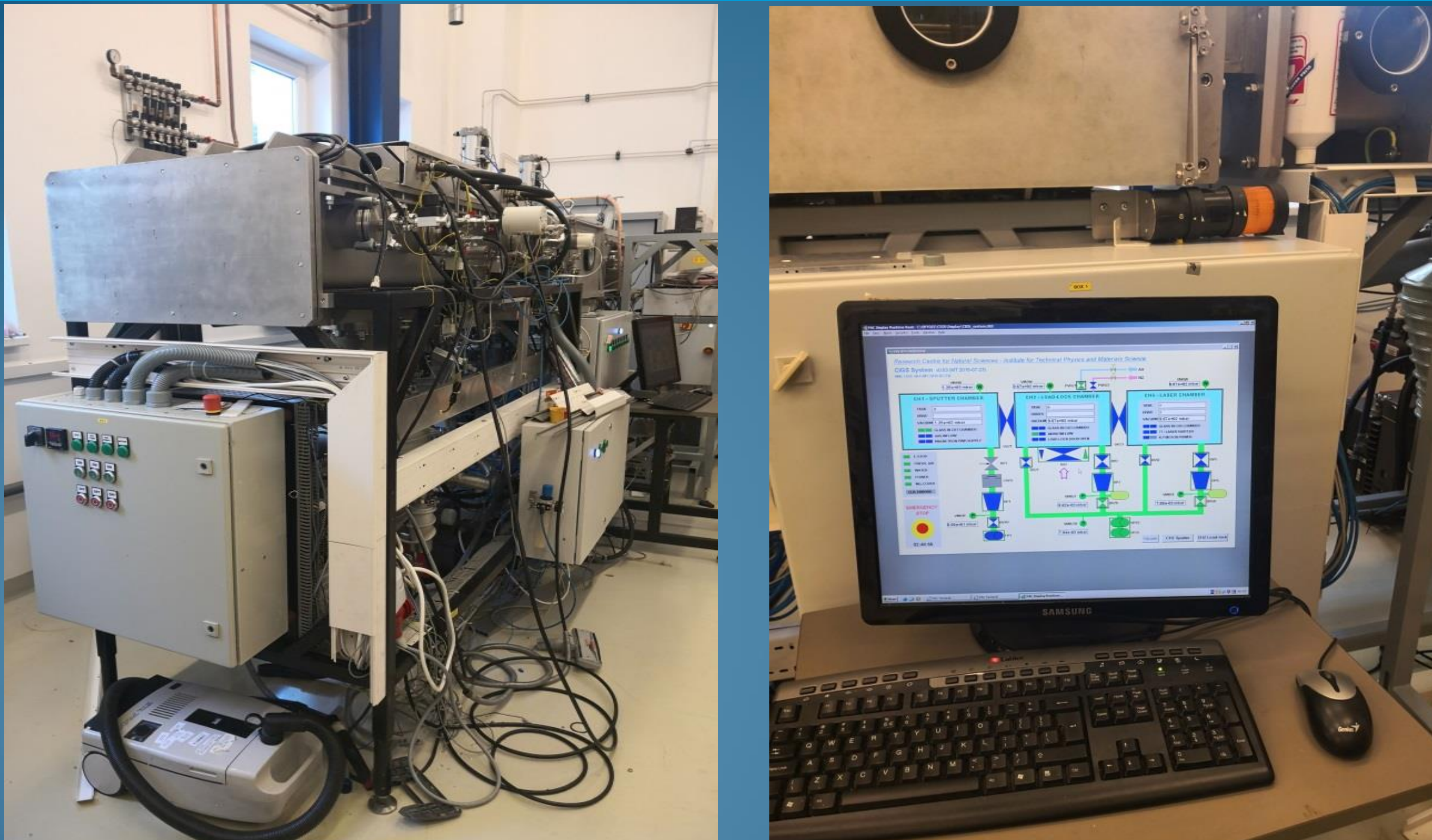


Figure (1) shows the DC magnetron sputtering systems, and its control screen

Figure (2) the chamber for DC magnetron sputtering device after air vacuumed. Blue light is from the Ar-O_2 plasma.

Figure (3) a) Spectroscopic Ellipsometry device, Woollam M-2000DI, Wavelength range from 191-1690 nm (photon energies from 0.7-6.5 eV), Automatic scan with a micro-focused 0.2 mm spot. Angle of incidence: 45-75 degree. Measurement time 1 sec per spot.

b)

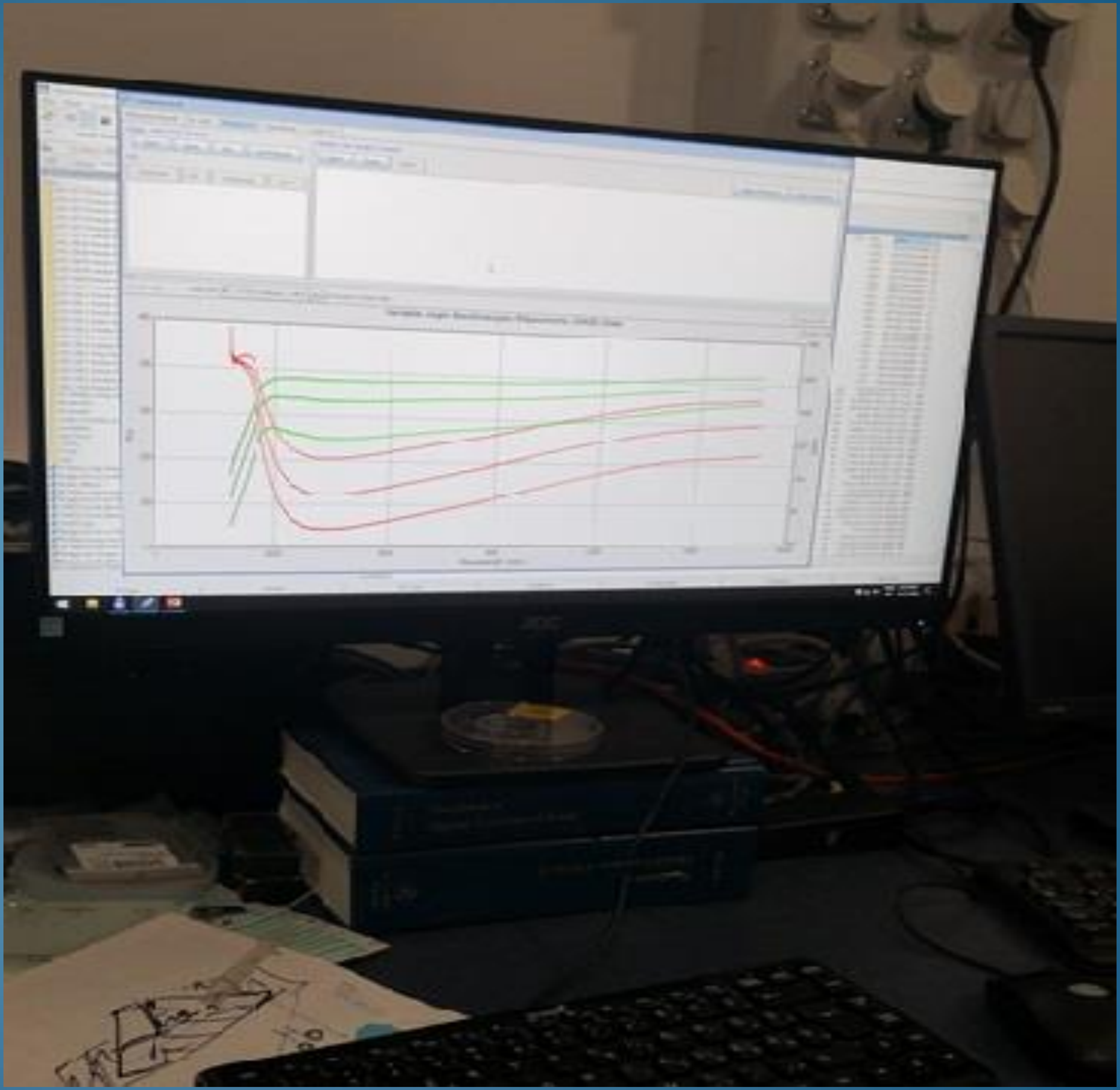
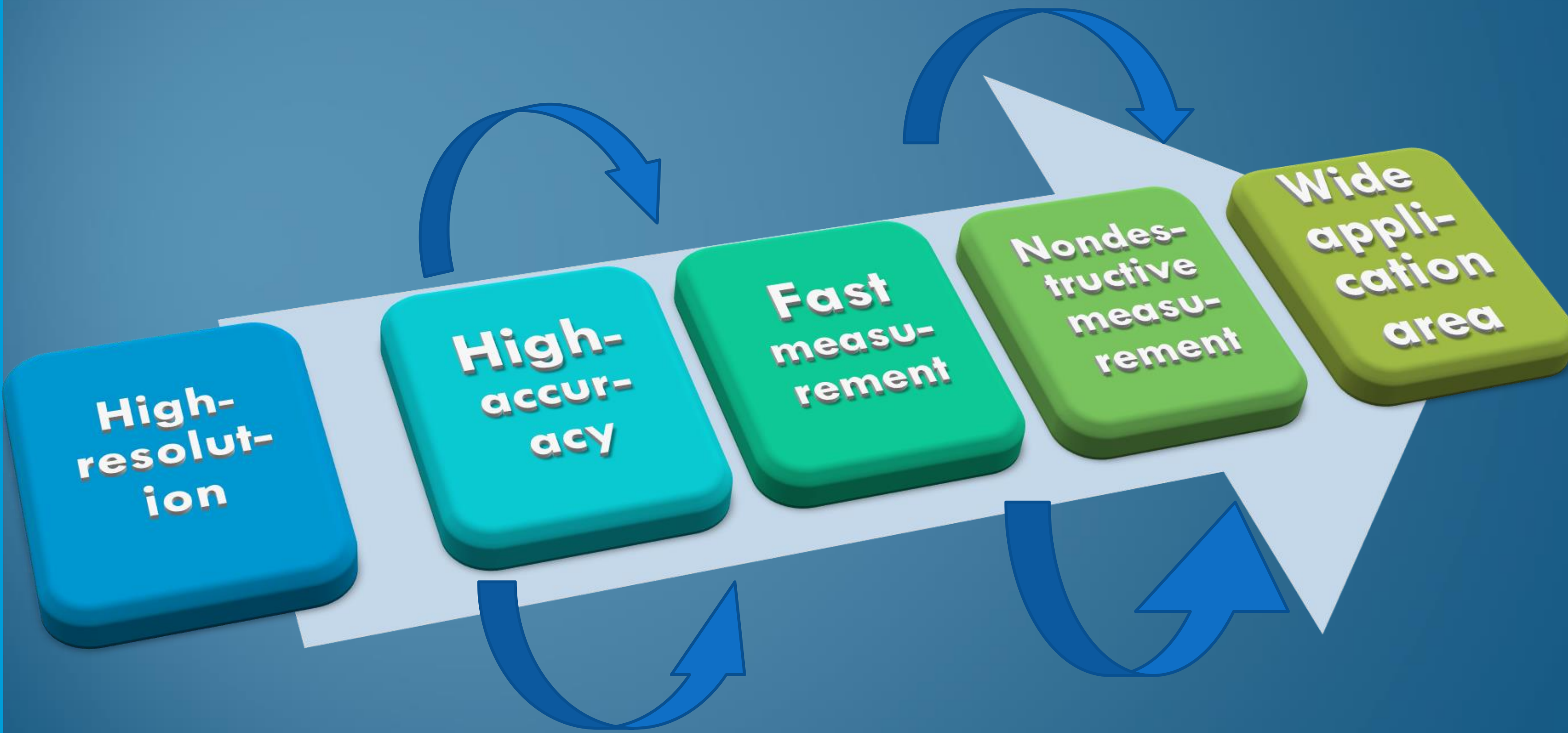
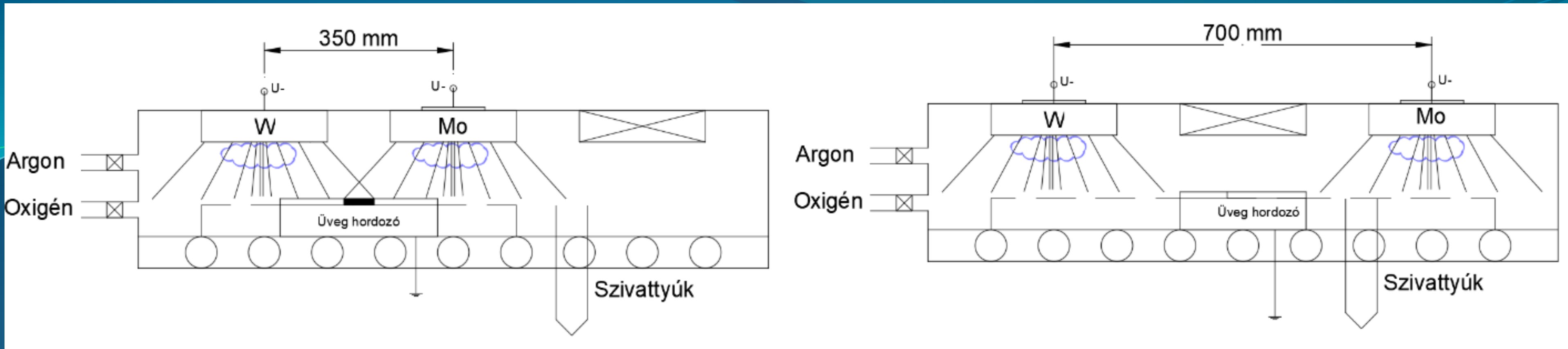


Figure (3) b) is the data analysis screen.

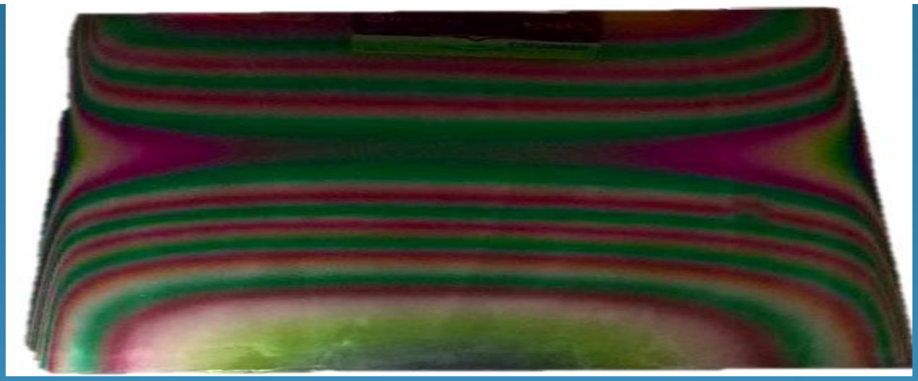
The Advantages of this device



Using spectroscopic ellipsometry, we can obtain quickly and non-destructive manner compositional maps if we have appropriate optical model. In this work, we compare the “goodness” of different optical models depending upon the sample preparation conditions during magnetron sputtering, for instance, the speed and cycle number of the substrate motion.

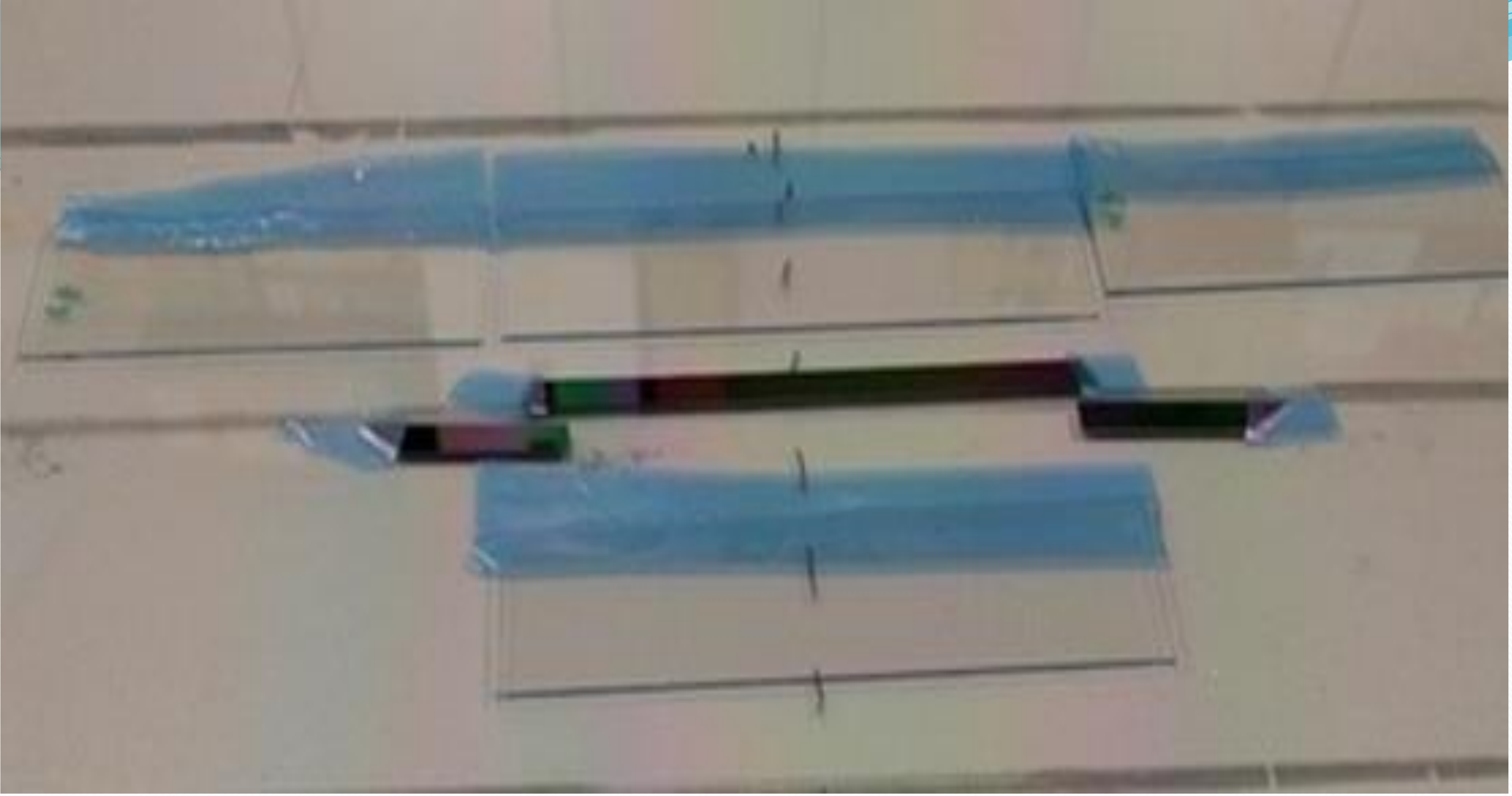


(a)



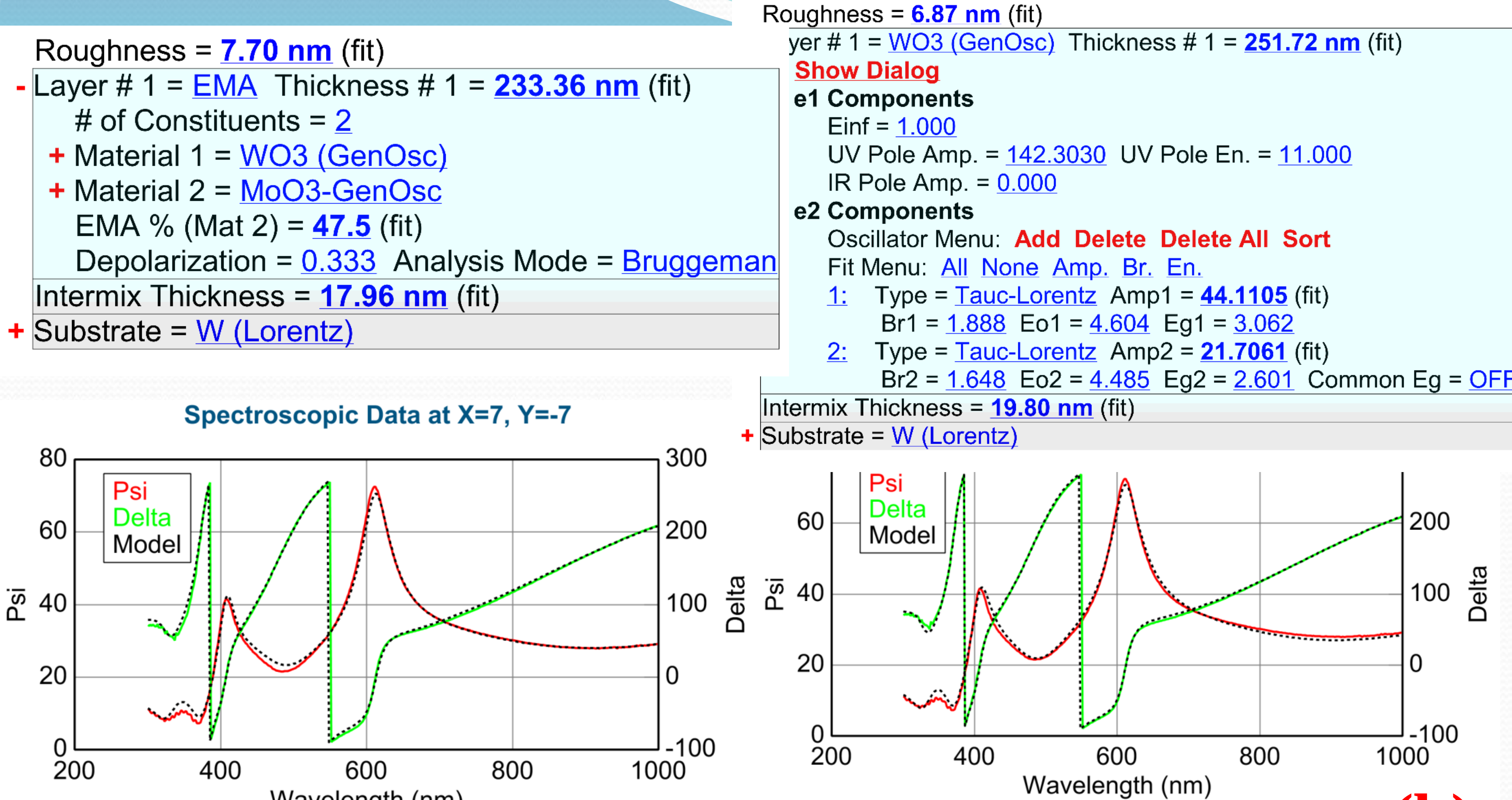
(b)

Figure (4) Schematic picture of the deposition, two arrangements of the targets: a) the two targets in closer position (35 cm from each other) b) the two targets in distant position (70 cm from each other). Colored bands show thickness and composition gradient.



(c)

Figure (4) c) WO_3-MoO_3 combinatorial mixed layers on glass- and Si-substrates on top of a 30x30 cm glass sheet. The pale colored bands show the changing thicknesses and compositions.

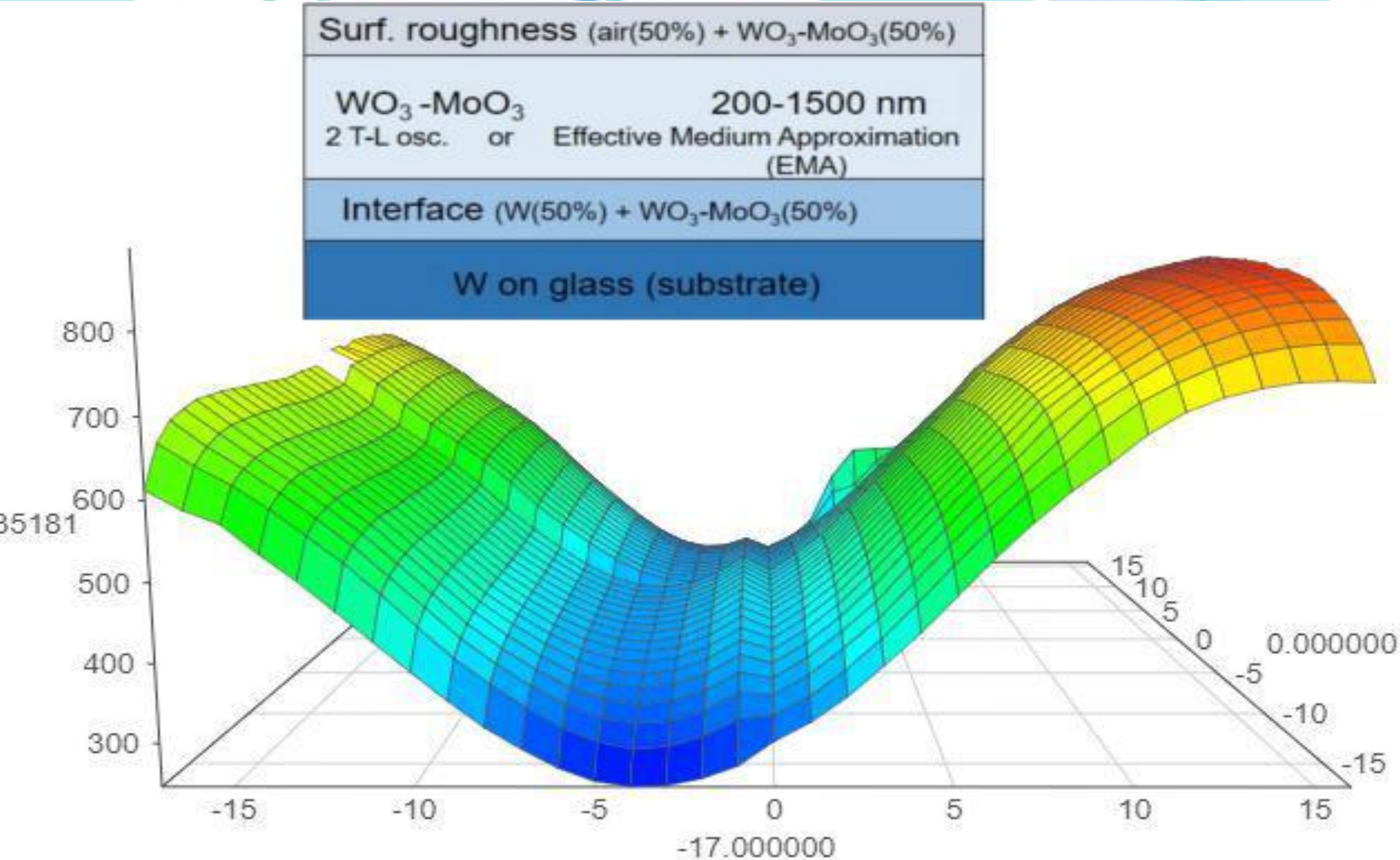


(a) MSE (Mean Squared Error) = 29.5
Roughness (nm) = 7.7 ± 0.2
EMA % (Mat 2) = 47.5 ± 1.4
Intermix Thickness (nm) = 17.9 ± 0.1

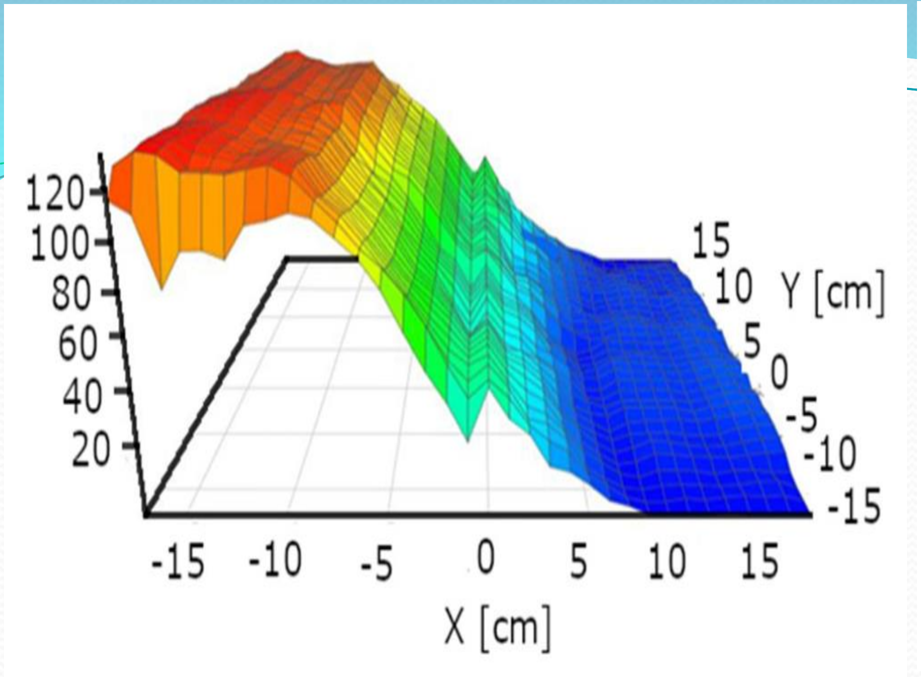
MSE = 27.4 **(b)**
Roughness (nm) = 6.9 ± 0.2
Amp1 = 44.1 ± 1.4 Amp2 = 21.7 ± 0.6
Intermix Thickness (nm) = 19.8 ± 0.2

Figure (5) Comparison of (a) EMA, (b) 2T-L modelling (WO_3-MoO_3).

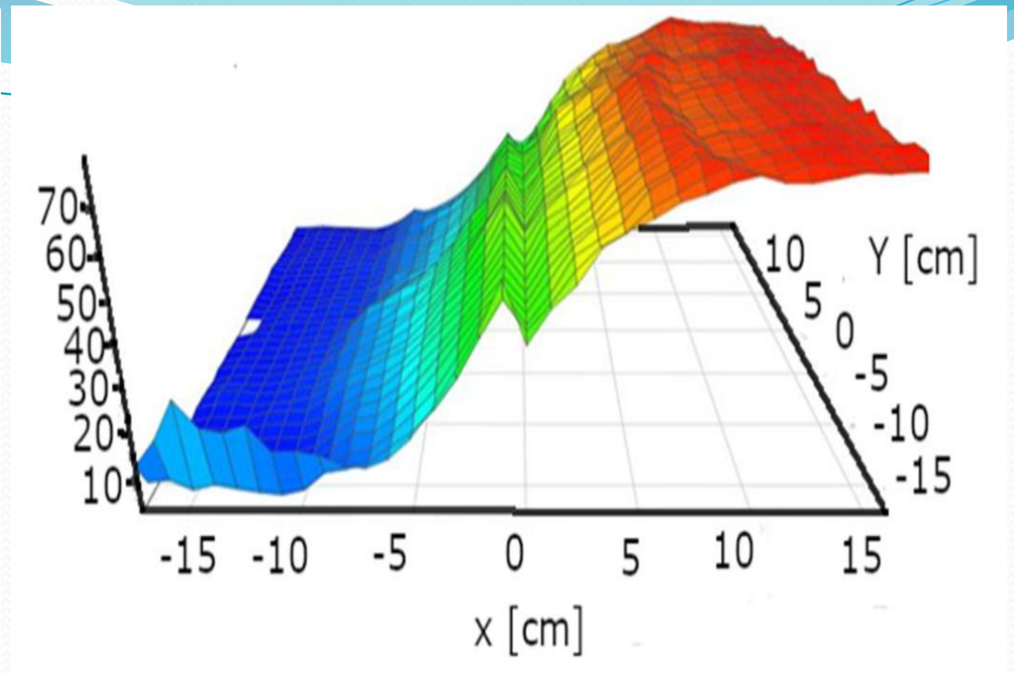
Results



Figure(5) c) Ellipsometric thickness mapping of the WO_3/MoO_3 combinatorial layer.



(d)



(e)

Figure(5) Shows the fitted parameters; d) Amp1: Amplitude-of-T-L(WO_3)–map; e) Amp2: Amplitude-of-T-L(MoO_3)–map (the wrinkles at the center lines are artefacts caused by the manual rotation during the SE measurement).

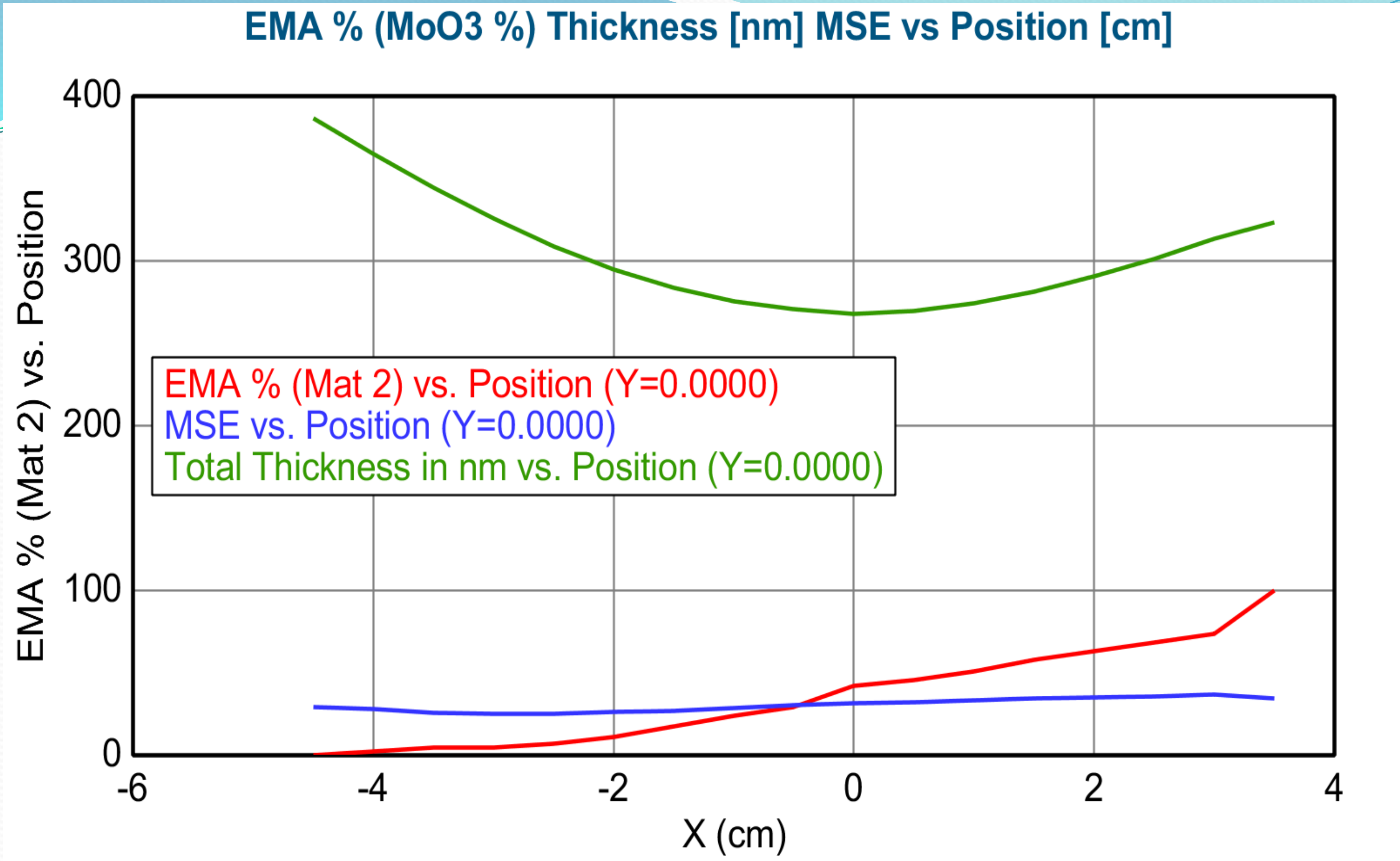
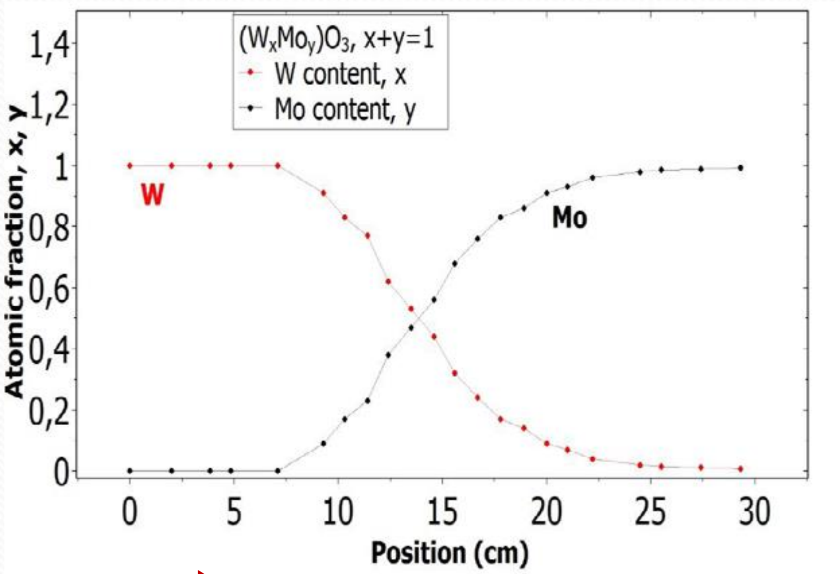
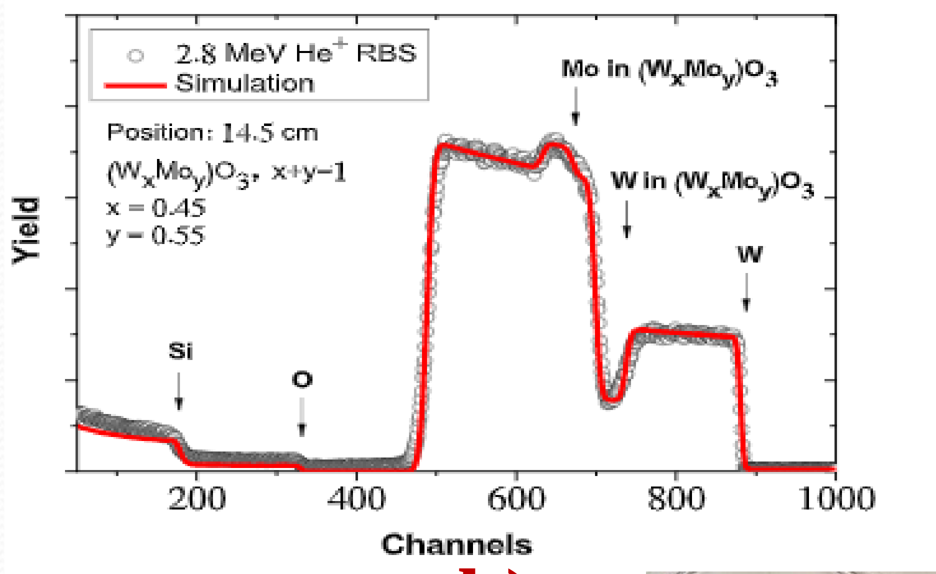


Figure (6) presented Ellipsometry mapping of the Effective Medium Approximation EMA % (MoO_3 %) Thickness (nm), MSE (fitting quality)

We measured the WO_3/MoO_3 samples (on Si-samples) and fit the SE measurement by the CompleteEASE program and compared the results with measurement by RBS.



a)



b)

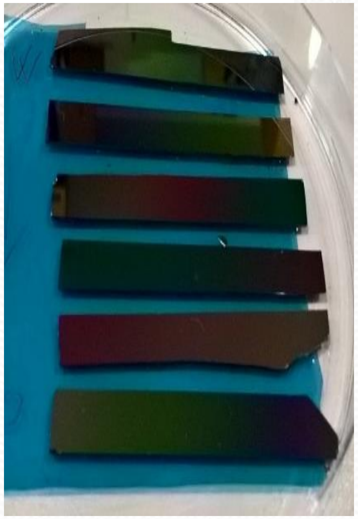
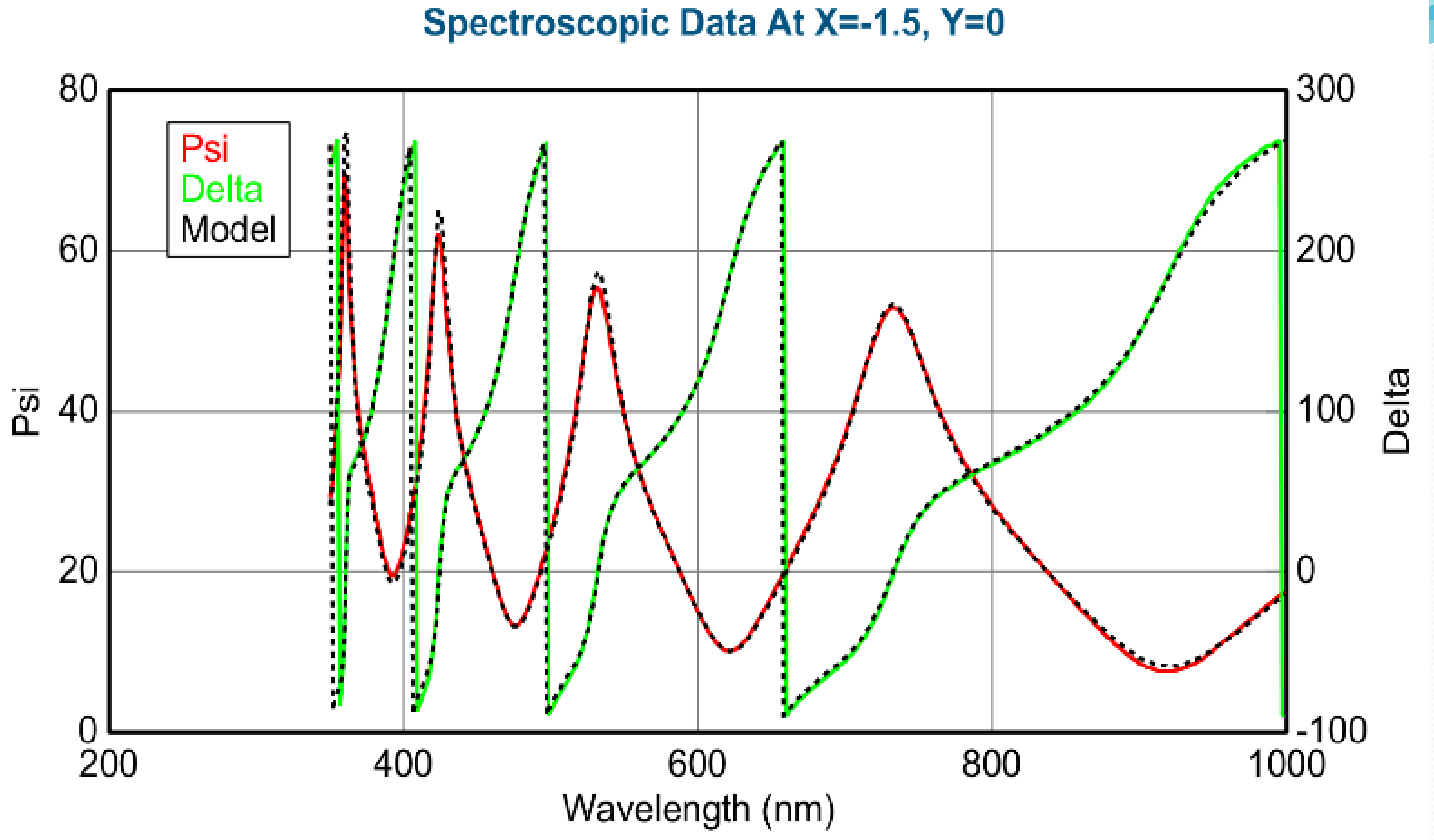


Figure (7) a) Composition-map along a line by Rutherford Backscattering Spectrometry.
b) One Rutherford Backscattering Spectrometry example near the center position.

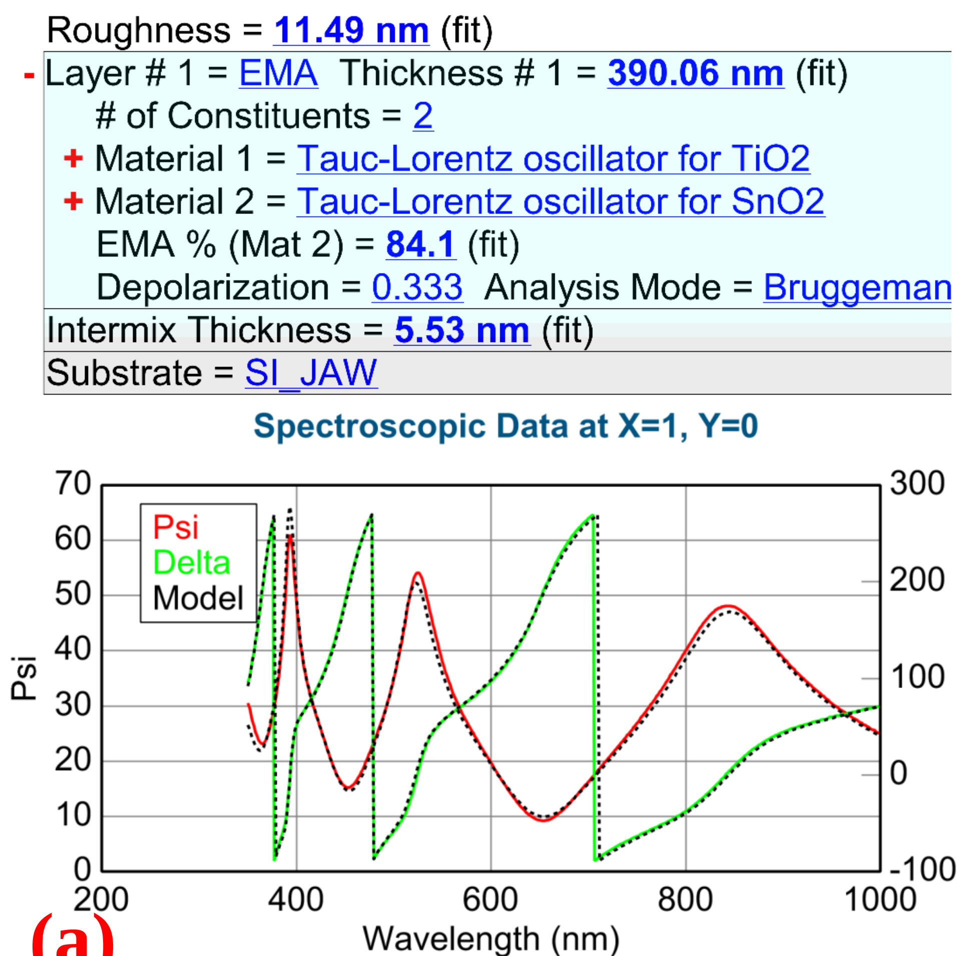
(a)

Figure (8) a)Ti and Sn oxides combinatorial deposition. Silicon probes to measure the thickness and composition map.



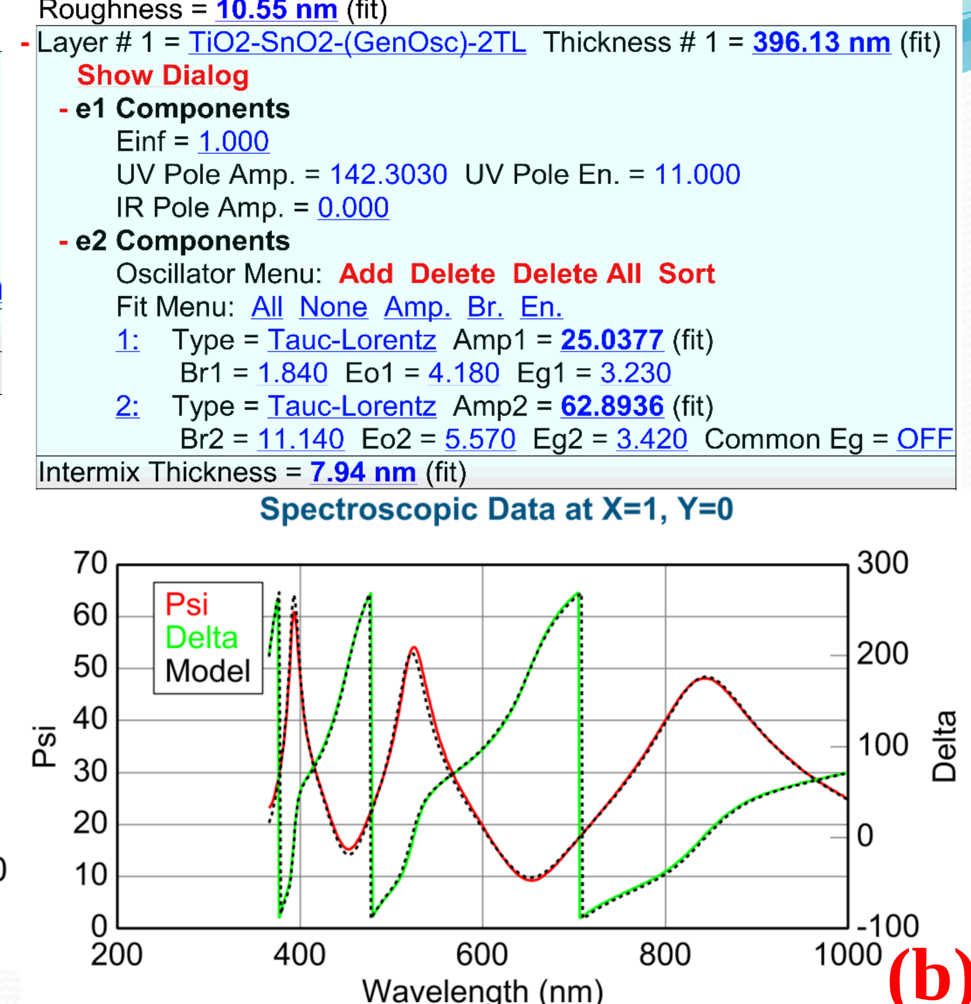
(b)

Figure (8) b)Measured and fitted spectra at one sample point: TiO_2-SnO_2-EMA-Si- stripe-right.



(a)

MSE (Mean Squared Error) = 31.6
Roughness (nm) = 11.5 ± 0.4
EMA % (Mat 2 – SnO2) = 84.1 ± 0.2
Intermix Thickness (nm) = 5.5 ± 0.4
Total Thickness (nm) = 390.1 ± 0.4



(b)

MSE = 27.2
Roughness (nm) = 10.6 ± 0.4
Amp1 = 25.0 ± 0.4 Amp2 = 62.9 ± 0.8
Intermix Thickness (nm) = 7.6 ± 0.3
Total Thickness (nm) = 396.1 ± 0.8

Figure (9) Comparison of (a) EMA and (b) 2T-L modelling (TiO_2-SnO_2)

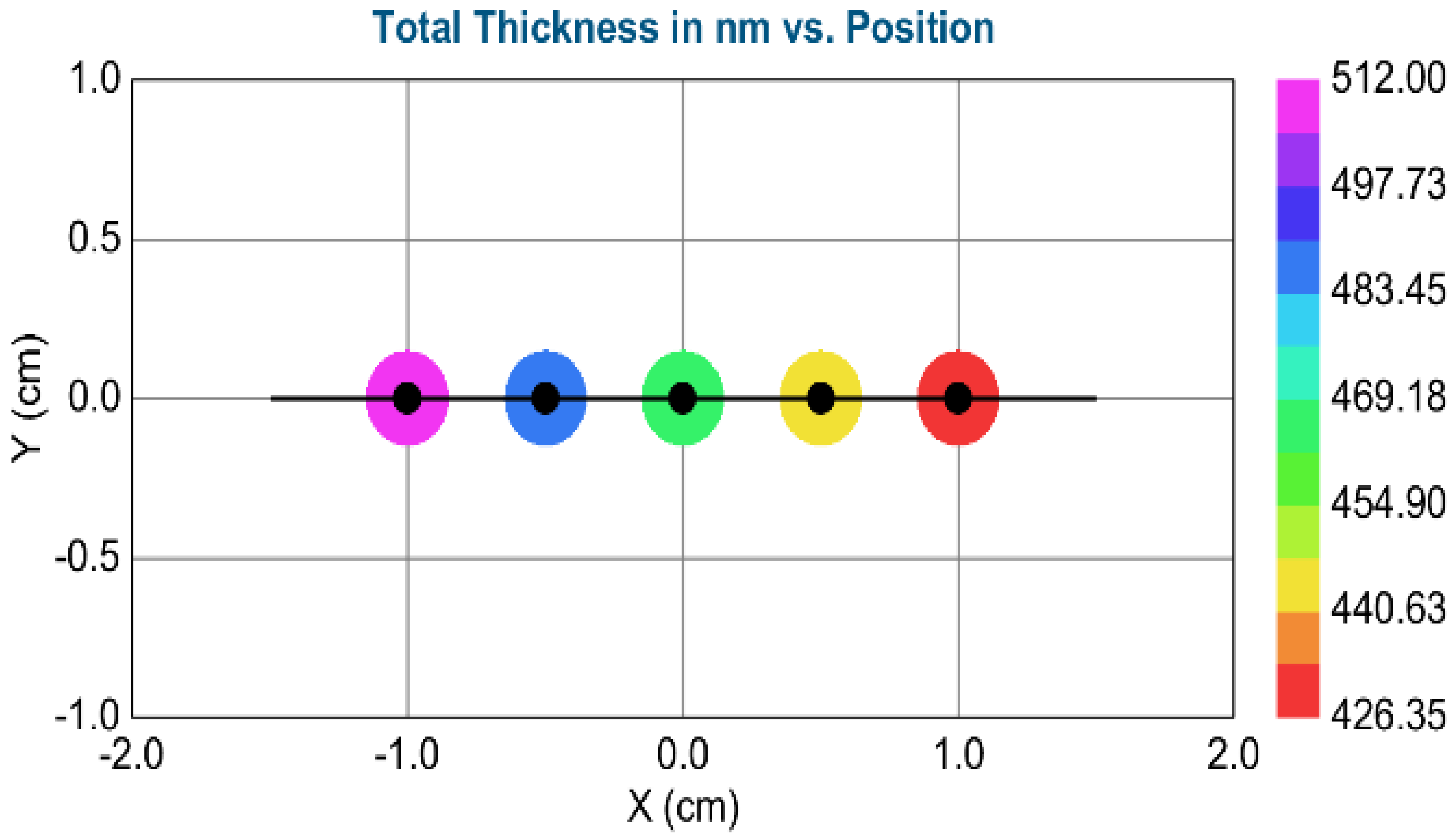


Figure (10) TiO_2-SnO_2-EMA-3cm-Si-stripe-left total Thickness.

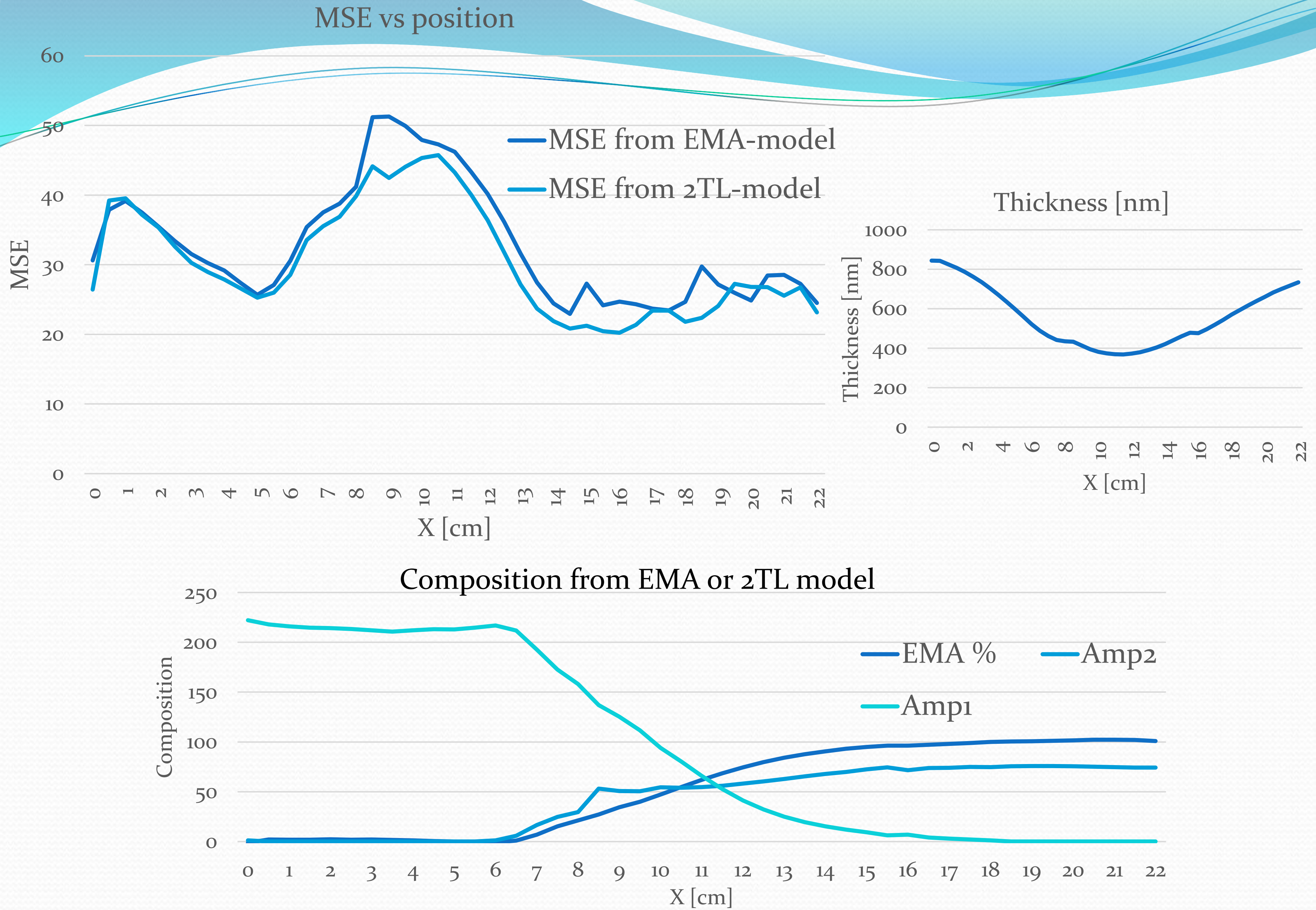


Figure (11) Comparison of EMA and 2T-L modelling (TiO_2-SnO_2).

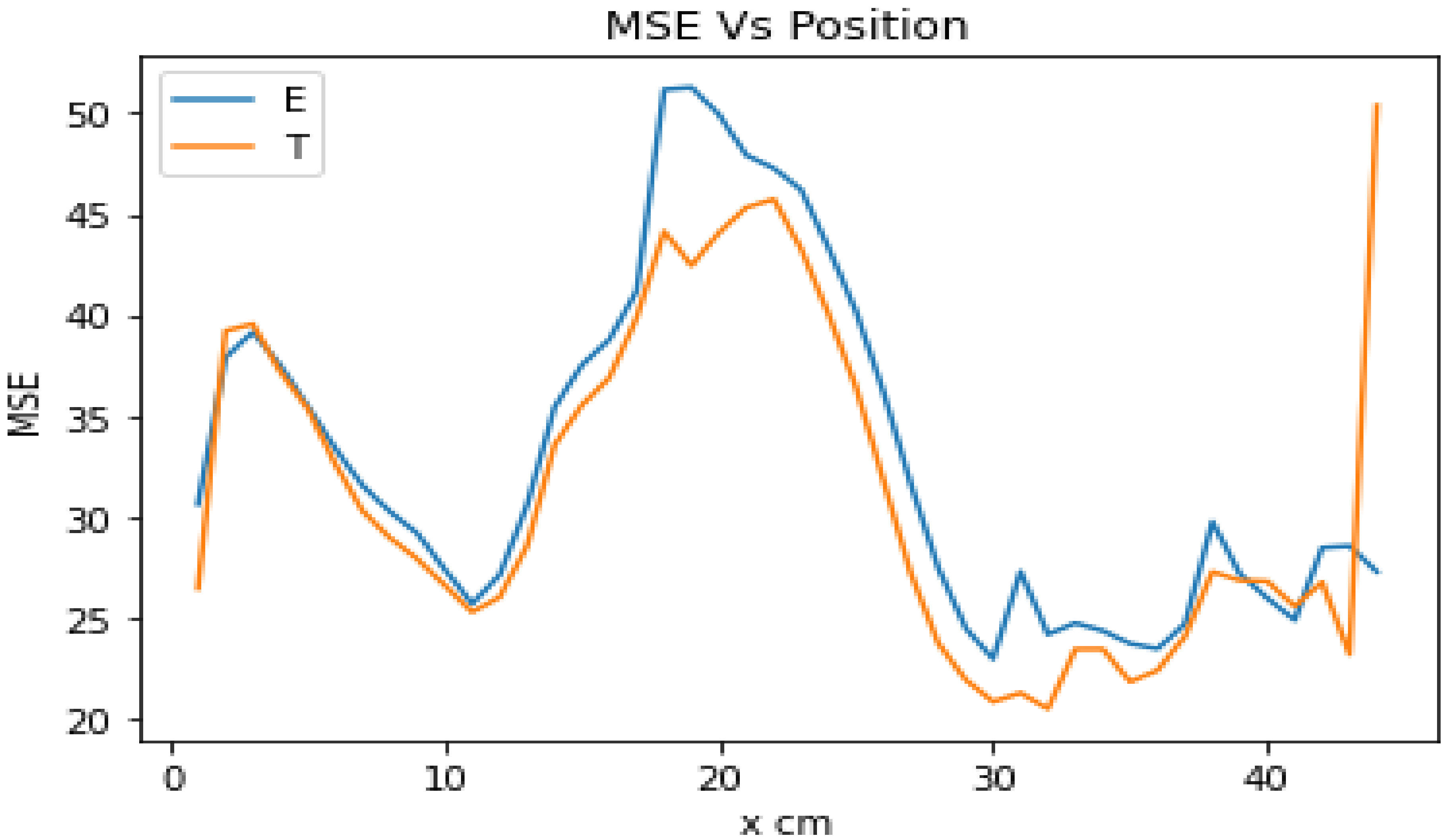


Figure (12) Comparison of EMA and 2T-L modelling (TiO_2-SnO_2) by home-made Python software.

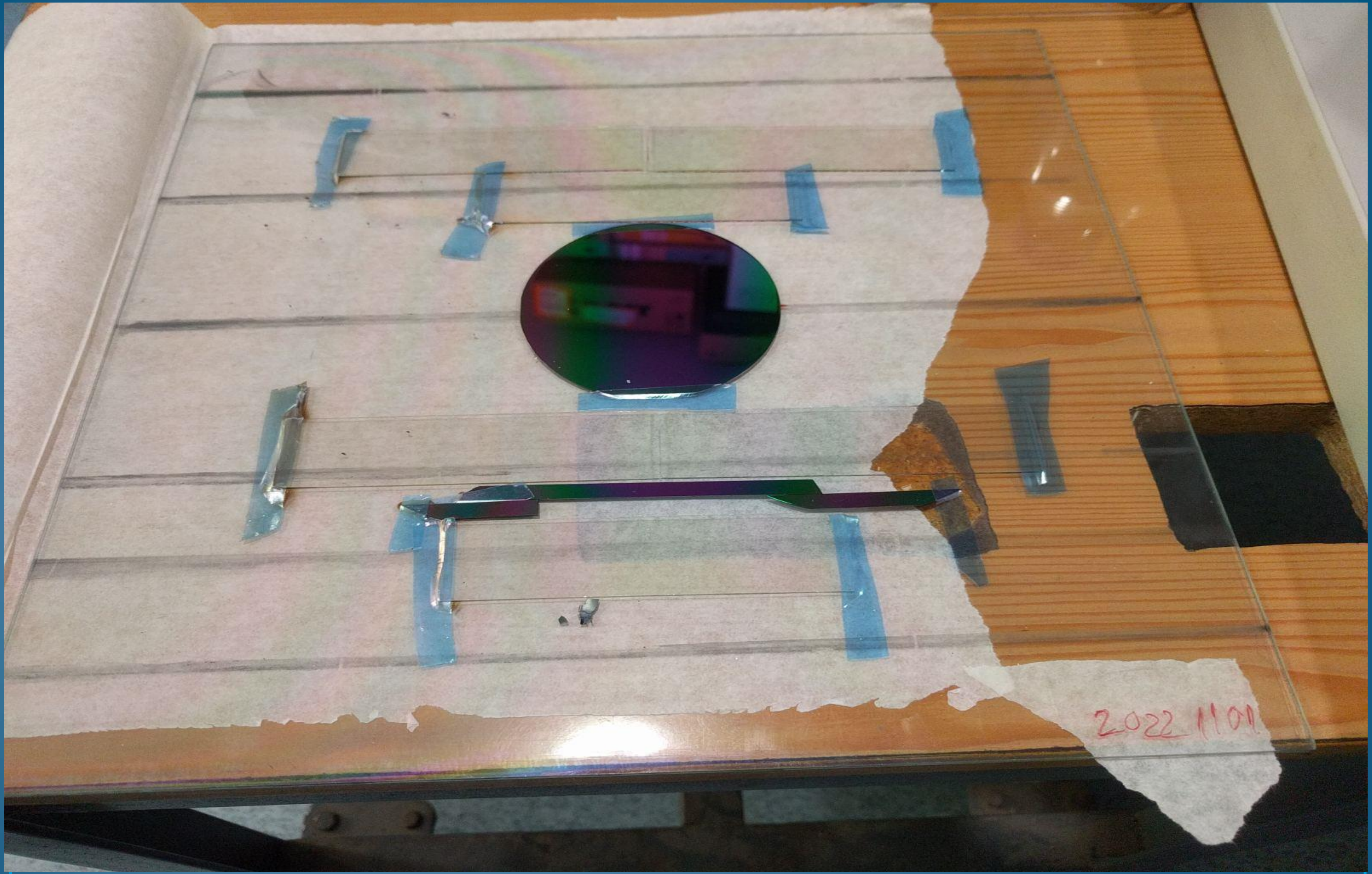


Figure (13) TiO_2-SnO_2-grad-on-3 inch-Si (circular sample, upper) and the Si-stripe samples, lower.

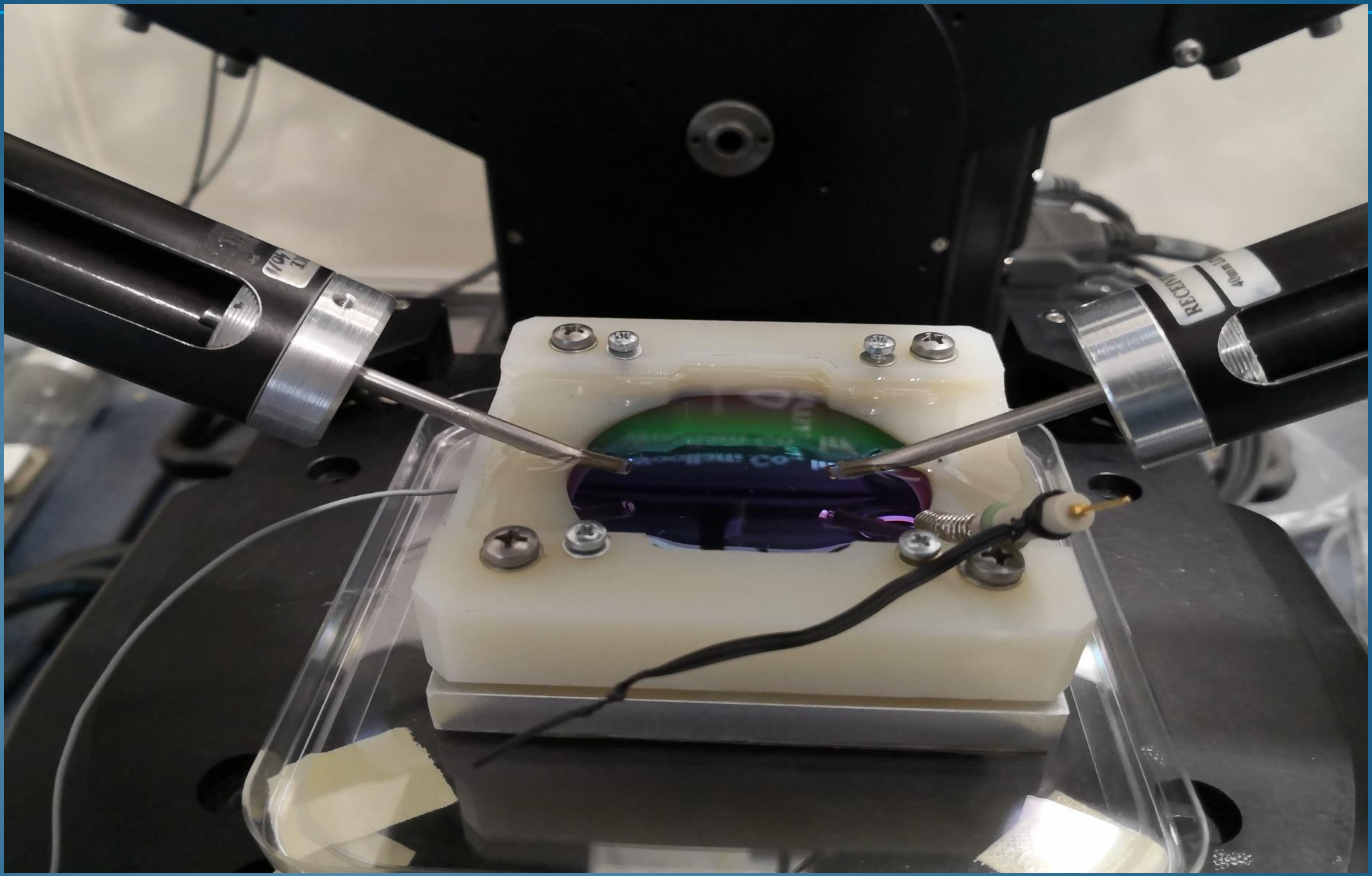


Figure (14) Liquid cell for elctrochromic measurements in reflection mode

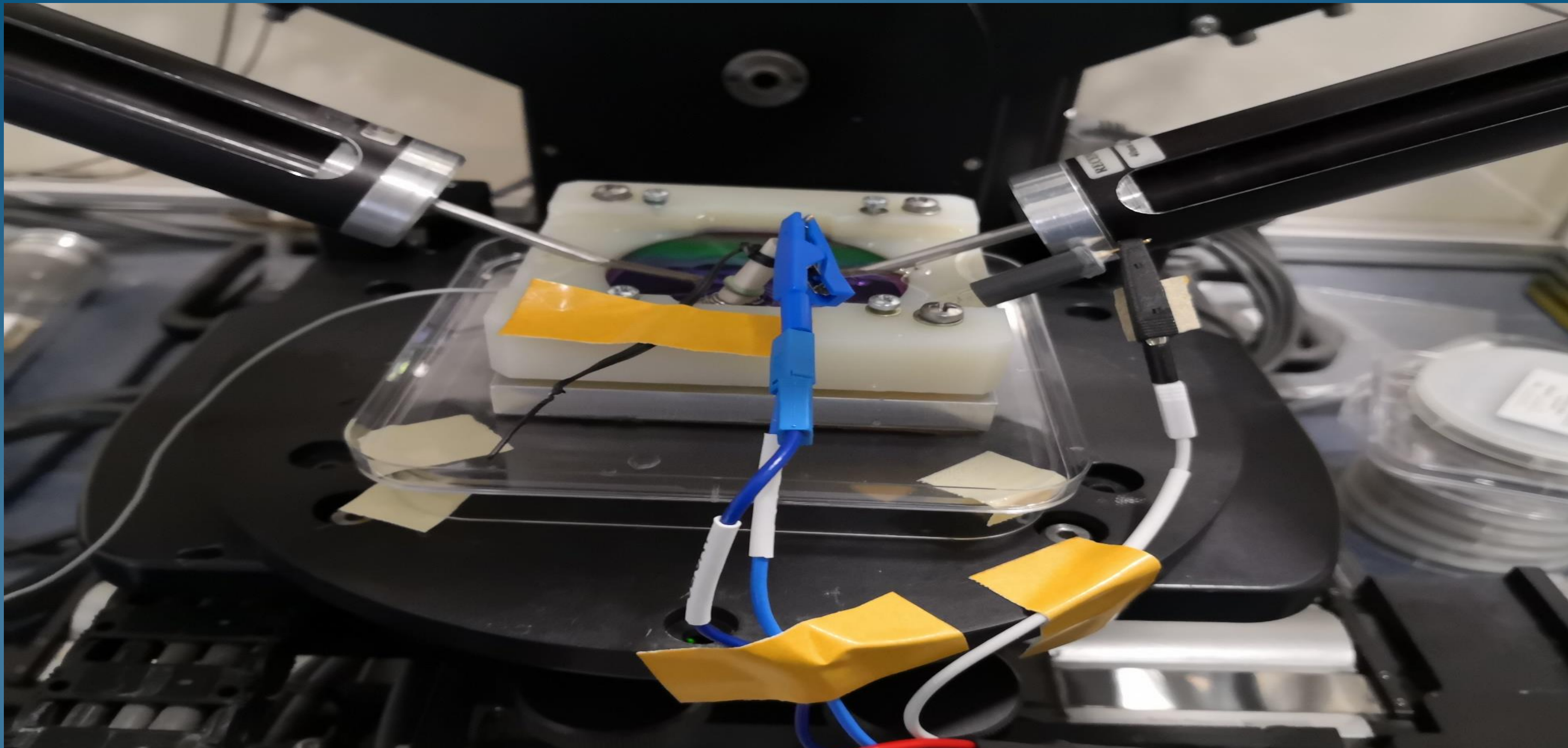
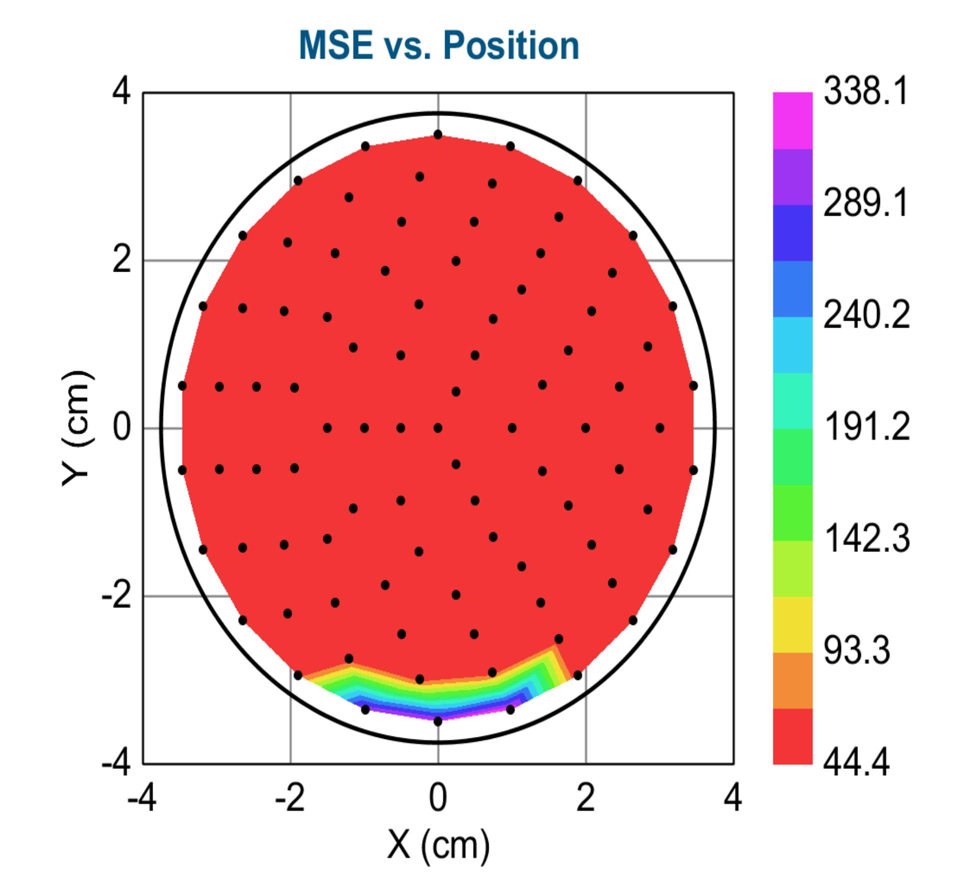
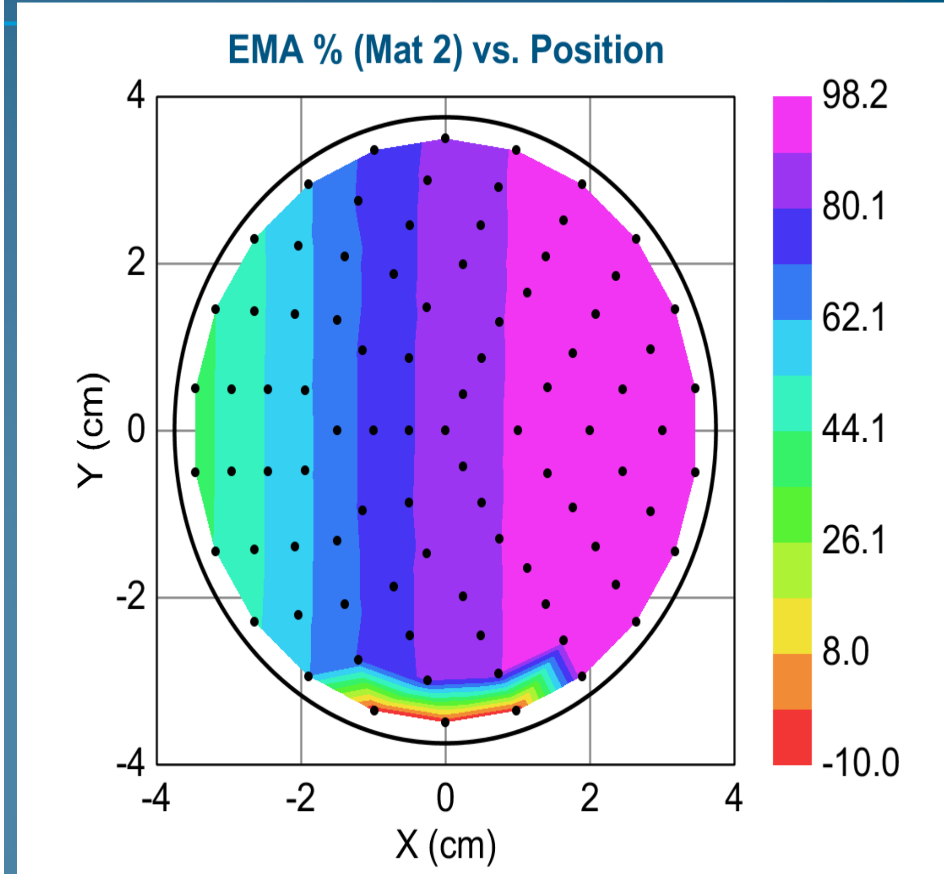


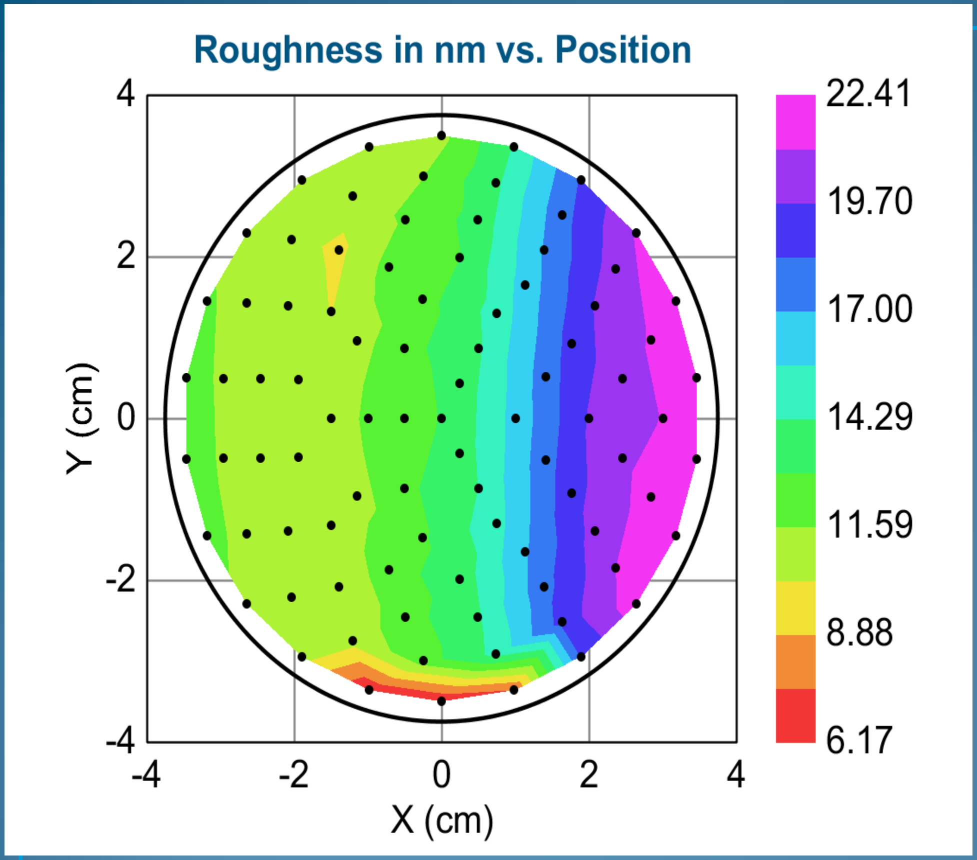
Figure (15) Electrochemical measurements were performed in a circukar cell filled with 1M lithium perchlorate ($LiClO_4$) / propylene carbonate electrolyte, and a Pt wire counter electrode was placed into the electrolyte alongside with a reference electrode.



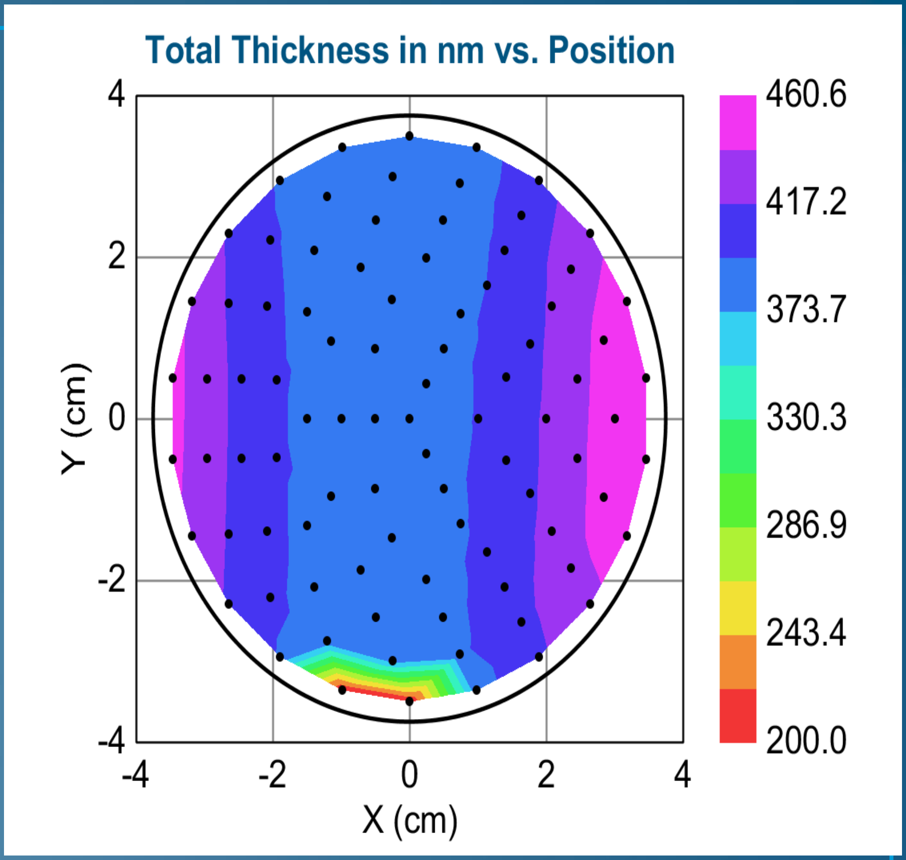


(a) **(b)**

Figure (16) a) MSE and b) Volume fraction % of TiO_2-SnO_2-3inch-Si by EMA model.



(c)



(d)

Figure (16) c) Roughness and d) Thickness of TiO_2-SnO_2-3inch-Si by EMA model.

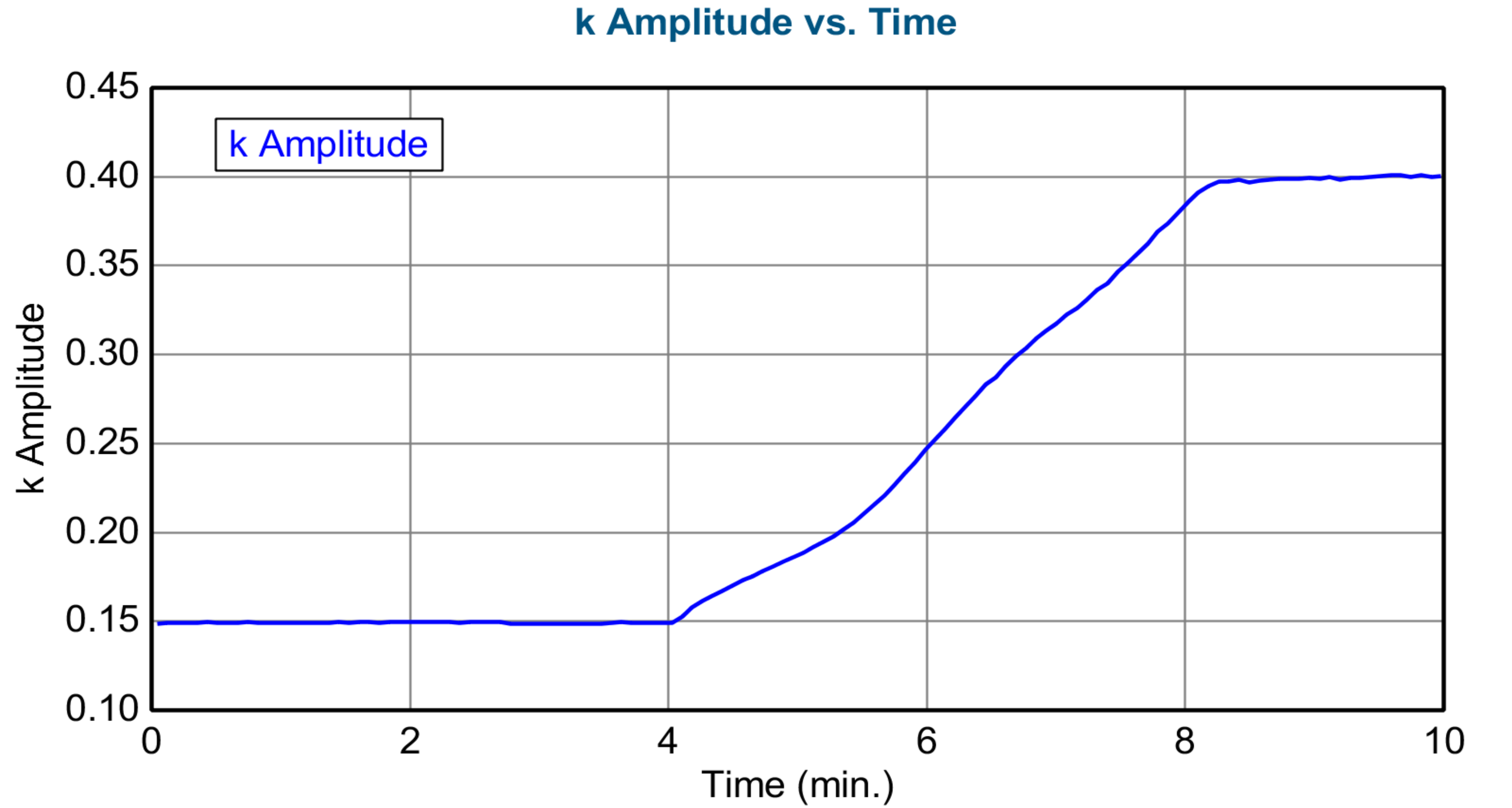


Figure (17) a) Imaginary part of the Refractive index (k Amplitude) as a function of time for highly-conductive-Si in liquid-cell during colorization (time-scan, simple Cauchy-model).

Here we can mention that from (0-4) minute's there is low absorption but from (4-8) minute's there is a growing absorption.

Fit Results

MSE = 11.760
A = 2.052 ± 0.006368
B = -0.00784 ± 0.001943
C = 0.00832 ± 0.00028127
k Amplitude = 0.14888 ± 0.001320
Exponent = 0.273 ± 0.0202
Thickness # 1 = 47.70 ± 0.358 nm
n of Cauchy @ 632.8 nm = 1.68854
Total Thickness = 97.70 ± 0.358 nm

Optical Model

- Graded Layer Thickness # 2 = 50.00 nm
  Grade Type = Simple # of Slices = 5
  % Inhomogeneity = 0.00
  + Material = Cauchy
+ Layer # 1 = Cauchy Thickness # 1 = **47.70 nm** (fit)
Substrate = Si_JAW

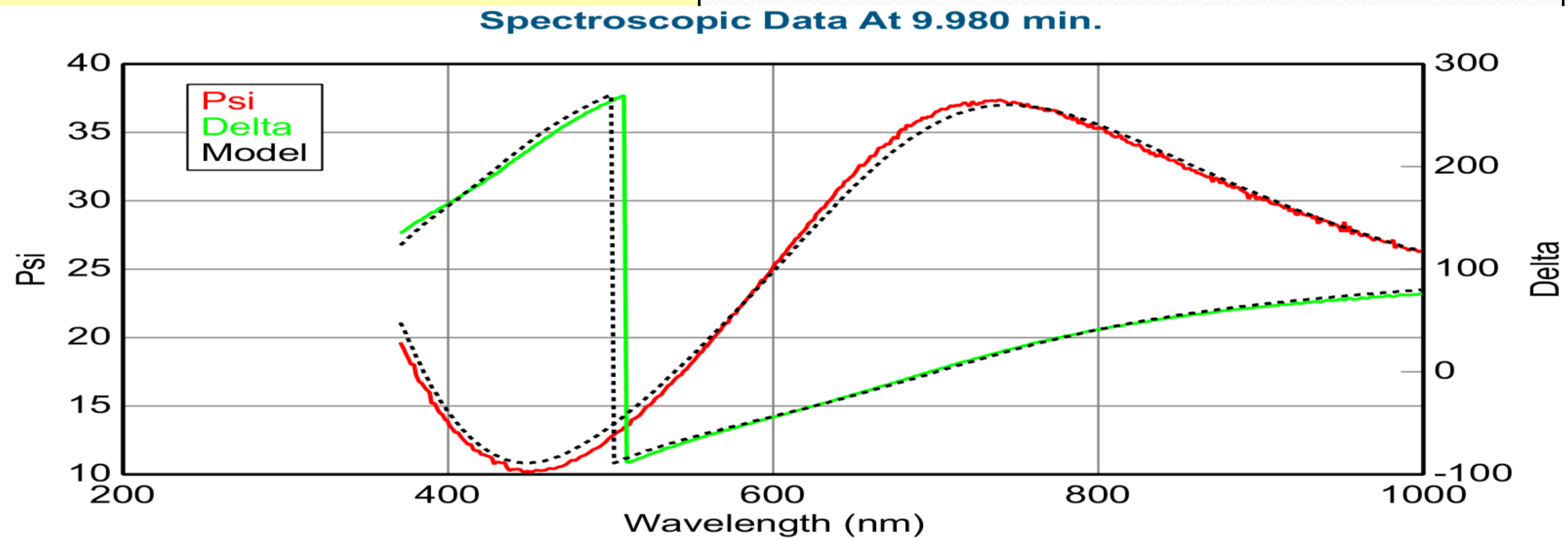


Figure (17) b) shows a typical example of a fitted SE spectrum for the details of the model structure, SE spectra were evaluated using a multi-layer, multi-parameter optical model applying graded Cauchy-dispersion.

Plans for the future:

Planned steps forward:-

1. Further investigation of stoichiometric and sub-stoichiometric oxides for gas sensoric purposes (Fig. 18 and 19).

2. Comparison of MSE for EMA and 2TL modelling TiO_2-SnO_2- 4inch-ref-Si and their measurements.

Figure (18) ***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. Left hand side is W-rich, right one is Mo-rich. No. 6 (middle one) is expected to be 50-50% in both cases. The upper rows show sub oxides (semi-transparent layers, No. 2 was broken during tweezer handling) The bottom rows show oxides (transparent layers).***

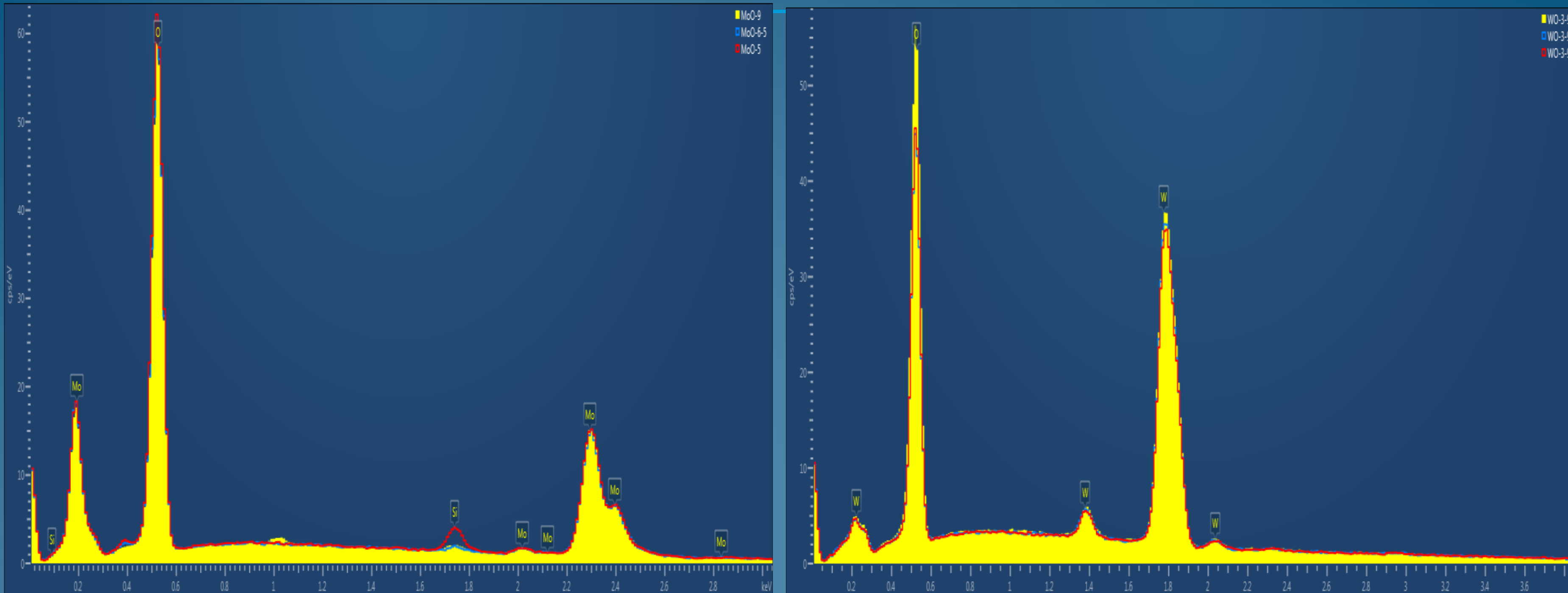


Figure (19) **EDS spectra of stoichiometric oxides and sub oxides of W and Mo Semi-quantitave analysis shows 10% oxygen vacancy.**

Conclusions

We can produce combinatorial samples on large scale in a magnetron sputtering system. We can choose between appropriate 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.

Subjects fulfilled in the semester:

Teaching activity

1- I presented my research in the XXXVIII. Kandó Conference (XXXVIII. Kandó Konferencia, 3-4 November 2022), 1084 Budapest, Tavaszmező u. 17, which held at Obuda University. ISBN 978-963-449-299-3, (https://konf2022.kvk.uni-obuda.hu/program) Elektronikai és kommunikációs rendszerek - Mikroelektronika, nanotechnológia, szenzortechnika szekció, Noor Taha, Lábadi Zoltán, Fried Miklós: {Combinatorial Preparation and Characterization Methods for High Throughput Study of Advanced Functional Materials}.

Teaching activity

2- I attend the Public defense of Mr. Hassanen Jaber's PhD dissertation in 6th of December in ÓE 1081.

3- I attended the autumn's doctoral ball, which taken in 07.10.2022. Evening of socializing, in Óbuda University.

4- I responded to the invitation of rector Prof. Dr. Levente Kovács. The Mini Symposium that held on 6th of September 2022.

5- I attended the academic year opening ceremony on 5th of September 2022. in Budapest, Várkert Bazár, 1013.

Thanks for your attention

Köszönöm a figyelmet