

Combinatorial Investigation of WO₃-MoO₃ Mixed Layers by Spectroscopic Ellipsometry to assess Effective Medium Approximation

M. Fried^{a,b}, R. Bogar^a, Z. Lábadi^b, Z. E. Horvath^b, Z. Zolnai^b,

^a Institute of Microelectronics and Technology, Óbuda University, Tavaszmező u. 17, H-1084 Budapest, Hungary

^b Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

Keywords: thin films, combinatorial preparation, spectroscopic ellipsometry

Currently, the protection against heat waves through the glass windows, the electrochromic film as a smart window [1] is the most useful tool to reduce heat in buildings. This type of glass consists of a layer of electrochromic film bounded by metal oxide layers. It controls the transmitted amount of light by supplying electric charge to the film system. There are many types of such as TiO₂, CrO, Nb₂O₅, SnO₂, NiO, IrO₂ [2], WO₃, and MoO₃ [3, 4]. Researchers have different methods of deposition as sputtering [5], atmospheric pressure chemical vapor deposition (APCVD) [6], dipping [7], sol-gel method [1, 4], and sintering [8]. This later paper investigated mixed materials but only limited number of compositions: (MoO₃)_x - (WO₃)_{1-x} for x=0, 0.2, 0.4, 0.6, 0.8.

During the present work we used reactive (in Ar-O₂ plasma) magnetron sputtering to create all combinations of WO₃-MoO₃ mixed layers along a line/band. Using combinatorial approach, we have all the compositions after one sputtering process in the same sputtering chamber. Our further aim is to investigate the goodness of WO₃-MoO₃ mixed layers as electrochromic materials for „smart” windows (transparency ratio, switching speed, coloration efficiency).

Layer depositions were performed in a reactive (Ar + O₂) gas mixture in high vacuum (~2x10⁻⁶ mbar base and ~10⁻³ mbar process pressure). 30 sccm/sec Ar and 30 sccm/sec O₂ volumetric flow rate was applied in the magnetron sputtering chamber. The substrates were 30 cm * 30 cm soda lime glasses. First, a W-mirror (W sputtered only in Ar-plasma) was prepared to avoid the back-reflection of the measuring light-beam during the Spectroscopic Ellipsometry (SE) measurements. The plasma powers of the two targets were chosen in the 0.75-1.5 kW range independently. We used 1, 5 or 25 cm/sec walking speed (back and forth) which was the speed of the 30x30 cm glass sample between the end positions (the edges of the targets).

The sputtering targets were placed in two arrangements as it can be seen in Fig. 1. In the first arrangement, the two targets were placed at 35 cm, in the second arrangement they were placed at 70 cm distance from each other. According to the measurements, in the first arrangement the two „material streams” overlapped around the center position, while in the second arrangement the two „material streams” were separated.

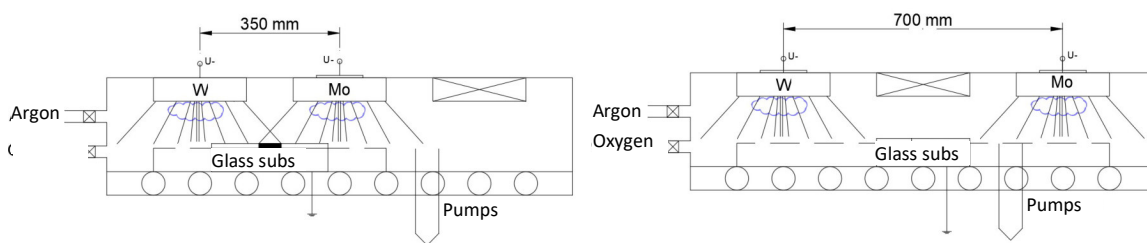


Fig 1 Two arrangements of the targets: a) the two targets in closer position (35 cm from each other) b) the two targets in distant position (70 cm from each other).

We used a Woollam M2000 SE device [9] to map the thickness and the composition change. We used CompleteEASE program (from Woollam Co., <https://www.jawoollam.com/ellipsometry-software/completeease>) to evaluate the mapping measurements using the built-in optical models and oscillator functions: Tauc-Lorentz (T-L) oscillators or Effective Medium Approximation. Note, that the maps from the M2000 measurements are compiled from four 15*15 cm parts. Our M2000 device can measure only one 15*15 cm part at once. The mapping measurements were performed with mm-sized beam-spot on a 15x15 grid with one spectra-pair per cm!

After sputtering, we investigated and mapped the samples by Spectroscopic Ellipsometry (SE) which is a relatively quick, cheap and a contactless method. We used different (oscillator- and Effective Medium Approximation, EMA-based) optical models to obtain the thickness and composition map of the sample layer. We checked the SE results using Rutherford Backscattering Spectrometry. In a set of experiments, we changed the position of the sputtering targets, the speed and cycle number of the substrate motion. Our aim was to compare the “goodness” of the different optical models depending upon the sample preparation conditions.

We used Si-probes which were placed at the centre line (6x5 cm long) of some samples for Rutherford Backscattering Spectrometry (RBS, see Fig. 4) and X-ray Diffractometry (XRD) measurements.

We used the Tauc-Lorentz oscillator model (Fig. 2) which is built-in (CompleteEASE program) and can be used as pre-determined component in the Bruggeman's Effective Medium Approximation (EMA or B-EMA [12]). In the EMA calculation, the mixed-layer is considered as being a physical combination of two distinct phases formed by WO_3 and MoO_3 with an appropriate volume fraction. The constituents are considered equivalent – neither of the components is considered as a host material. In this case, it holds that

$$0 = \sum_i^N f_i \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon}$$

where ε is the effective complex dielectric function of the composite layer; f_i and ε_i denote volume fraction and the complex dielectric function of the i^{th} component. In the case of two components, (WO_3 and MoO_3) the formula is a complex quadratic equation where ε (the effective dielectric function) is the unknown and we can choose easily between the two solutions. (The wrong one is physically meaningless.)

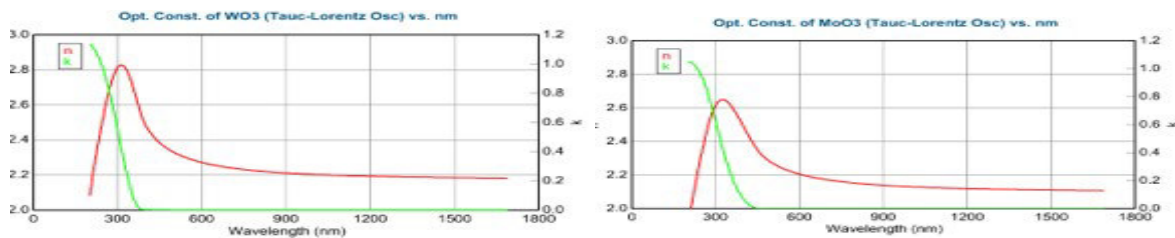


Fig. 2 Determined complex refractive indices using the Tauc-Lorentz oscillator model for pure WO_3 (left) and MoO_3 (right)

The Tauc-Lorentz (T-L) oscillator model is a combination of the Tauc and Lorentz models [11] T-L model contains 4 parameters: the transition Amplitude, the Broadening coefficient of the Lorentz oscillator, the peak position for the Lorentz oscillator, and the Bandgap Energy (E_g), which is taken to be the photon energy where $\varepsilon_2(E)$ goes to zero. When the E photon energy is less than the bandgap energy, E_g , $\varepsilon_2(E)$ is zero. The real part of the dielectric function $\varepsilon_1(E)$ can be obtained from $\varepsilon_2(E)$ through the Kramers–Kronig relation.

During the following optical modelling, we used the determined complex refractive indices (and complex dielectric functions) of the pure WO_3 and MoO_3 using the Tauc-Lorentz oscillator model, see Fig. 2. Finding the best match between the model and the experiment is typically achieved through regression analysis. An estimator, like the Mean Squared Error (MSE), is used to quantify the difference between curves.

First, we performed single-target experiments to assess the deposition rate dependence on the power and on the distance from the target. (This way, we determined the angle dependence of “the material stream”.) We used 1.5, 1, and 0.75 kW powers. The layer deposition rate is non-linear: double power results in 7 times higher rate in the case of WO_3 . We adjusted the used powers for the “double-target” experiments because of the different “walking” speeds and distances.

Double-target samples

1 Targets in closer position

The first (combinatorial) experiment was performed in the „targets in closer position” (Fig. 1 a) The power of the W-target was 0.75 kW, the power of the Mo-target was 1.5 kW. 300 walking cycles were applied with 5 cm/sec walking speed. (We can calculate ~ 1 nm „sublayer thickness” around the center part where the 50 % mixture is expected.) We used a 2-Tauc-Lorentz-oscillator optical model: W-

substrate/interface-layer/T-L(WO_3)+T-L(MoO_3)-mixed-layer/surface-roughness-layer. (This model layer is better for atomic mixture.) 5 fitted parameters were used: the layer thicknesses and the 2 Amplitudes (oscillator strengths). The basic parameters (the Broadenings, the Peak positions and the Bandgap Energies) of the clean materials were determined from the measurements at near the edges of the samples.

Fig. 3 shows the resulted maps (with the schematic optical model): Thickness-map and two Amplitude-maps (T-L(WO_3)-map and T-L(MoO_3)-map) One can see that the composition (Amplitudes) change from 0 % to 100 % in the middle 10-15 cm interval. The composition at the different lateral positions were checked by RBS measurements, too, (see Fig. 4 and 5) which shows good agreement between the results of the two methods.

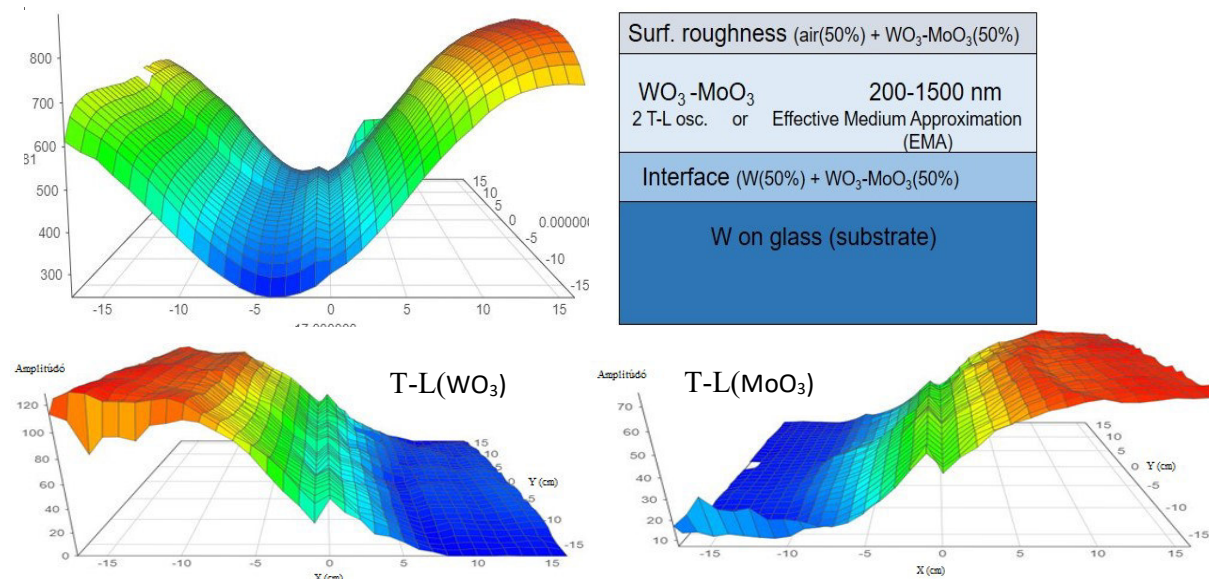


Fig.3 Thickness-map and the schematic optical model (a) Amplitude-of-T-L(WO_3)-map (b) Amplitude-of-T-L(MoO_3)-map (c) (The wrinkles at the centre lines are artefacts caused by the manual “rotation” during the SE measurement.)

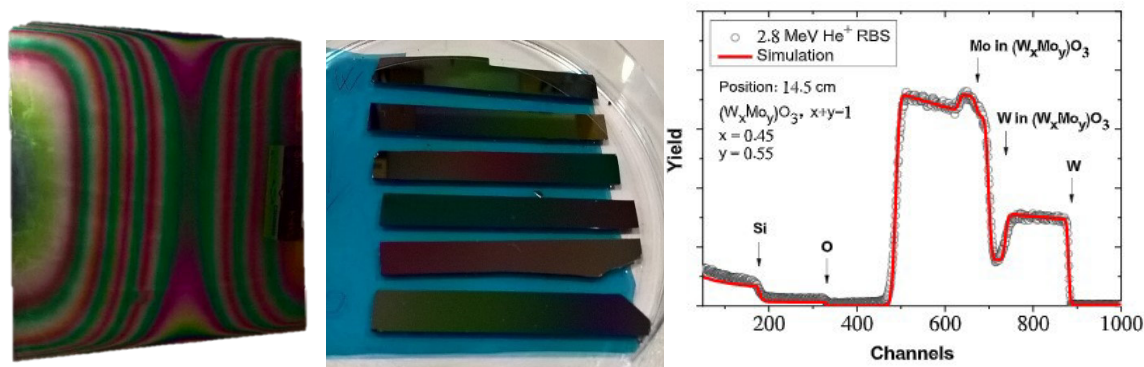


Fig. 4 Photograph of one sample (left) Photograph of the Si-probes which were placed at the centre line of some samples for RBS and XRD (centre) One Rutherford Backscattering Spectrometry example near the centre position. We used the RBX-code [10] to simulate the RBS-spectra.

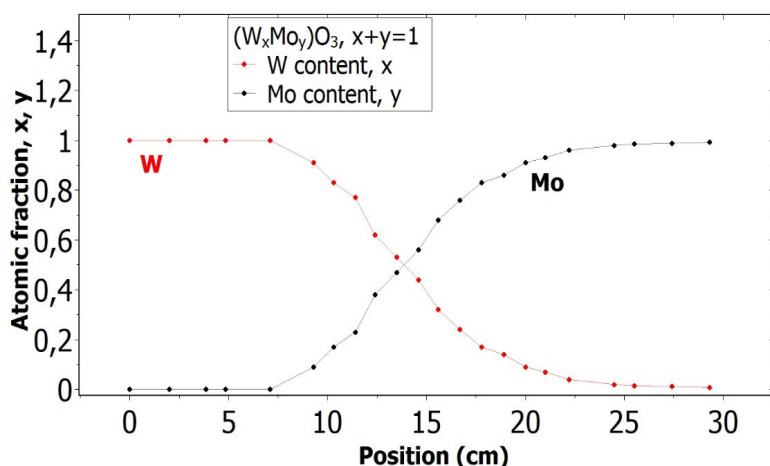


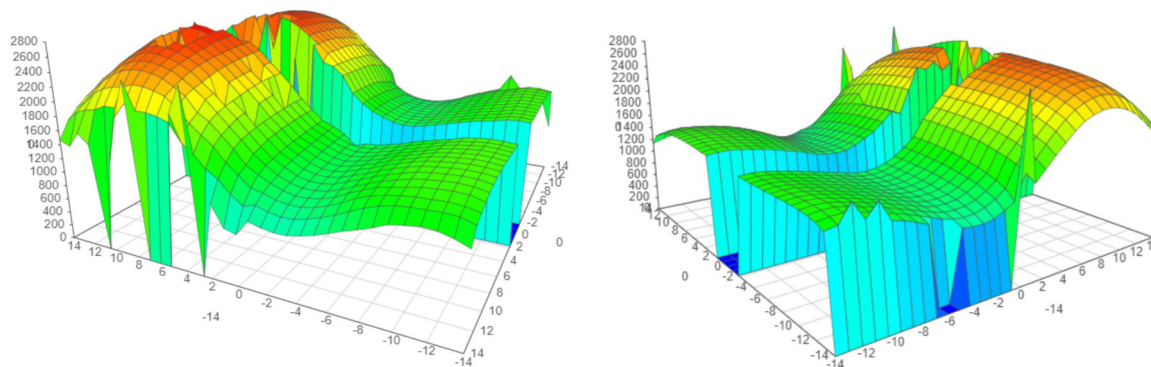
Fig. 5 Composition-map along a line by Rutherford Backscattering Spectrometry

2 Atomic (or „molecular”) mixture vs „superlattice”

We prepared two different samples in the „targets in distant” position (Fig. 1 b). The difference was the walking speed (and the number of the walking cycles): one „Fast” (walking speed: 25 cm/sec) and one „Slow” (walking speed: 1 cm/sec) sample. The different speed results in different „sublayer thickness”: ~ 0.5 nm for the „Fast” sample and 3-5 nm for the „Slow” sample, calculating from the final thicknesses and the number of the walking cycles around the center part where the 50-50 % mixture is expected. We used two types of optical models: the 2-T-L-oscillator model and the Effective medium approximation (EMA [12]) model (see Fig. 3, upper right) Finding the best match (see Fig. 7 and 9) between the model and the experiment is typically achieved through regression. An estimator, like the Mean Squared Error (MSE), is used to quantify the difference between curves. We can choose between the optical models seeing the MSE-maps: better the model if the MSE values are significantly lower at the relevant (around 50-50 % composition) positions (see Fig. 6 and 8).

2.1 “Fast” sample, 25 cm/sec walking – ~ 0.5 nm „sublayer thickness”

The thickness of the layer around the center part is app. 700 nm. We can calculate a „sublayer thickness” ~ 0.5 nm for this „Fast” sample from the number of the walking cycles (1500) and we can consider it an atomic mixture. Thickness-maps (Fig. 6, upper) show nearly the same results for both optical models. The Amplitude-of-T-L(only WO_3)–map and the EMA(volume percent of WO_3)–map (Fig. 6, middle) and MSE-maps (Fig. 6, lower) show similar tendencies, however the 2-T-L-oscillator model shows significantly lower MSE values against the Effective Medium Approximation model, see the Fig. 10 where the $\text{MSE(EMA)} - \text{MSE(2 T-L)}$ values are shown. The significantly positive values around the center part (especially around the 50-50 % ratio) show that the 2-T-L-oscillator model is better for this type (atomic mixture) of layer structure. The measured and fitted example spectra on Fig. 7 show that the 2-T-L model is better especially under the 450 nm wavelength region where the light absorption is significant.



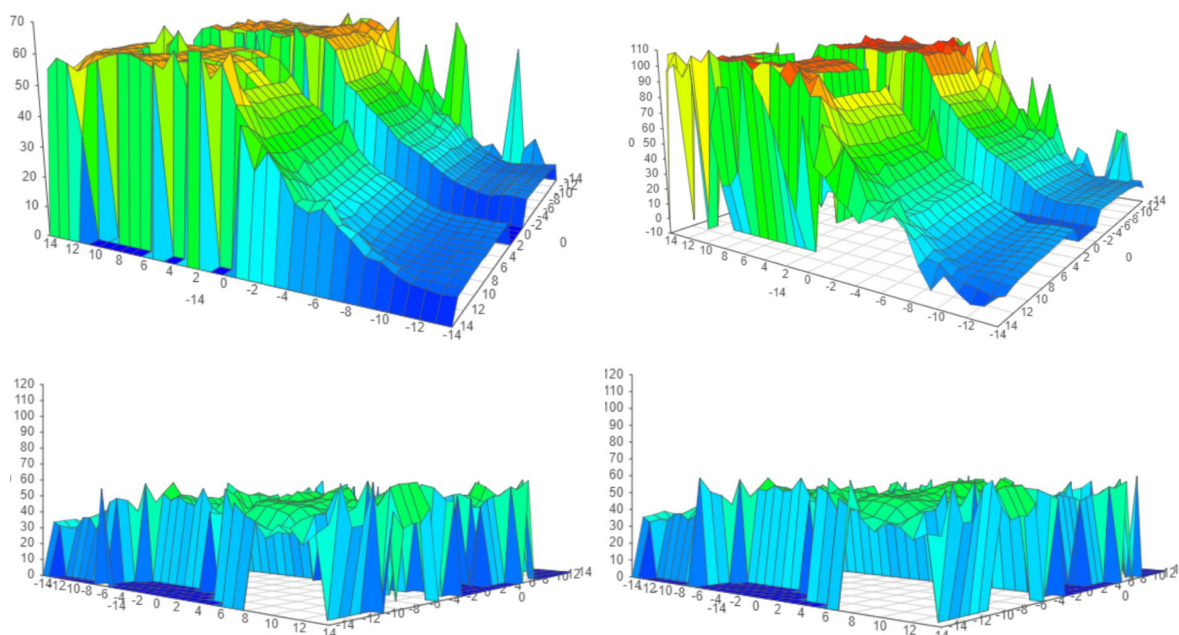


Fig. 6 Thickness-maps (upper), Amplitude-of-T-L(only WO_3)-map and EMA(WO_3)-map (middle) and MSE-maps (lower) using the 2-T-L-oscillator model (left column) and the Effective medium approximation model (The “gaps” around the centre line are due to the Si-probes.)

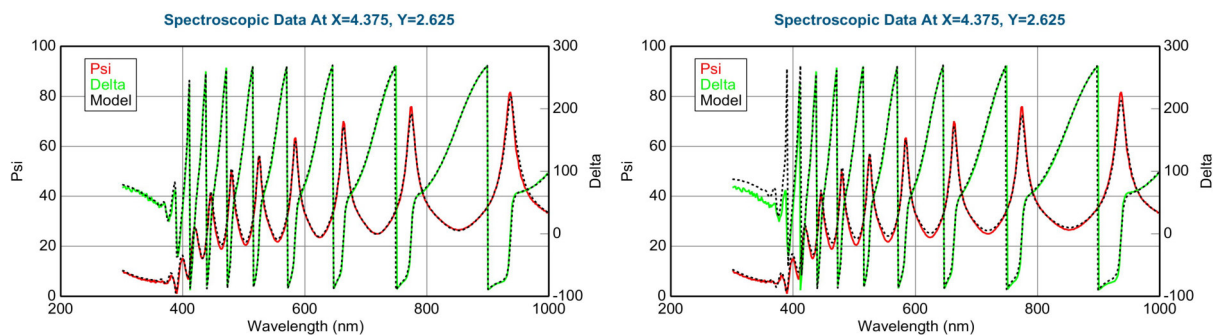


Fig. 7 Measured and fitted spectra at one sample point: 2-T-L-oscillator-model (left, Fit error (MSE) = 30.4, Thickness = 1159.6 ± 2.9 nm, Amp1 = 39.2 ± 1.1 , Amp2 = 26.7 ± 0.4) and Effective medium approximation model (right, Fit error (MSE) = 40.1, Thickness = 1081.7 ± 0.1 nm, EMA % (Mat 2) = 41.8 ± 0.8)

2.2 “Slow” sample, 1 cm/sec walking – 3-5 nm sublayer thickness

The thickness of the layer around the center part is app. 300 nm. We can calculate a „sublayer thickness” ~ 4 nm for this „Slow” sample from the number of the walking cycles (70) and we can consider it as a „superlattice”. (We can say it superlattice only at 50-50 %, otherwise we can call it superlattice-type.) Thickness-maps (Fig. 8, upper) show nearly the same results for both optical models. The Amplitude-of-T-L(only WO_3)–map and the EMA(volume percent of WO_3)–map (Fig. 8, middle) and MSE-maps (Fig. 8, lower) show similar tendencies, however the Effective Medium Approximation model shows significantly lower MSE values against the 2-T-L-oscillator model, see the Fig. 10 where the $\text{MSE(EMA)} - \text{MSE(2 T-L)}$ values are shown. The significantly negative values around the center part (especially around the 50-50 % ratio) show that the Effective Medium Approximation oscillator model is better for this type („superlattice”) of layer structure. The measured and fitted example spectra on Fig. 9 show that the Effective Medium Approximation model is better with an 1.3 % precision of the composition (volume fraction) parameter.

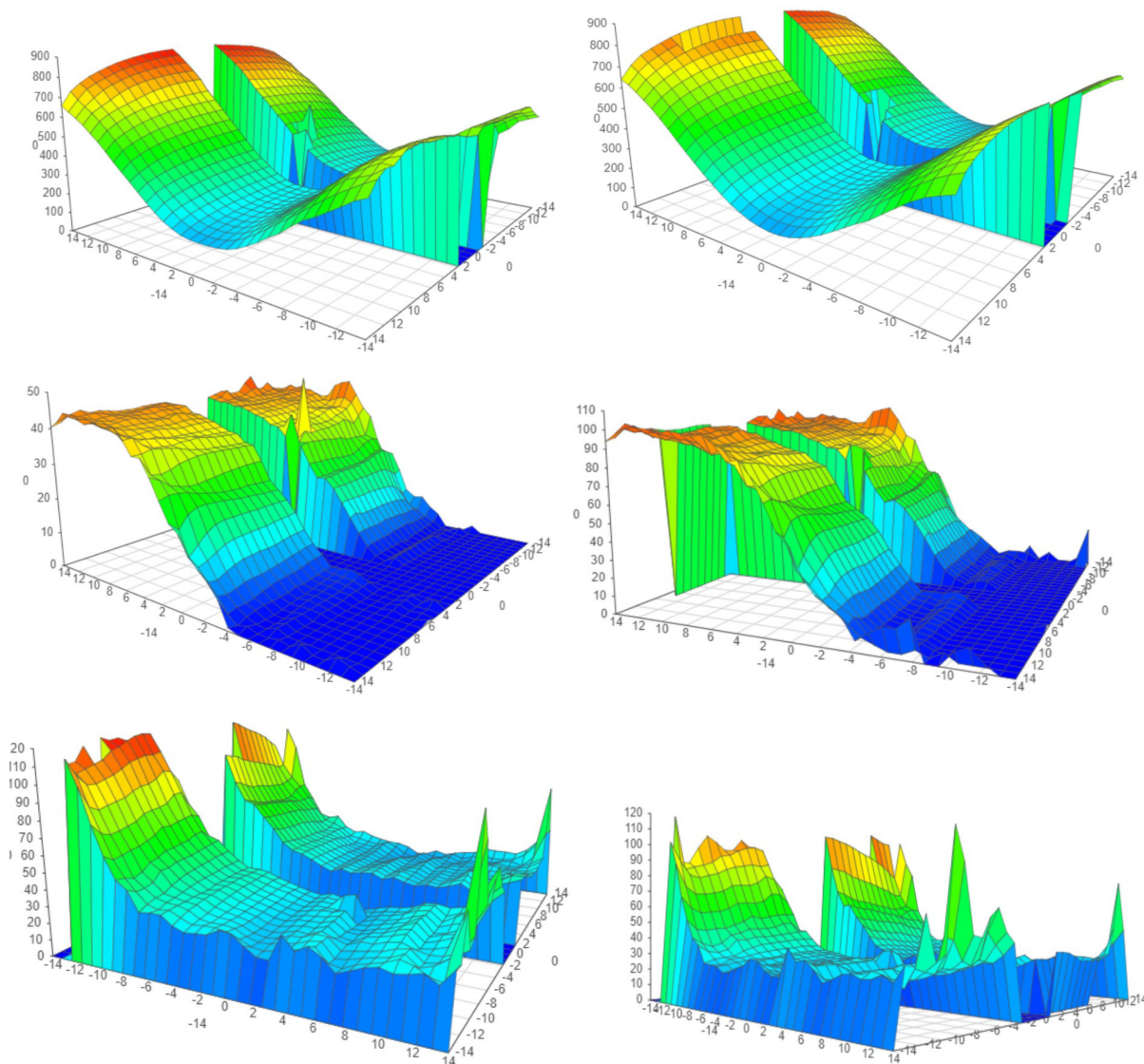


Fig. 8 Thickness-maps (upper), Amplitude-of-T-L(WO_3)–map and EMA(MoO_3)–map (middle) and MSE-maps (lower) using the 2-T-L-oscillator model (left column) and the Effective medium approximation model (The “gaps” around the centre line are due to the Si-probes.)

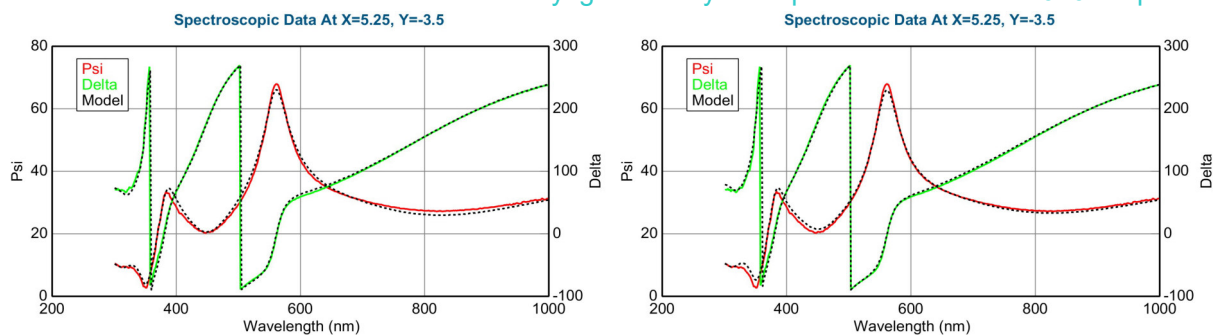


Fig. 9 Measured and fitted spectra at one sample point: 2-T-L-oscillator-model (left, Fit error (MSE) = 29.2, Thickness = 230.4 ± 0.8 nm, Amp1 = 58.0 ± 1.5 , Amp2 = 11.4 ± 0.7) and Effective medium approximation model (right, Fit error (MSE) = 24.8, Thickness = 218.0 ± 0.1 nm, EMA % (Mat 2) = 28.5 ± 1.3)

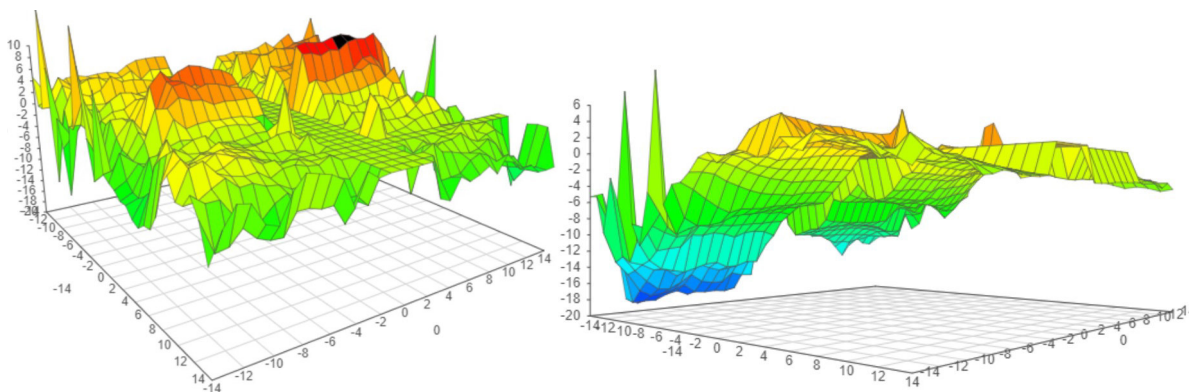


Fig. 10 The MSE(EMA) – MSE(2 T-L) map shows that the 2-T-L-oscillator model is better for the “fast”, atomic mixture sample (left), while the Effective Medium Approximation model is better (lower MSE) for “slow”, sublayer-type sample (right), especially around the 50-50 % ratio (central) region. (The “gap” (with 0 values) around the centre line are due to the Si-probes.)

Conclusion: We can produce combinatorial samples on large scale in a magnetron sputtering system. These samples can be mapped (thickness and composition maps, too) by fast and non-destructive manner by Spectroscopic Ellipsometry. We can choose between appropriate optical models (2-Tauc-Lorentz-oscillator model versus the Bruggeman Effective Medium Approximation, BEMA) depending on the process parameters. One can conclude that if you have more than one „molecular layer” in the „sublayers” you can use BEMA.

Acknowledgment: Support form VOC-DETECT M-ERA.NET Transnational Call 2018 (OTKA NN 131269) and OTKA K129009 projects are acknowledged.

References

- [1] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials (Elsevier, Amsterdam, 1995) P. P. Gonzalez-Borrero, F. Sato, A.N. Medina, M.L. Baesso and A.C. Bento: Applied Physics Letters. Vol. 96, 061909 (2010); doi: <http://dx.doi.org/10.1063/1.3313945>
- [2] J. Livage and D. Ganguli: Solar Energy Materials & Solar Cells. Vol. 68 (2001), p. 365-381
- [3] C.S. Hsu, C.C. Chan, H.T. Huang, C.H Peng and W.C Hsu: Thin Solid Films. Vol. 516 (2008), p. 4839-4844
- [4] S.Y. Lin, C.M. Wang, K.S. Kao, Y.C. Chen and C.C. Liu: Journal of Sol Gel Science and Technology. Vol. 53 (2010), p. 51
- [5] V. Madhavi, Jeevan Kumar Padarti, Paruchuri Kondaiah, Owais Hussain, S. Uthanna, Ionics vol. 20(12) (2014) 1737-1745
- [6] T. Ivanova, K.A. Gesheva, M. Kalitzova, F. Hamelmann, F. Luekermann and U. Heinzmann: Journal of Optoelectronics and Advanced Materials. Vol. 11 (2009), p. 1513-1516

- [7] A. Novinrooz, M. Sharbatdaran and H. Noorkojouri: Central European Science Journals (2005), p. 456-466
- [8] Ch.Prameelaand, K.Srinivasarao; International Journal of Applied Engineering vol. 10(4) (2015) pp. 9865-9875
- [9] <https://www.jawoollam.com/products/m-2000-ellipsometer>
- [10] E. Kótai, Computer Methods for Analysis and Simulation of RBS and ERDA spectra, Nucl. Instr. Meth. B 85 (1994) 588 - 596.
- [11] G.E. Jellison, Jr. and F.A. Modine, Appl. Phys. Lett. 69, 371 (1996), Erratum, Appl. Phys. Lett. 69, 2137 (1996)
- [12] D. A. G. Bruggeman, Ann. Physik (Leipzig) 24, 636 (1935)