

Preparation and Characterization of Mixed Metal Oxide Layers using Reactive Combinatorial Sputtering

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Abstract

Combinatorial DC sputtering method of metal oxides is presented onto a 30x30cm substrate. Specifically tungsten and molybdenum oxides were deposited and characterized for electrochromic and sensoric purposes. Mapping ellipsometry combined with RBS proves the presence of the continuous composition range in the layers. Samples of amorphous character were tested for electrochromic properties in organic electrolyte. Combinatorial deposition of non-stoichiometric suboxides for VOC gas sensing also presented.

Keywords: sputtering, electrochromism, gas sensors

Introduction

The physical, chemical and structural properties of the cutting-edge materials are strongly dependent on their composition. Using the combinatorial material synthesis approach, materials libraries can be produced in one experiment that contain the full composition range on a single substrate. We use pulsed mode reactive DC sputtering for preparation and Spectroscopic Ellipsometry (SE), RBS-Rutherford Backscattering Spectrometry (RBS) Transmission Electron Microscopy (TEM) for layer characterization. These methods can help us to search more efficient advanced functional materials for electrochromic and gas sensing properties.

Experimental

Reactive (in Ar-O₂ plasma) W- and Mo-target were placed separately into the sputtering chamber and a proper single axis movement program of the 30x30 cm glass substrates ensured the composition graded final layer from the two (W and Mo) separated targets. (Fig. 1.)

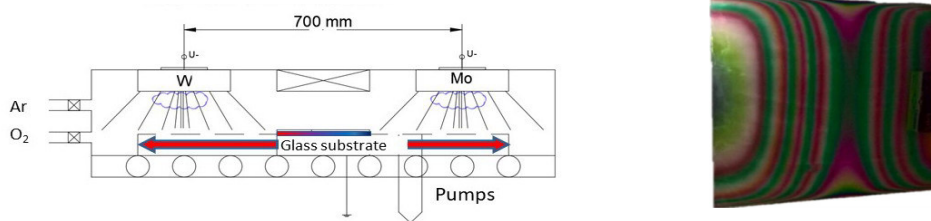


Figure 1. Schematic draw of the combinatorial deposition and layout of a combinatorial layer. Newtonian rings indicate thickness gradient

Results and discussion

Figure 2. shows the ellipsometric mapping of the combinatorial layer (a) together with the schematic optical model (b), while Figure 2c shows the composition of the layer alongside the substrate movement axis. It can be seen from these figures that the layer contains the full compositional range of the MoO₃- WoO₃ binary oxide system.

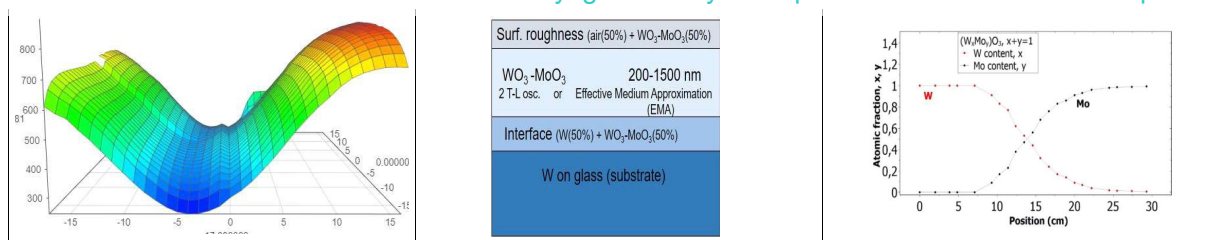


Figure 2. Ellipsometry mapping and optical model of the combinatorial layer (a,b) and lateral composition curves taken by RBS (c)

The layer thicknesses are in the 300-800nm range. Since the number of the uniaxial movement cycles during the deposition was 1750, no sublayers are expected in the structure.

Figure 3. shows the cross-sectional TEM micrographs of the deposited oxide layers. Presence of the amorphous phase can be seen in the electron diffraction pattern.

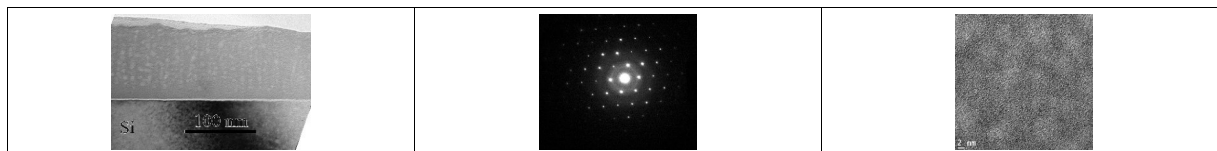


Figure 3. (a) Cross-sectional TEM of the amorphous MoO₃ layer (Ar/Ox =40/25 P=100W) Note the porous structure (b)Electron diffraction pattern shows amorphous rings (c) HI-RES TEM of the amorphous MoO₃

Figure 4. shows the coloured and bleached state of the (Mo,W) oxide layer in 0,1M LiClO₄ – propylene carbonate solution. The deposited sample series makes possible to measure the coloration efficiency

$$CE(\lambda) = \Delta OD(\lambda) / q \text{ cm}^2 \text{ C}^{-1}$$

where $\Delta OD(\lambda)$ represents the change in single-pass, transmitted optical density at the wavelength of interest λ , because of transfer of charge q of the mixed oxide. This parameter can be measured in the full visible wavelength range, and the combinatorial approach allows 2% composition resolution.

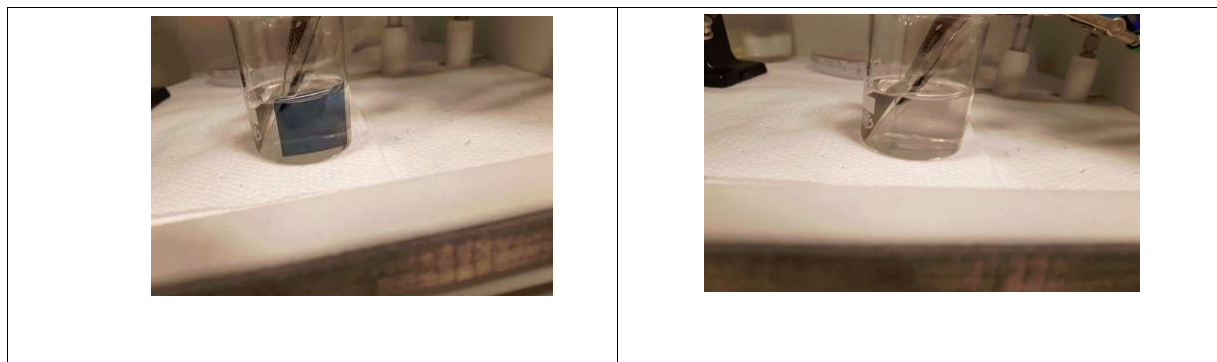


Figure 4: Coloured and bleached state of the (W,Mo) oxide film

Combinatorial samples were also deposited under oxygen depleted conditions. Figure 5 shows the electron dispersive spectrum of the suboxides.

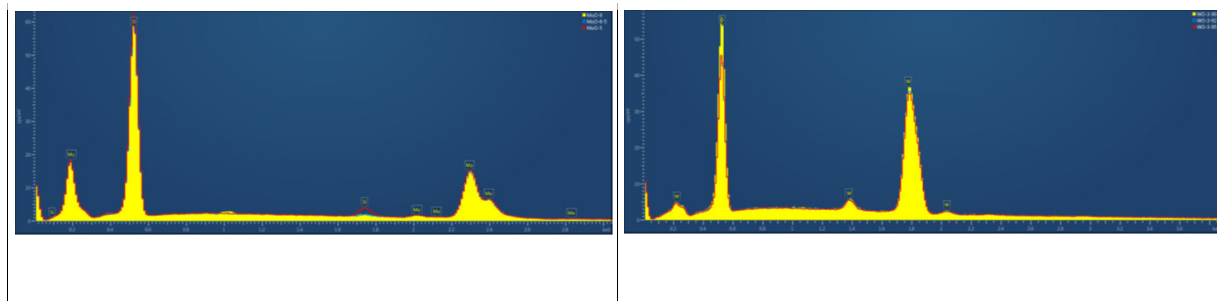


Figure 5. EDS spectra of stoichiometric oxides and suboxides of W and Mo

Semi-quantitative analysis shows 10% oxygen vacancy

The non-stoichiometric samples are tested for VOC gas sensing properties (benzene and formaldehyde sensing).

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References

- [1] M. Fried, R. Bogar, Z. Lábadi, Z. Zolnai: *Combinatorial Investigation of WO₃–MoO₃ Mixed Layers by SE*; ICSE-8, 8. Int. Conf. on Spectroscopic Ellipsometry, 2019, Barcelona, Spain, oral presentation , submitted to Thin Solid Films