

Characterization of MAPLE deposited WO₃ thin films for electrochromic applications

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Abstract. Tungsten trioxide (WO₃) is a widely studied material for electrochromic applications. The structure, morphology and optical properties of WO₃ thin films, grown by matrix assisted pulsed laser evaporation (MAPLE) from monoclinic WO₃ nano-sized particles, were investigated for their possible application as electrochromic layers. A KrF* excimer ($\lambda=248$ nm, $\zeta_{FWHM}=25$ ns) laser source was used in all experiments. The MAPLE deposited WO₃ thin films were studied by atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXRD) and Fourier transform infrared spectroscopy (FTIR). Cyclic voltammetry measurements were also performed, and the coloring and bleaching were observed. The morpho-structural investigations disclosed the synthesis of single-phase monoclinic WO₃ films consisting of crystalline nano-grains embedded in an amorphous matrix. All thin films showed good electrochromic properties, thus validating application of the MAPLE deposition technique for the further development of electrochromic devices.

1. Introduction

Tungsten trioxide is studied for many applications, such as photocatalysis [1,2], sensing various toxic and inflammable gasses [3–7], water splitting [8] and solar energy conversion [9]. Also, WO₃ is the best known electrochromic material and its application in fields like large scale electrochromic devices as displays, smart windows and optical switching coatings is widely investigated [9–11].



Matrix Assisted Pulsed Laser Evaporation (MAPLE) technique has been validated for successful obtaining of thin films of sensitive materials avoiding thermal decomposition and irreversible degradation [12–15]. In MAPLE the target is frozen and consists of material to be ablated prepared as suspension or dissolved in an optically absorbing solvent with a high vapour pressure (*e.g.*, water, toluene). The purpose of the volatile solvent in the target is to aid desorption by absorbing most of the laser energy and vaporising when the laser energy is converted to thermal energy by photochemical processes, thus entraining the particles of interest to the substrate [16].

The expulsed substance is assembled on substrates where it forms a thin film with a thickness from a few to several hundreds of nm. The incident laser pulse used for MAPLE initiates two photo-thermal processes in the matrix: evaporation of the frozen composite target and transfer of the material onto the substrate [17]. Typically, the target consists of starting material (less than 10 wt.%) dissolved or suspended into a laser wavelength absorbing solvent when in frozen state. The material molecules reach sufficient kinetic energy by collective collisions with the evaporating solvent molecules so that a controlled transfer on the substrate in gas phase is ensured. Since the receiving substrate is usually kept at room temperature and the sticking coefficient of the solvent is nearly zero, the evaporated solvent is efficiently pumped away by the vacuum system. The solvent and solute concentration should be selected so that: the solute can be dissolved to form a dilute, particulate-free solution; most of the laser energy has to be absorbed by the solvent molecules rather than the solute ones; and no photochemical reaction is produced between solvent and solute [18]. By optimization of the MAPLE deposition parameters (solvent type, laser wavelength, repetition rate, laser fluence, solute concentration, substrate temperature, background gas and pressure), the process can proceed without significant material decomposition [19]. It was demonstrated that MAPLE could provide more crystalline layers as compared to PLD method from the same materials [12].

Highly transparent WO₃ thin films with as high as possible specific surface area are desirable for electrochromic applications, as the electrochromic properties depend not only on the nature and structure of the material, but also on its surface properties. Attainment of 5:1 ratios between the coloured and the bleached state (as required for many electrochromic devices), was preliminarily attempted here by such MAPLE.

2. Experimental

2.1. Materials and thin films preparation

Monoclinic WO₃ (m-WO₃) nano-sized particles were prepared by controlled annealing of hexagonal ammonium tungsten bronze, (NH₄)_xWO_{3-y}, in synthetic air at heating rate of 10 °C/min and purge gas flow rate of 130 mL/min [2]. The final annealing temperature was 600 °C. At temperatures over 550 °C WO₃ crystalizes predominantly monoclinic [20]. The MAPLE targets were fabricated using the as-synthesized m-WO₃ nano-sized particles.

The MAPLE set-up used in the experiments is presented schematically in figure 1. WO₃ thin films have been deposited using a KrF*excimer laser source ($\lambda = 248\text{nm}$, $\zeta_{\text{FWHM}} \leq 25\text{ ns}$), running at a repetition rate of 20 Hz. The substrates were ITO glass with sheet resistance of $\sim 10\text{ ohm/sq.}$ (supplied by Sigma-Aldrich), as well as $\langle 110 \rangle$ single-crystalline Si wafers and glass for reference. Prior to deposition, all substrates were degreased in acetone for 30 min, washed in ethanol in an ultrasonic bath for 30 min, and then rinsed with deionised water.

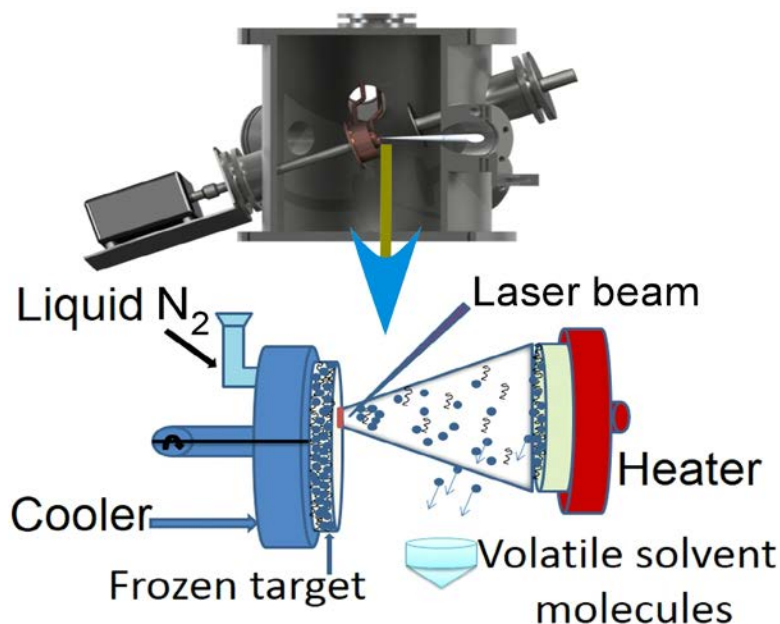


Figure 1. Typical MAPLE experimental set-up (schematics reproduced after Refs. 12 and 15).

The deposition parameters are summarized in table 1. The target-to-substrate distance (D_{T-S}), the oxygen pressure and the frequency of the ablation pulses (f) were constant for all samples. The deposition variables were: substrate temperature (T), number of pulses (consequently the thickness of the films), and fluence.

Table 1. Experimental conditions for WO_3 thin films deposited by MAPLE.

Sample code	D_{T-S} (mm)	Fluence (J/cm^2)	f (Hz)	O_2 pressure (Pa)	T ($^\circ\text{C}$)	No. Of pulses ($\text{K}=10^3$)
WO_3 -251	40	1	20	16	250	12 K
WO_3 -252		0.8			250	6 K
WO_3 -253		0.6			250	4 K
WO_3 -201		0.6			200	4 K

2.2. Characterization techniques

(i) The surface morphology of films was analysed by atomic force microscopy (AFM) in non-contact mode using an NT-MDT NTEGRA Probe NanoLaboratory system (NT-MDT NSG01 cantilever with tip radius of 10 nm).

(ii) The structure of the films was investigated by grazing incidence X-ray diffraction (GIXRD) using a Bruker D8 Advance diffractometer, in parallel beam setting, with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) incident radiation. The incidence angle was set to 2° , and the scattered intensity was scanned within the range $(20-60)^\circ$ (2θ), with a step size of 0.04° , and 5 s per step.

(iii) Fourier transform infrared (FTIR) spectrometry studies were performed in transmission mode with a Shimadzu 8400S instrument. The investigated range was chosen between $500-4000 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

(iv) Cyclic voltammetry experiments were performed by a Bio-Logic Potentiostat/Galvanostat/ SP-200 in a standard three-electrode set-up. The cell used Pt as a counter electrode and a saturated calomel electrode as a reference electrode, altogether with the studied WO_3 films deposited onto ITO glass as working electrodes. The electrodes were immersed in electrolyte of 1 mol/l LiClO_4 dissolved in propylene carbonate.

3. Results and Discussion

FTIR spectrum of parent powder used for preparing the target for the MAPLE depositions is shown in figure 2. The IR characteristic vibration bands of monoclinic WO_3 were observed at the following wave numbers: 641 ($\nu(\text{W-O})$ vibrational modes), 782 (WO_3 bending (δ) vibrations), 870 (WO_3 stretching (ν) vibrations) and 1010–1050 cm^{-1} (possible $\nu(\text{W-O-W})$ vibrations) [21,22]. Supplemental bands positioned at (i) 1420 and (ii) 1630 cm^{-1} are ascribed to (i) stretching vibrations of hydroxyl groups ($\nu(\text{OH})$) which are strongly bonded to either water molecules or to surface oxygen atoms and/or of carbonate groups, and to (ii) in plane bending $\delta(\text{HOH})$ of water molecules, respectively [22,23]. It has to be noted that the partial hydroxylation due to adsorption might negatively affect the long-term stability of such MAPLE deposited films used for electrochromic applications.

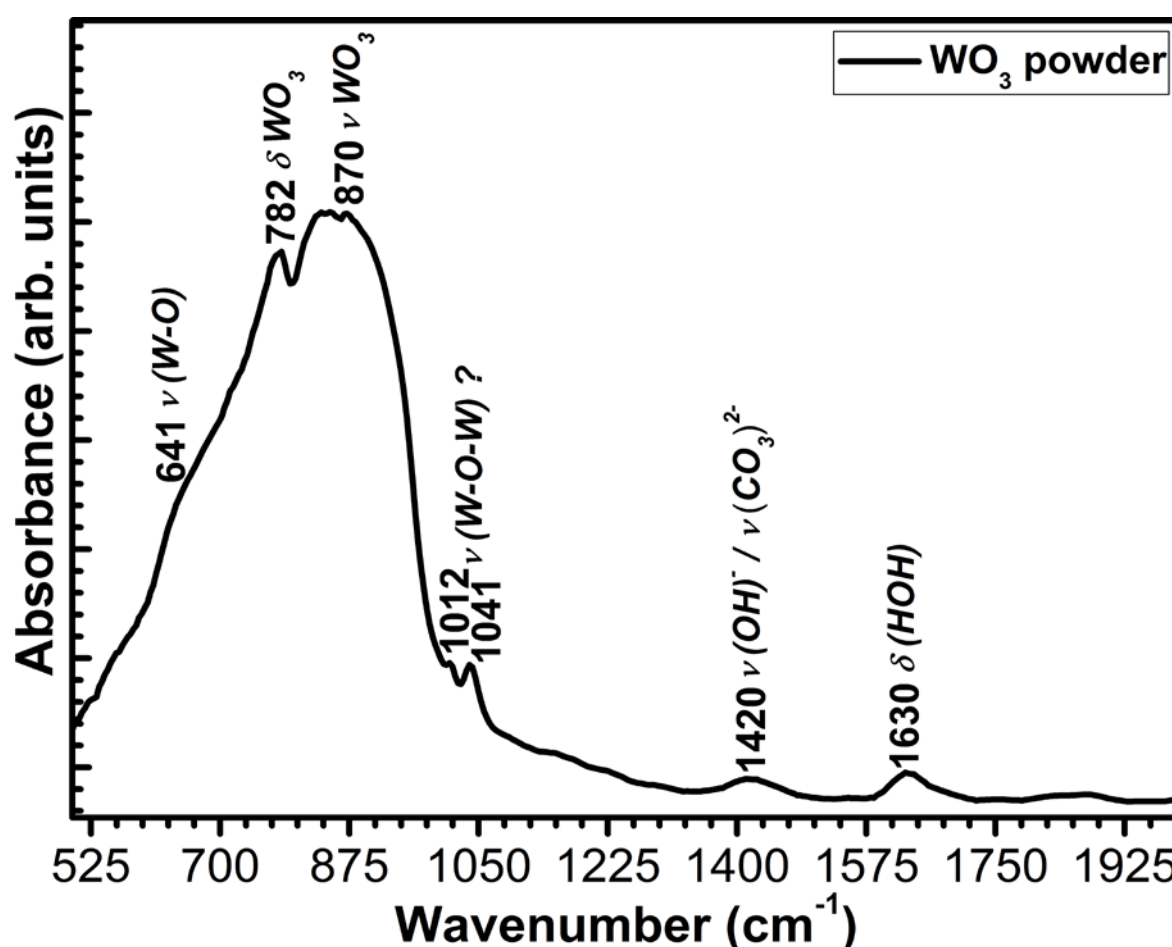


Figure 2. FTIR spectra of m- WO_3 powder used for preparing the target for the MAPLE depositions.

The morphology of the MAPLE deposited WO_3 films was studied by AFM on $0.4 \mu\text{m} \times 0.4 \mu\text{m}$ areas. The typical morphology of films together with the root mean square roughness (R_{RMS}) are exemplified in figure 3 for three of the synthesized samples (*i.e.*, WO_3 -201, WO_3 -253, and WO_3 -252). All films consisted of spheroidal grains with sizes in the range of about 10–50 nm. With the rise of the substrate temperature an increase of the larger grains population has been noticed (figure 3-bc), most probably due to coalescence processes. However, at a 200 °C (figure 3-a), the film surface appears more uniform and homogenous, which is indicative of a more well-ordered structure. The presence of the coalescence grains in the case of films deposited at 250 °C (figure 3-bc) results in an increase of the surface roughness from ~7 nm to ~12–13 nm.

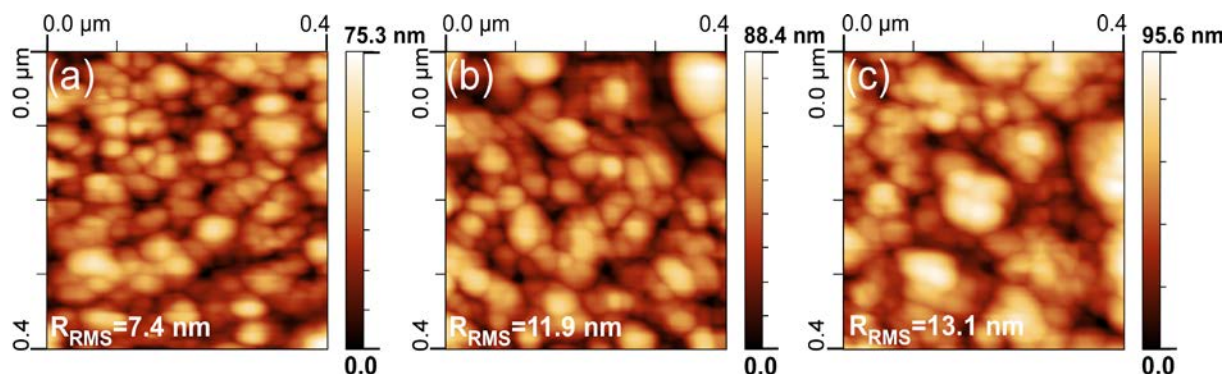


Figure 3. Characteristic AFM images of the WO_3 thin films deposited by MAPLE at substrate temperature of 200 °C (a) and 250 °C (b,c), using a laser fluence of 0.6 J/cm² (a,b) and 0.8 J/cm² (c). The R_{RMS} values are inserted on the micrographs.

The GIXRD patterns (figure 4) indicated that all MAPLE films consist of monoclinic WO_3 (ICDD: 01-083-0950) as single phase. One can note that the samples exhibited also an amorphous component as indicated by the broad humps on which the diffraction maxima of WO_3 are superimposed. This suggests that the studied films are composed of nano-sized crystallites embedded in an amorphous matrix. Differences in the crystallinity/amorphous ratios could be depicted between the films. The crystallinity of the WO_3 samples increased in the following order: 251<252<253<201. This is indicated by both the well-resolved WO_3 peaks and by the more reduced intensity of the amorphous halo. The laser fluence plays a prominent role on the structural features of the film. The GIXRD results suggested that a lower laser fluence (*e.g.*, samples 201 and 253 deposited at 0.6 J/cm²) is propitious for the synthesis by MAPLE of films with improved crystallinity. Additionally, a moderate deposition temperature (*i.e.*, 200 °C) favors the overall structural quality of films (in good agreement with the AFM results), as at higher temperatures desorption phenomena can intensify during film growth, which can result in a (potentially) more faulty structure. In the case of the most crystalline sample (*i.e.* 201), having the most well-resolved peaks, the crystalline coherence length (“crystallite size”) was estimated from the full-width at half maximum of the 200 diffraction line using the Scherrer equation. The line width was corrected for instrumental broadening using a corundum standard reference (NIST SRM 1976). A crystalline coherence length of ~26 nm has been calculated. The presence of a well-crystallized component in the MAPLE samples was considered encouraging, as could foster electrochromic performance of the films. Our previous studies suggested that WO_3 thin films with higher degree of crystallinity showed better electrochromic properties [24].

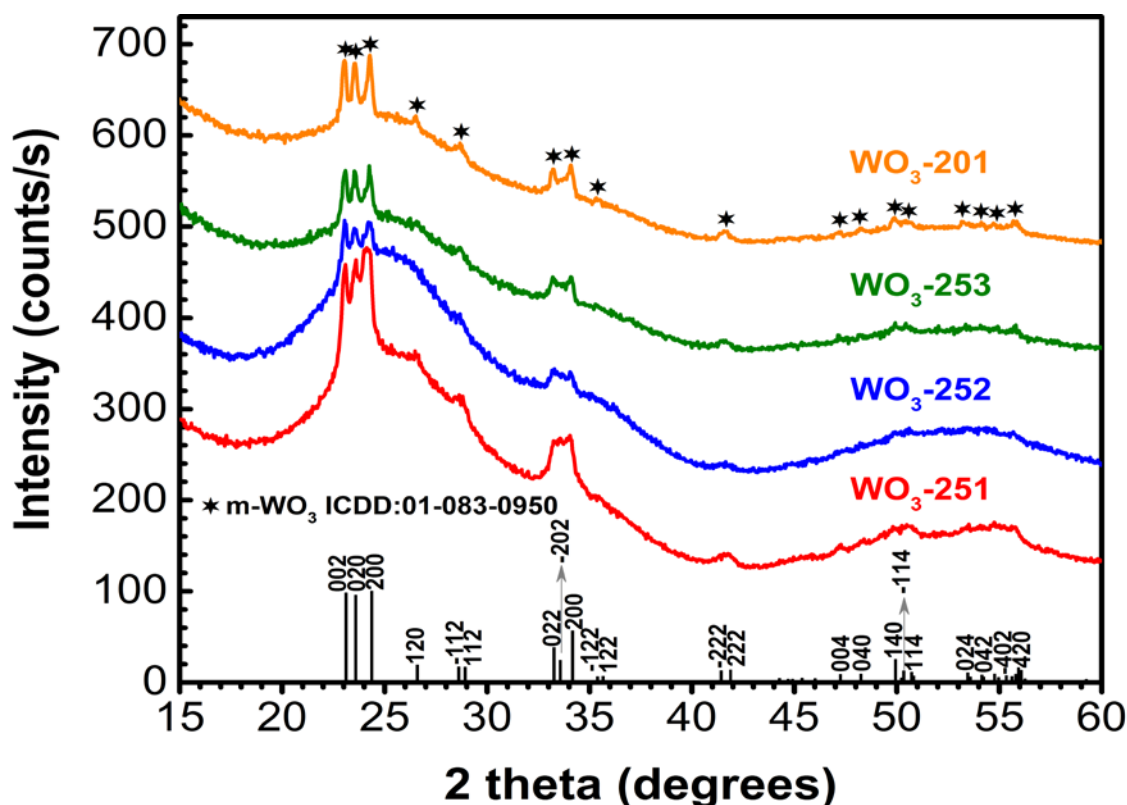


Figure 4. Comparative GIXRD patterns of MAPLE deposited WO_3 films.

Cyclic voltammetry measurements were performed on the WO_3 thin films fabricated by MAPLE, and the electrochromic effect was observed. The films showed strong coloration (the real value to be determined in further experiments), and fast (in a few seconds at the scanning rate of 20 mV/s) and full bleaching was observed. The effect was reversible for many cycles at comparably low voltages in the range $-0.7/+0.4$ V. For these MAPLE deposited WO_3 films, which are with higher specific surface, it was observed stronger coloration with respect to previously studied films deposited by magnetron sputtering or chemical vapour deposition (CVD). A characteristic cyclic voltammetry curve for 20 cycles measured at scanning rate of 20 mV/s is presented in figure 5.

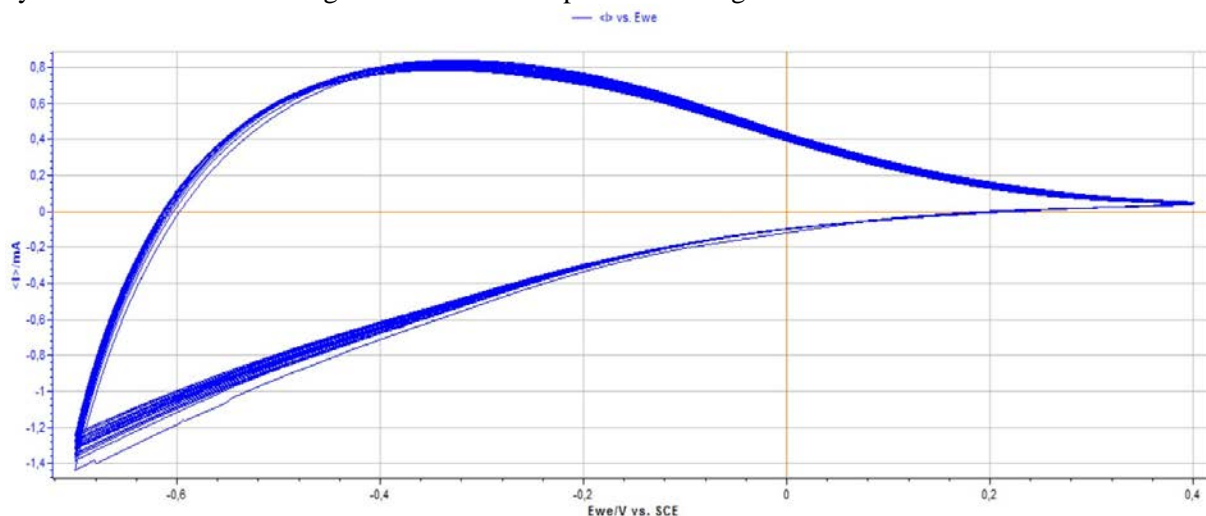


Figure 5. Typical cyclic voltammetry curve of MAPLE deposited WO_3 thin film (sample 251) measured for 20 cycles.

The intercalation of ions into the film happens in the first measured period when the voltage goes from 0 to negative. Then the positive Li^+ ions are attracted to the electrode and go into the free sites of the lattice, which consequently leads to the coloration of the film. When the voltage is reversed, the process starts to go backwards and when the applied voltage turns positive, big part of the ions de-intercalate, and the film bleaches. The coloration process started at -0.2 to -0.3 V, the bleaching started very close to 0, in the positive voltages. The voltages needed for ion injection and extraction, and consequently for coloration and bleaching, were with around 0.2 – 0.3 V lower compared with CVD prepared WO_3 films studied previously [25].

4. Conclusions

MAPLE deposited WO_3 thin films were fabricated and investigated for their possible application in electrochromic devices. The films showed good crystallinity, consisting of a monoclinic WO_3 phase. From morphological point of view the films elicited a typical MAPLE topology, being constituted of spheroid nano-grains with diameters varying mainly in the range 10 – 50 nm.

The preliminary tests indicated that the MAPLE deposited WO_3 thin films possess good electrochromic properties: strong coloration and fast and full bleaching. The effect was observed for many cycles, the strong coloration and full bleaching being preserved. These results are promising for future application of MAPLE deposited WO_3 thin films in the development of electrochromic devices.

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References

- [1] Wicaksana Y, Liu S, Scott J and Amal R 2014 *Molecules* **19** 17747
- [2] Szilágyi I M, Forizs B, Rosseler O, Szegedi A, Nemeth P, Kiraly P, Tarkanyi G, Vajna B, Varjú Josepovits K, Laszlo K, Tóth A L, Baranyai P and Leskelä M 2012 *J. Catal.* **294** 119
- [3] Blo M, Carotta M C, Galliera S, Gherardi S, Giberti A, Guidi V, Malagù C, Martinelli G, Sacerdoti Vendemiati B and Zanni A 2004 *Sens. Actuator B-Chem.* **103** 213
- [4] Balázs C, Wang L, Zayim E O, Szilágyi I M, Sedlacková K, Pfeifer J, Tóth A L and Gouma P-I 2016 *J. Eur. Ceram. Soc.* **28** 913
- [5] Szilágyi I M, Saukko S, Mizseic J, Tóth A L, Madarász J and Pokol G 2010 *Solid State Sci.* **12** 1857
- [6] Guatwei L, Xian-ju T, Choongyew C, Gaikun A and Zailani A B M 2011 *J. Mater. Sci. Eng.* **5** 27
- [7] Szilágyi I M, Wang L, Gouma P-I, Balázs C, Madarász J and Pokol G 2009 *Mater. Res. Bull.* **44** 50
- [8] Marsen B, Miller E L, Paluselli D and Rocheleau R E 2007 *Int. J. Hydrogen Energy* **32** 3110
- [9] Gesheva K A 2007 Thin film optical coatings for effective solar energy utilization (New York: Nova Science)
- [10] Granqvist C G 1995 Handbook of Inorganic Electrochromic Materials (Amsterdam: Elsevier)
- [11] Monk P M S, Mortimer R J and Rosseinsky D R 2007 *Electrochromism and Electrochromic Devices* (Cambridge: Cambridge university press)
- [12] Boanini E, Torricelli P, Fini M, Sima F, Serban N, Mihailescu I N and Bigi A 2012 *J. Inorg. Biochem.* **107** 65
- [13] Jankovic A, Erakovic S, Ristoscu C, Mihailescu (Serban) N, Duta L, Visan A, Stan G E, Popa A C, Husanu M A, Luculescu C R, Srdic, V V, Janackovic Dj, Miskovic-Stankovic V, Bleot C, Chifiriuc M C and Mihailescu I N 2015 *J. Mater. Sci.–Mater. Med.* **26** 17
- [14] Visan A, Stan G E, Ristoscu C, Popescu-Pelin G, Sopronyi M, Besleaga C, Luculescu C, Chifiriuc C, Hussien M D, Marsan O, Kergourlay E, Grossin D, Brouillet F and Mihailescu I N 2016 *Int. Pharmaceut.* **511** 505

- [15] Visan A, Grossin D, Stefan N, Duta L, Miroiu F M, Stan G E, Sopronyi M, Luculescu C, Freche Marsan O, Charvilat C, Ciuca S and Mihailescu I N 2014 *Mater. Sci. Eng. B* **181** 56
- [16] Mercado A L, Almond C E, Hoekstra J G and Fitzgerald J M 2005 *Appl. Phys. A* **81** 591
- [17] Caricato A P and Luches A 2011 *Appl. Phys. A* **105** 565
- [18] Mihailescu I N, Bigi A, Gyorgy E, Ristoscu C, Sima F and Oner E T 2014 Biomaterial thin film by soft pulsed laser technologies for biomedical applications *Lasers in Materials Science (Springer Series in Materials Science vol 191)* eds M Castillejo, P M Ossi and L Zhigilei (Berlin: Springer) chapter 11 pp 271–294
- [19] Mihailescu I N, Ristoscu C, Bigi A and Mayer I 2010 Advanced biomimetic implants based nanostructured coatings synthesized by pulsed laser technologies *Laser-Surface Interactions, New Materials Production Tailoring Structure and Properties* (Springer Series in Materials Science vol 130) eds A Miotello and P M Ossi (Berlin: Springer) chapter 10 pp 235–260
- [20] Szilágyi I M, Sajó I, Király P, Tárkányi G, Tóth A L, Szabó A, Varga-Josepovits K, Madarász J and Pokol G 2009 *J. Therm. Anal. Calorim.* **98** 707
- [21] Burdis M S, Siddle J R and Taylor S 1994 Proc. SPIE 2255, Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII, 371 (September 9, 1994); doi:10.1117/12.185380
- [22] Sharma N, Deepa D, Varshney P and Agnihotry S A 2001 *Thin Solid Films* **401** 45
- [23] Diaz-Reyes J, Dorantes-Garcia V, Perez-Benitez A and Balderas-Lopez J A 2008 *Superficies y Vac.* **21** 12
- [24] Boiadjiev S, Ivanova T, Rassovska M and Gesheva K A 2007 *J. Optoelectron. Adv. Mater.* **9** 264
- [25] Gesheva K A, Ivanova T, Marsen B, Zollo G and Kalitzova M 2008 *J. Cryst. Growth* **310** 2103