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MDPI

Reactive Dual Magnetron Sputtering: A Fast Method for Preparing Stoichiometric Microcrystalline $ZnWO_4$ Thin Films

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Supplementary Materials

Supporting Figures

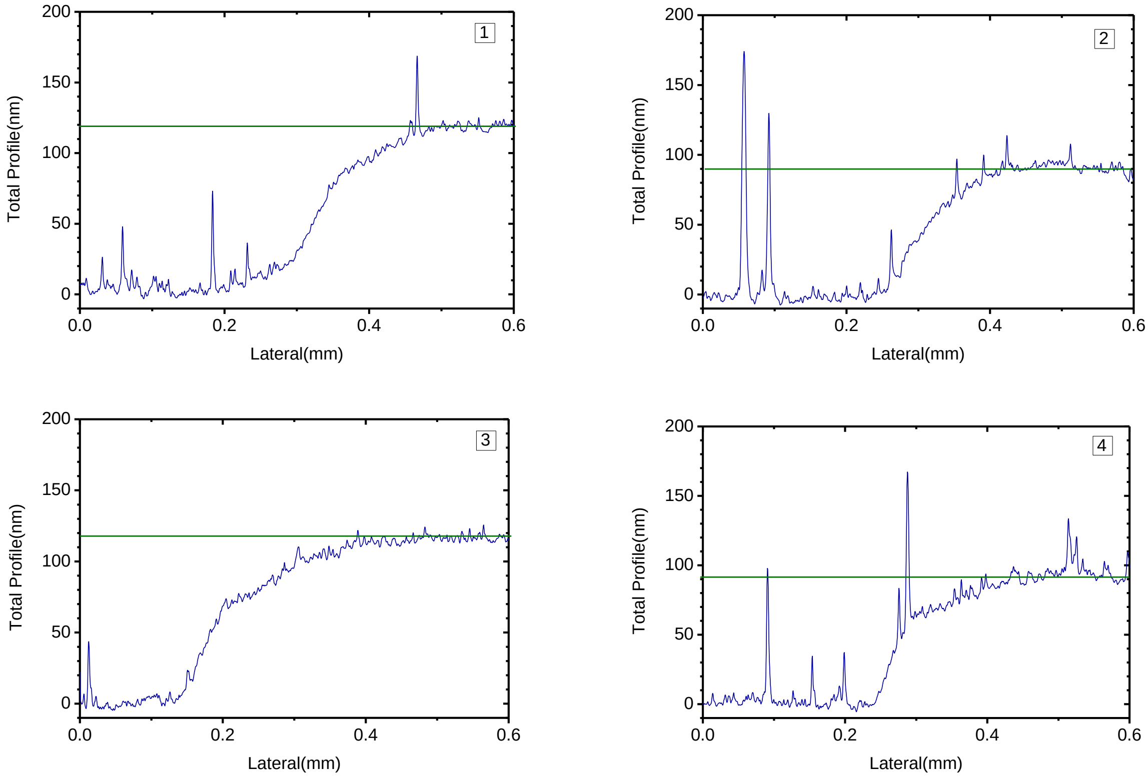

Figure S1. Sputter profiles of WO_3 deposited using standard DC sputter deposition parameters. The standard parameters comprise a process atmosphere of 50% O_2 and 50% Ar, an FTO substrate hold at room temperature, a sputter power of 25 W, a process pressure of 0.005 mbar and a substrate-magnetron distance of 20 cm. The spikes in the figure are due to dust.

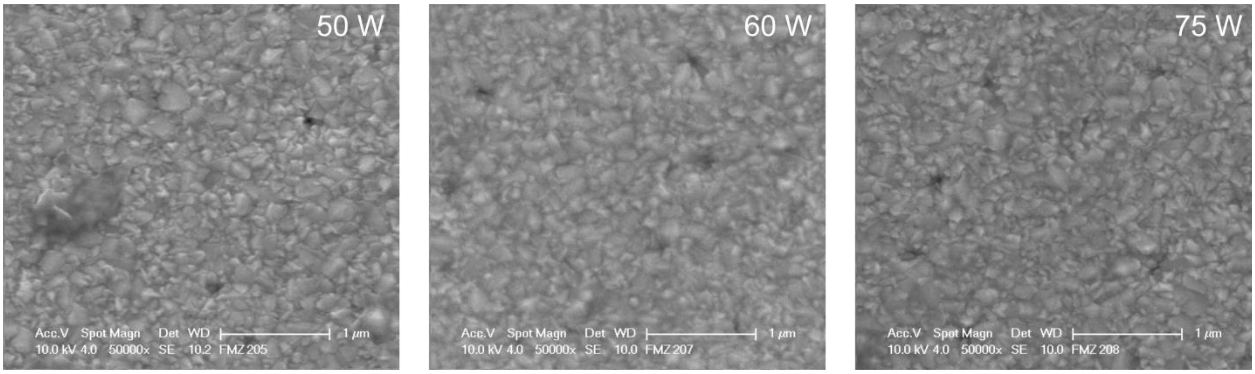

Figure S2. SEM images of ZnO thin films deposited at different sputtering powers keeping other deposition parameters constant (50%/50% O_2/Ar).

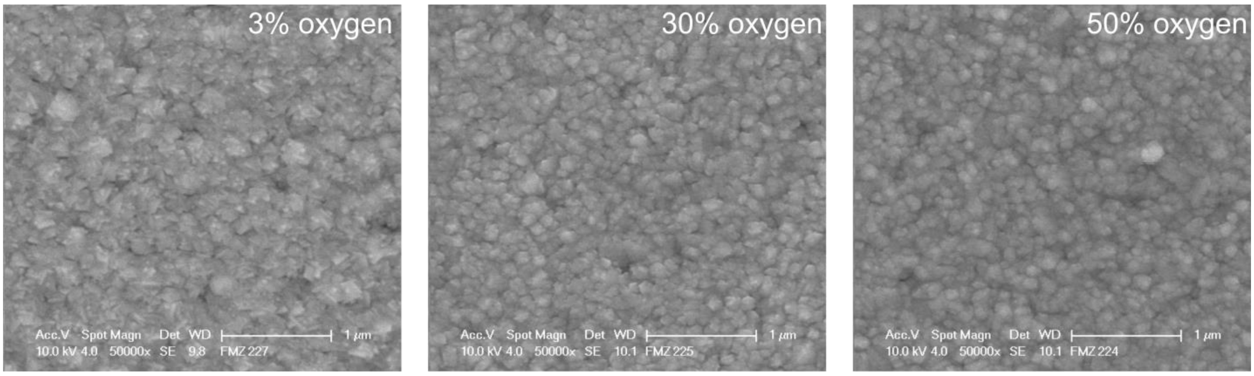

Figure S3. SEM images of ZnO thin films deposited using different oxygen contents in the process gas keeping other deposition parameters constant (*P* = 60 W). Argon is used as filler gas.

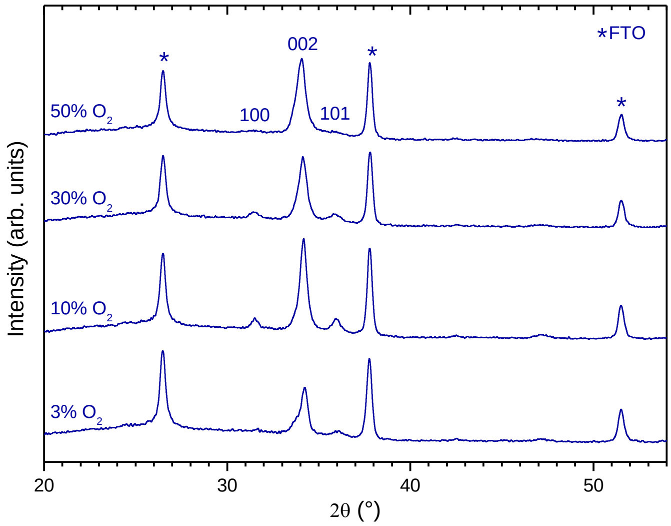

Figure S4. X-ray diffractograms of ZnO thin films deposited using different oxygen contents in the process gas keeping other deposition parameters constant (*P* = 60 W). Argon is used as filler gas.

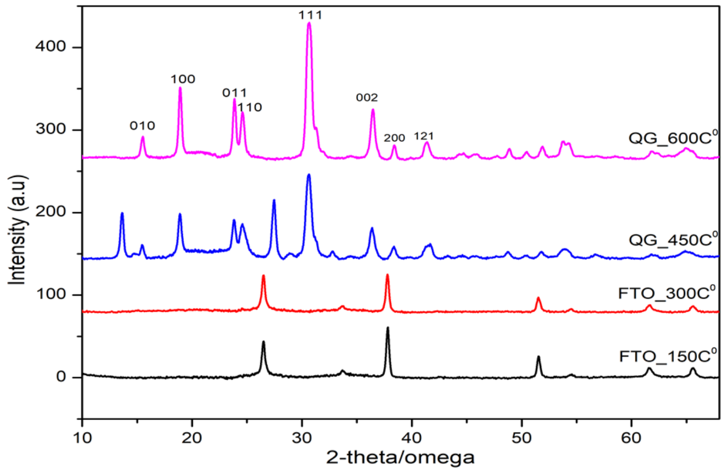

Figure S5. X-ray diffractograms of $ZnWO_4$ thin films annealed at different temperatures for 10 h in air. FTO: glass/FTO substrates and QG: quartz glass substrates. The indices in the graph correspond to $ZnWO_4$. For 150 °C and 300 °C mostly FTO reflexes can be seen and a small peak at 34° which could be of ZnO. At 600 °C phase pure $ZnWO_4$ was obtained. The extra reflexes for the 450 °C annealed sample could not be assigned.

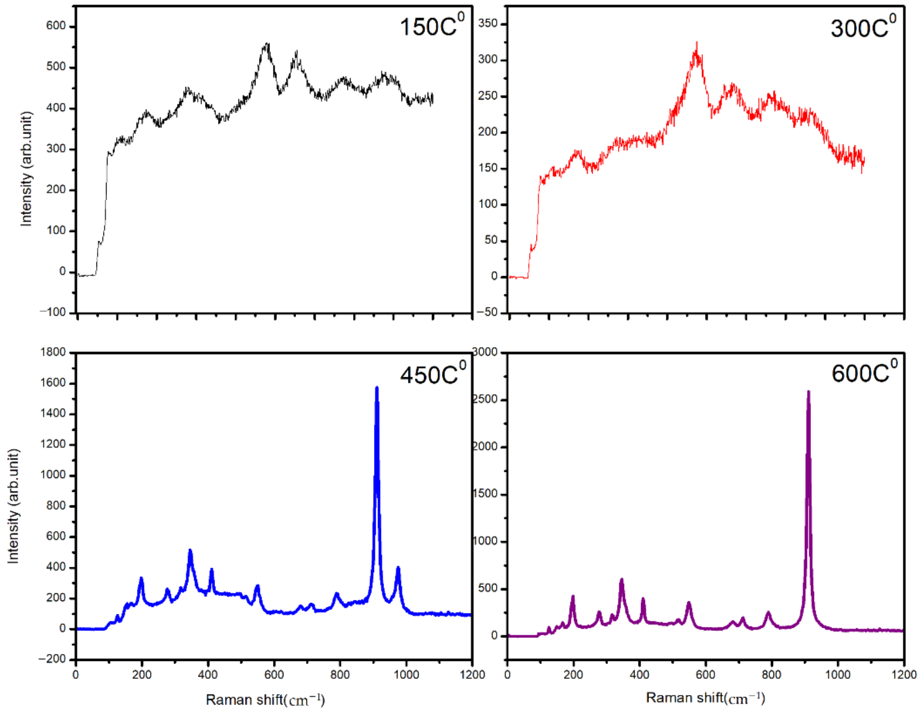

Figure S6. Raman spectra of $ZnWO_4$ thin films annealed at different temperatures for 10 h in air. The samples annealed at 150 °C and 300 °C appear to be amorphous, while the sample annealed at 450 °C does not appear to be phase pure (additional peak at 970 cm^{-1}).

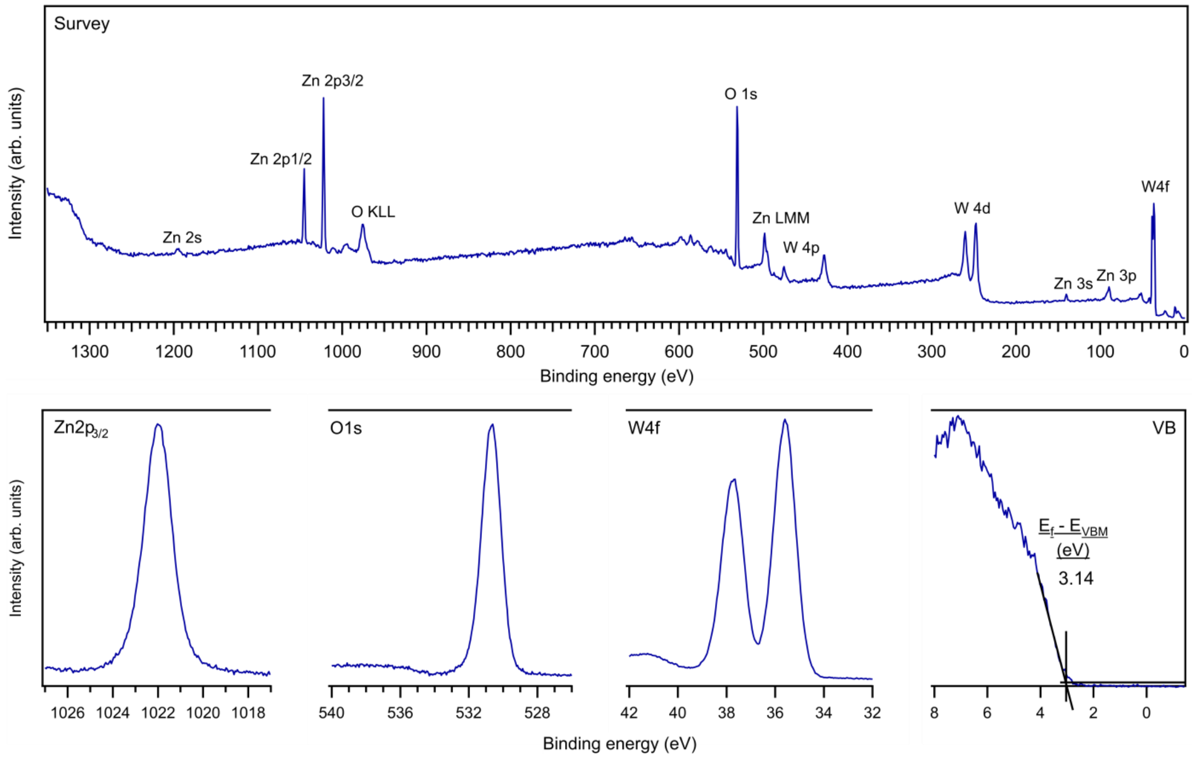

Figure S7. Survey, Zn $2p_{3/2}$, O 1s and W 4f core level, and valence band (VB) XP spectra of a 15 nm thick amorphous $ZnWO_4$ film.

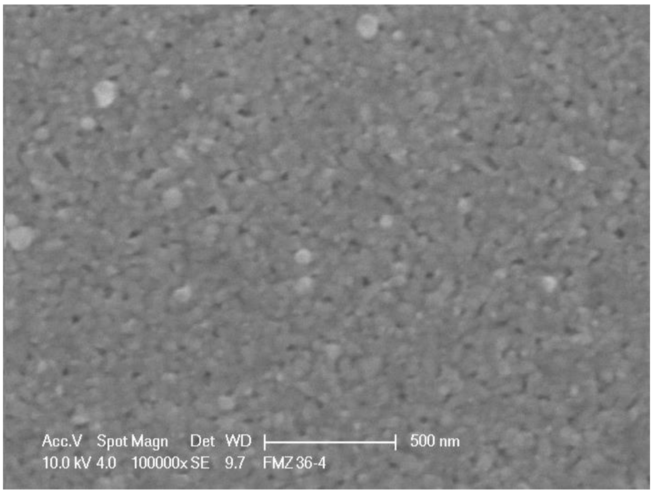

Figure S8. SEM image of 100 nm monoclinic $ZnWO_4$ thin films annealed in air at 600 °C for 10 h.

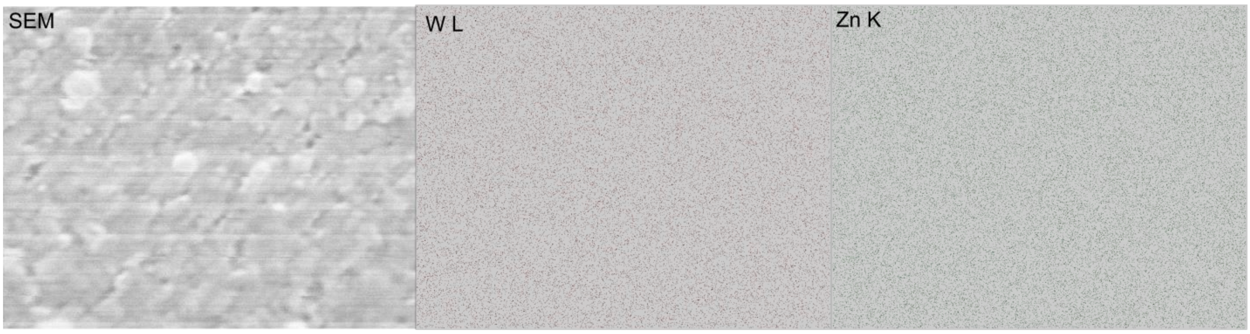

Figure S9. SEM-EDS of 100 nm monoclinic $ZnWO_4$ thin films annealed in air at 600 °C for 10 h. In green Zn K and in red W L.

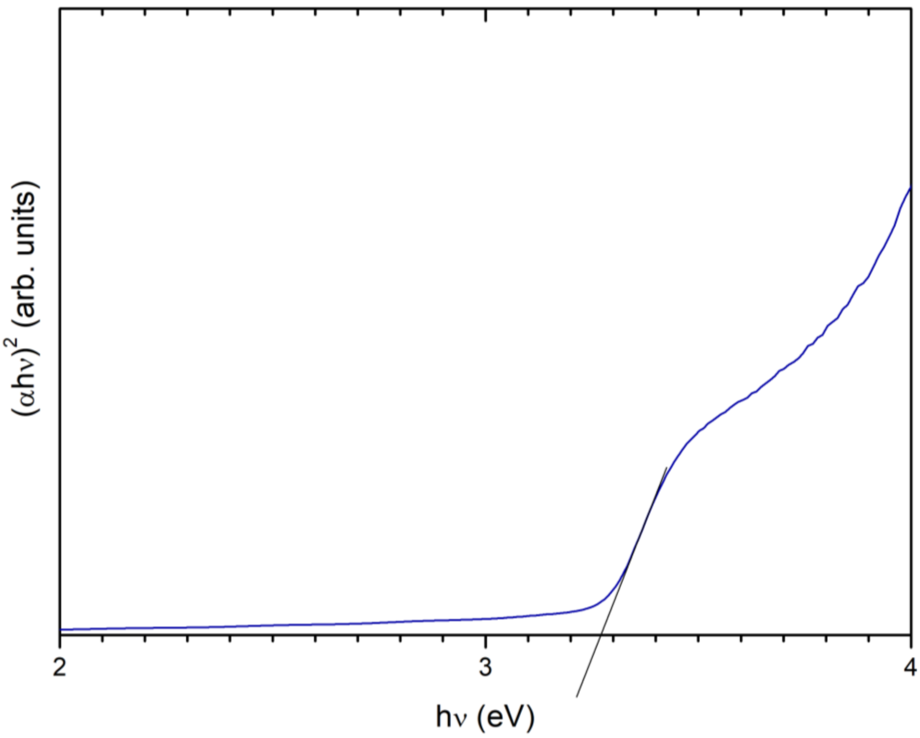

Figure S10. Tauc plot for the direct optical transition of the monoclinic $ZnWO_4$ thin film.

Supporting Methods

The relative XPS surface stoichiometries were determined using CasaXPS according to:

$$[i]\% = \frac{A_i}{s_i \sum_n \frac{A_n}{s_n}} \cdot 100\%$$

with [i]% the atomic percentage of species i using core level i, A_i the area of core level i, s_i the sensitivity factor of core level i. The sensitivity factors can be described by:

$$s = \sigma \cdot \lambda \cdot T$$

with σ being the photoionization cross section, λ being the inelastic mean free path (IMFP) and T being the transmission function. SPECS tabulated photoionization cross sections for the Phoibos 150 analyzer were used and amounted for Zn $2p_{3/2}$, O 1s and W 4f to 15.13, 2.77, 10.35, respectively. According to Powell [1] and Ebel [2] the IMFP can be approximated by:

$$\lambda = E_k^p$$

with E_k being the photoelectron kinetic energy and p being equal to 0.7414 [3]. The transmission function of the PHOIBOS analyzer is determined according to a modified method developed by Hemminger et al [4]. The transmission function is expressed by:

$$T \propto E_P \cdot (E_K/E_P)^{b(E_K/E_P)}$$

with E_k being the photoelectron kinetic energy and E_P being the pass energy. The transmission function equation is automatically fitted to the experimental data using the Specslab 2 measurement software.

Reference

1. Powell, C.J. The quest for universal curves to describe the surface sensitivity of electron spectroscopies. *J. Electron. Spectros. Relat. Phenomena* **1988**, *47*, 197–214, doi:10.1016/0368-2048(88)85012-6.
2. Ebel, H.; Ebel, M.F.; Baldauf, P.; Jablonski, A. The energy dependence of attenuation lengths in elements. *Surf. Interface Anal.* **1988**, *12*, 172–173, doi:10.1002/sia.740120226.
3. Jablonski, A. Universal energy dependence of the inelastic mean free path. *Surf. Interface Anal.* **1993**, *20*, 317–321, doi:10.1002/sia.740200409.
4. Hemminger, C.S.; Land, T.A.; Christie, A.; Hemminger, J.C. An empirical electron spectrometer transmission function for applications in quantitative XPS. *Surf. Interface Anal.* **1990**, *15*, 323–327, doi:10.1002/sia.740150505.