

Optical Response to Hydrogen of WO₃ Thin Films Prepared by Magnetron Sputtering

Wiktoria Weichbrodt¹, Jarosław Domaradzki¹, Michał Mazur¹

¹ Wrocław University of Science and Technology, Faculty of Electronics, Photonics and Microsystems, Janiszewskiego 11/17, 50-372 Wrocław, Poland

Corresponding Author's e-mail address: michal.mazur@pwr.edu.pl

Summary:

Tungsten oxide thin films were prepared using gas impulse magnetron sputtering and as-deposited samples were additionally annealed at 400°C to obtain nanocrystalline structure. Surface studies revealed good homogeneity of the prepared coatings. Thin films were exposed to hydrogen with different concentrations and their optical response, that is the decrease of transmission coefficient, was measured in the spectral range from 200 to 1000 nm. The change of resistance upon exposure to hydrogen, was also measured to compare optical and electrical response.

Keywords: WO₃, thin film, magnetron sputtering, gasochromic properties, hydrogen gas sensor

Introduction

Gasochromic WO₃ thin film sensors typically require noble metal nanoparticles as catalysts to facilitate the absorption and dissociation of H₂ molecules. One proposed mechanism, known as the “generation of oxygen vacancies” model, suggests that H⁺ ions reduce W⁶⁺ on the WO₃ surface, forming oxygen vacancies that lead to coloration process [1,3]. Bleaching occurs via the re-oxidation of W⁵⁺ to W⁶⁺ by atmospheric oxygen, restoring transparency [1,3]. WO₃ thin films can be prepared using many various methods, including sol-gel, electron beam evaporation, thermal evaporation and magnetron sputtering. Noble metals like Pd, Pt, or Au can be applied as very thin adlayers at the top of thin films or used as dopants to improve sensing response. Nishizawa et al. [15] showed that Pt-doped WO₃ films respond faster to 4% H₂ than Pd-doped ones, and both showed high repeatability. Garavand et al. [8] reported that Pt/WO₃ coatings had higher coloration efficiency at 90–200 °C, while Pd/WO₃ performed better below this range. Lee et al. [10] deposited Pd on amorphous WO₃ by e-beam evaporation, which resulted in a 50% transmittance decrease as a response to 1% H₂.

In this work we show the gasochromic properties of nanocrystalline tungsten oxide thin films prepared by gas impulse magnetron sputtering. We compared optical and electrical response of this thin films to hydrogen exposure with different concentrations, up to 2.5%. The highest optical response was nearly twenty, while electrical

resistance changed by several orders of magnitude.

Experimental methods

Tungsten oxide thin films were deposited using the gas impulse magnetron sputtering process with. The deposition process was conducted for 45 minutes with the average pressure of around 5·10⁻³ mbar. Metallic tungsten target (purity of 99.95%) was sputtered with a mixture of argon and oxygen with a ratio of 7:1. The gas impulses were injected directly above the target surface with a frequency of 10 Hz, while the powering cycles were synchronized with gas pulses and lasted for 30 ms. Thin films were deposited at various substrates including fused silica for X-ray diffraction (XRD) and optical studies including gasochromic measurements, silicon for scanning electron microscope (SEM) investigations and aluminum with interdigitated electrodes for determination of electrical response to hydrogen. Moreover, a very thin Pt catalyst with a thickness of ca. 2 nm was deposited at the top of WO₃ thin films using electron beam evaporation. Directly after deposition thin films were annealed in a tubular quartz furnace in an ambient air and pressure for 4 hours at 400°C.

SEM studies were performed with the aid of high-resolution field-emission scanning electron microscope FE-SEM (FEI Helios Xe-PFIB). XRD investigations were done with the use of Empyrean PANalytical X-ray diffractometer containing a PIXel3D detector and CuK_{α1} radiation.

Transmission coefficient measurements were performed in the wavelength range of 300 to

1000 nm with the use of an Ocean Optics QE65000 spectrophotometer and a coupled deuterium-halogen light source. Gasochromic investigations were done at a temperature of 150°C using Janis ST-100H optical cryostat. Gas flow of hydrogen mixed with air was controlled MKS mass flow controllers. Measurement cycles consisted of coloring in diluted hydrogen with concentrations up to 2.5% and bleaching in pure air. Each cycle lasted for 30 minutes. The optical response (OR) was calculated according to the eq. (1):

$$OR = \frac{T_{air}}{T_{H_2}} \quad (1)$$

where: T_{air} – transmission coefficient in air, T_{H_2} – transmission coefficient in H_2 with specific concentration.

Furthermore, studies of sensor response (SR) in terms of resistance change upon exposure to hydrogen were conducted.

Results

WO_3 thin films directly after deposition had uniform surface with low roughness and were amorphous. After post-process annealing, a phase transition to WO_3 -monoclinic occurred, and the average crystallite size was about 23 nm.

Figure 1 shows the optical response of annealed tungsten oxide thin films exposed to hydrogen concentrations from 0.5 to 2.5%. As can be seen from the transmission coefficient spectra, increasing the hydrogen concentration to 1% resulted in a significant decrease of the transparency of the thin films in the near-infrared wavelength region. Moreover, for a concentration of 2.5% and a wavelength of 900 nm, the transmission decreased from 84.6% to 4.5%, which gives the optical response of 18.9.

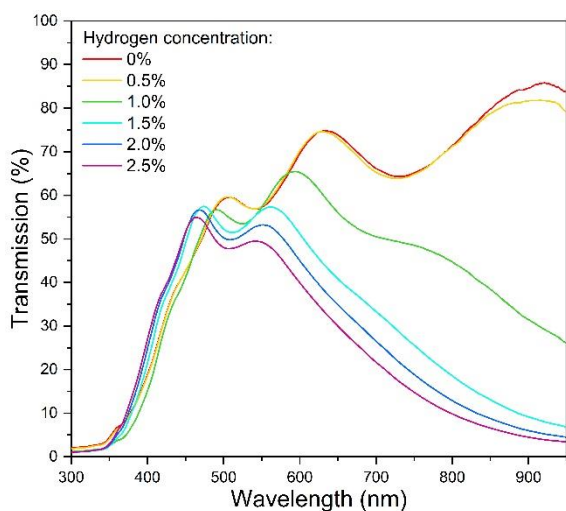


Fig. 1. Optical transmission spectra change upon exposure to hydrogen (in air) with various concentrations.

The sensor response of these thin films in terms of resistance change was over 6 orders of magnitude, i.e. it changed from $10^8 \Omega$ to a value well below $10^2 \Omega$.

Summary

Tungsten oxide thin films revealed very good gasochromic properties as the optical response for the highest concentration was almost 19. It is also worth to emphasize that the resistance of the same thin films measured at the same conditions was decreased of several orders of magnitude. This means there was a significant change from dielectric to conducting behavior of the tested thin films. The in-situ studies of X-ray photoelectron spectroscopy and Raman spectroscopy will be performed in the future to determine changes in the surface and structural properties of WO_3 thin films exposed to hydrogen.

References

- [1] A. Mirzaei, J.H. Kim, H.W. Kim, S.S. Kim, Gasochromic WO_3 nanostructures for the detection of hydrogen gas: An overview. *Applied Sciences* 9, 9, (2019); doi: 10.3390/app9091775
- [2] C. Gao, X. Guo, L. Nie, X. Wu, L. Peng, J. Chen, A review on WO_3 gasochromic film: Mechanism, preparation and properties. *International Journal of Hydrogen Energy* 48, 2442–2465, (2023); doi: 10.1016/j.ijhydene.2022.10.100.
- [3] K. Nishizawa, Y. Yamada, K. Yoshimura, Low-temperature chemical fabrication of WO_3 gasochromic switchable films: A comparative study of Pd and Pt nanoparticles dispersed WO_3 films based on their structural and chemical properties. *Thin Solid Films* 709, 138201, (2020); doi: 10.1016/j.tsf.2020.138201.
- [4] N. T. Garavand, S. M. Mahdavi, A.I. Zad, Pt and Pd as catalyst deposited by hydrogen reduction of metal salts on WO_3 films for gasochromic application. *Applied Surface Science* 273, 261-267, (2013); doi: 10.1016/j.apsusc.2013.02.027.
- [5] Y. A. Lee, S.S. Kalanur, G. Shim, J. Park, H. Seo, Highly sensitive gasochromic H_2 sensing by nanocolumnar WO_3 -Pd films with surface moisture. *Sensors and Actuators B: Chemical* 238, 111-119, (2017); doi: 10.1016/j.snb.2016.07.058.

Acknowledgements

This work was co-funded from the sources given by the Polish National Science Centre (NCN) as a Sonata research project No UMO-2020/39/D/ST5/00424 in the years 2021–2024 and under the OPUS call in the Weave programme, grant No 2023/51/I/ST11/02195.