

# Colour characteristics of nanocrystalline $\text{WO}_{3-x}$ thin films as a function of their stoichiometry

Cecilia Guillén  
José Herrero

Dep. Energy, CIEMAT, Avda. Complutense 40,  
Madrid 28040, Spain

[jose.herrero@ciemat.es](mailto:jose.herrero@ciemat.es)

Stoichiometric  $\text{WO}_3$  crystallizes in tetragonal or hexagonal structures based on corner-sharing  $\text{WO}_6$  octahedra. Each W ion is surrounded by six O ions, ideally forming an octahedron; whereas each O ion is bound to two W ions in a linear configuration, which can be represented as  $\text{W}^{6+}-\text{O}^{2-}-\text{W}^{6+}$  [1]. One may assume that the basic building blocks are similar in the amorphous material, although bond lengths and bond angles exhibit considerable disorder.

Although stoichiometric  $\text{WO}_3$  is a transparent oxide, there exist a number of sub-stoichiometric forms ( $\text{WO}_{3-x}$ ) that exhibit different colours, ranging from blue in the case of a slight oxygen deficiency to brownish for  $\text{WO}_2$  [2]. For the sub-stoichiometric oxides, the most common defects are the oxygen vacancies, which can be neutral ( $\text{V}_{\text{O}}^0$ ), singly charged ( $\text{V}_{\text{O}}^+$ ), or doubly charged ( $\text{V}_{\text{O}}^{2+}$ ) with respect to the unperturbed lattice. The formation of a doubly charged vacancy and two  $\text{W}^{5+}$  ions seems to be energetically advantageous [3]. Thus, absorption of light can arise from the phonon-mediated excitation of an electron in one such  $\text{W}^{5+}$  site to a neighbouring  $\text{W}^{6+}$  site [3, 4].

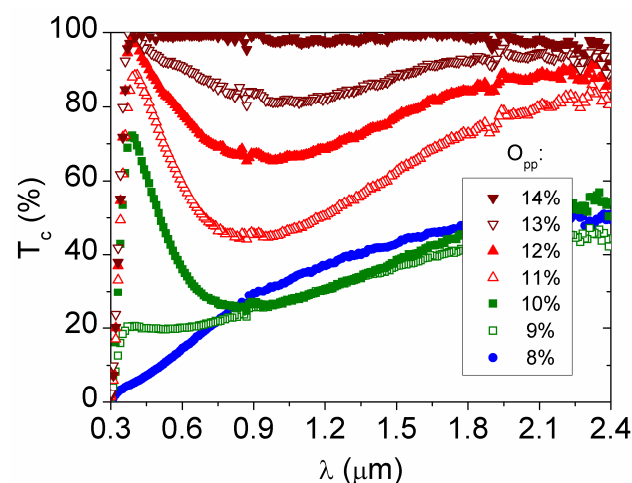
In the present work, nanocrystalline  $\text{WO}_{3-x}$  thin films have been obtained by reactive sputtering of a metallic target (99.9% purity) on unheated glass substrates. The oxygen to argon partial pressure ratio ( $O_{\text{pp}}$ ) has been changed to analyse its influence on the structural, optical and electrical properties of the samples. The main objective is to optimize their colour characteristics for smart windows and other related applications [4, 5].

Figure 1 shows the evolution of the optical transmittance of the sputtered films as a function of the  $O_{\text{pp}}$ . In parallel, the free carrier concentration is found increasing as the visible transmittance decreases. Then, the contribution of plasmonic absorption by free electrons has also been considered.

## References

- [1] Granqvist CG, *Thin Solid Films* 564 (2014) 1–38.
- [2] Thummavichai K, Xia Y, Zhu Y, *Prog. Mater. Sci.* 88 (2017) 281–324.
- [3] Niklasson GA, Granqvist CG, *J Mater Chem* 17 (2007) 127–156.
- [4] Granqvist CG, Arvizu MA, Bayrak Pehlivan I, Qu HY, Wen RT, Niklasson GA, *Electrochimica Acta* 259 (2018) 1170–1182.
- [5] Wang Z, Wang X, Cong S, Geng F, Zhao Z, *Mater. Sci. Engin. R* 140 (2020) 100524.

## Figures



**Figure 1:** Optical transmittance of  $\text{WO}_{3-x}$  thin films prepared by reactive sputtering at different oxygen partial pressures ( $O_{\text{pp}}$ )