Structural characterization of tungsten oxide thin films deposited by balanced and unbalanced magnetron sputtering.

A. Hemberg[1], C. Navío[2], F. Renaux[1], C. Bittencourt[2], R. Snyders[1,2], M. Hecq[1,2] and J.P. Dauchot[1,2]

1. Materia Nova Research Center - Parc Initialis, 1, Avenue Nicolas Copernic, B-7000 Mons, Belgium
2. Laboratoire de Chimie Inorganique et Analytique, Umons - 20, Place du Parc, B-7000 Mons

1° Frame of the work

Tungsten trioxide (WO_3) thin films were prepared through balanced and unbalanced magnetron sputtering using oxygen/argon. The effects of the substrate temperature, applied power and bias on the film characteristics were studied. X-ray diffraction and AFM were used to characterize the structure and the grain size of the WO_3 films.

2° Experimental

WO_3 films were prepared at 7 mbar using a tungsten target (99.9 %). A pulsed DC power at 50Hz and 1936ns was used to generate the plasma. The ratio of O_2 in mixed gas (Ar + O_2) was 15, 25, 47 and 83%. Silicon (100) was used as substrate. The cathode power was 125W. The substrate temperature during the deposition was varied from 150 to 550°C. The substrate can be at floating bias or grounded.

3° Results

a) Balanced Magnetron

Effect of the gas mixture

	002 (°)	Grain size (Å)
15 % O_2	22.54	113
25 % O_2	22.99	101
47 % O_2	22.87	111
83 % O_2	23.12	119

Tab. 1. Crystal size is determined through the Debye Scherrer method

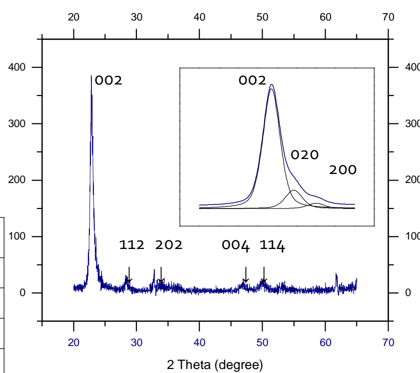


Fig. 1. XRD pattern of WO_3 films (1000 Å) at 550°C and 83 % in O_2

Fig. 1. shows the X-ray diffractograms of WO3 films. The XRD patterns show the (002), (020), (200), (112), (202), (004) and (114) reflections from the monoclinic phase. This phase is described with the space group P21/n (cell parameters: a= 7.301 Å, b= 7.539 Å, c= 7.689 Å, β =90.89°). From table 1 it can be seen that the grain size does not depend on the concentration of oxygen in the gas mixtures, whereas the position of the (002) peak does; this can be associate with strain in the films.

Effect of the thickness

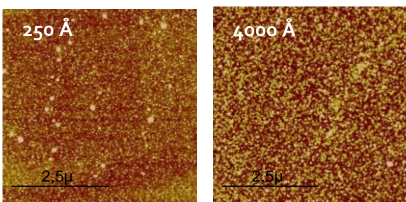


Fig. 2. AFM images (5 x 5 µm²) of thin films

Thickness	002 (°)	Grain size (Å)
4000 Å	22.91	183
2000 Å	22.91	142
1000 Å	23.12	119
500 Å	22.97	73
375 Å	23.22	67
250 Å	23.07	70

Tab. 2. Crystal size on (002) peak

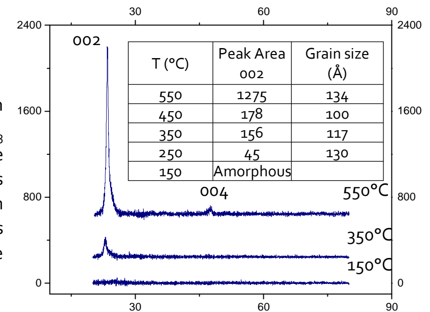
Square	4000 Å	2000 Å	500 Å	375 Å	250 Å	Silicon
5 x 5 µ	8.2 nm	6.3 nm	4.6 nm	3.2 nm	1.9 nm	1.8 nm

Tab. 3. Mean aggregate size deduced from AFM

Table 2 and 3 show the influence of the thickness on the morphology of the WO_3 films: for higher thicknesses the grain size is larger and the aggregate is also increased.

Effect of the temperature

Fig. 3. shows the XRD pattern recorded on annealed WO_3 films. It can be seen that the crystallinity of the films increases for annealing at high temperatures. The films deposited at 150°C are amorphous.



T (°C)	Peak Area 002	Grain size (Å)
550	1275	134
450	178	100
350	156	117
250	45	130
150	Amorphous	

Fig. 3. XRD pattern of WO_3 films (2500 Å) at 550, 450, 350, 250, and 150°C at 83 %.in O_2

b) Unbalanced Magnetron

Effect of the gas mixture

	200 (°)	Grain size (Å)
15 % O_2	24.01	51
25 % O_2	24.04	61
47 % O_2	23.94	60
83 % O_2	24.56	63

Tab. 4. Crystal size on (200) peak

Fig. 4. shows the X-ray diffractograms of WO_3. It can be seen that the monoclinic phase is prensent as for balanced deposition. However, the texture (preferential orientation) is different and the grain size smaller.

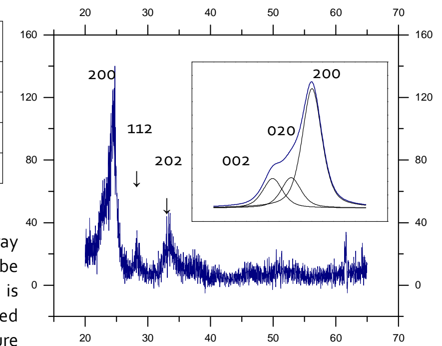


Fig. 4. XRD pattern of WO_3 films (1000 Å) at 550°C and 83 % in O_2

Effect of the power:

Power	200 (°)	Grain size (Å)
500 W	24.226	61
250 W	24.282	60
125 W	24.545	63
75 W	24.650	56

Tab. 5. Dependence of the crystal size on the applied power

Effect of the bias

Substrate	Peak Area 002	Peak Area 200	Grain size (Å)
Floating	34	139	61
Ground	650	553	68

Tab. 4. Crystal size and Peak area for floating and ground substrate

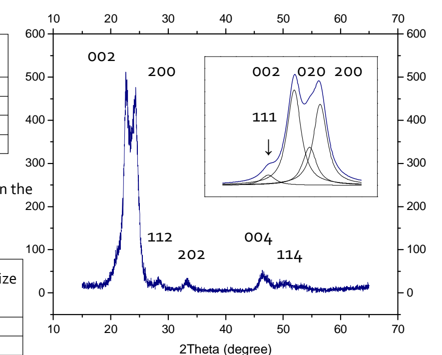


Fig. 5. XRD pattern of WO_3 films (1000 Å), T= 550°C, 83 % of O_2 and substrate grounded

The crystallinity of the grounded film is ~ 4X higher than the floating one (table 4).

4° Conclusions

The results show a close dependence between sputtering conditions and structural properties of the WO_3 films. Particularly, the use of unbalanced magnetron process leads to a modification of the texture and of the crystal size when compared to balanced magnetron. This may be due to different ion bombardment conditions during the thin films growth.

Acknowledgements : Special thanks to Région Wallonne (Programme First DO.C.A) , ARC-UMH and the Belgian government through the PAI P06/08 « Ψ » program for financial support