

## Supporting Information

# Influence of the Oxygen Substoichiometry and of the Hydrogen Incorporation on the Electronic Band Structure of Amorphous Tungsten Oxide Films

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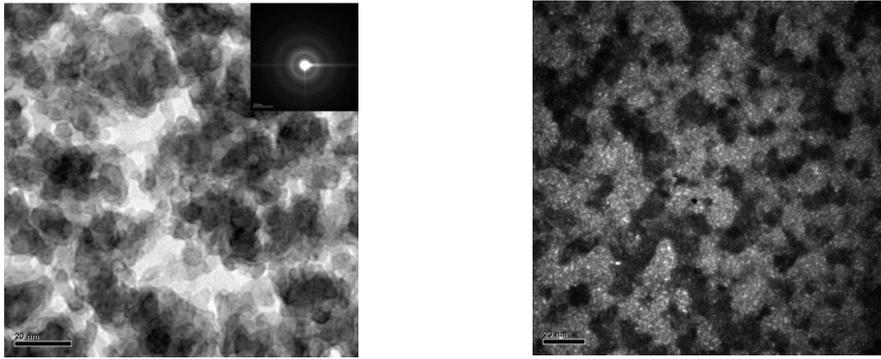
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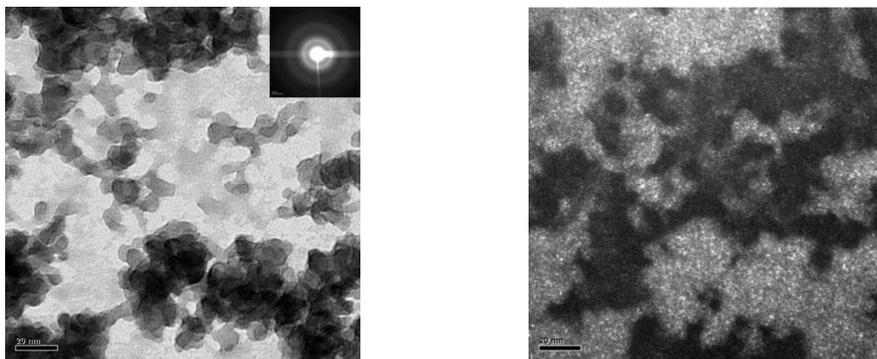
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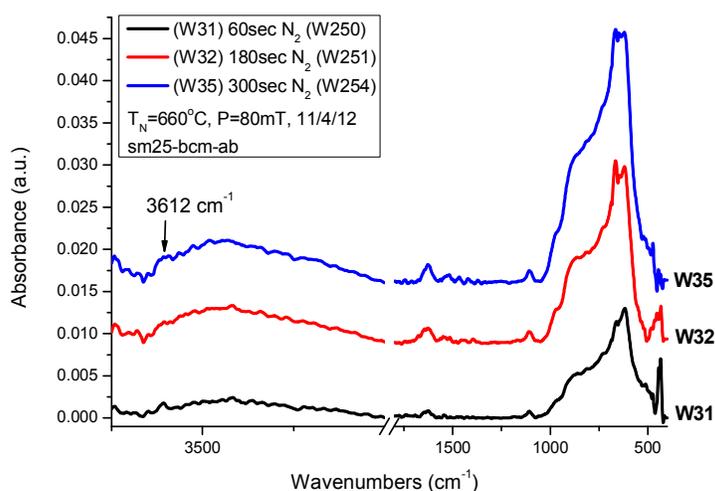
**Figure S1.** Bright field (left) and the corresponding dark field (right) TEM micrographs taken on a tungsten oxide sample grown in  $N_2$  environments. The corresponding electron diffraction pattern is also shown.



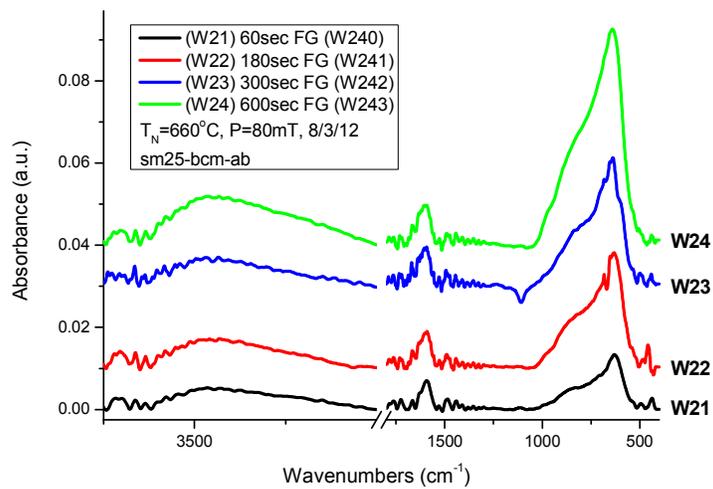
**Figure S2.** Bright field (left) and dark field (right) TEM images taken on a tungsten oxide sample grown in forming gas (FG) environment. Inserted in the left image the corresponding electron diffraction pattern.

The x-ray diffraction spectra taken on tungsten oxide films grown in  $N_2$  and forming gas (FG) were structureless.

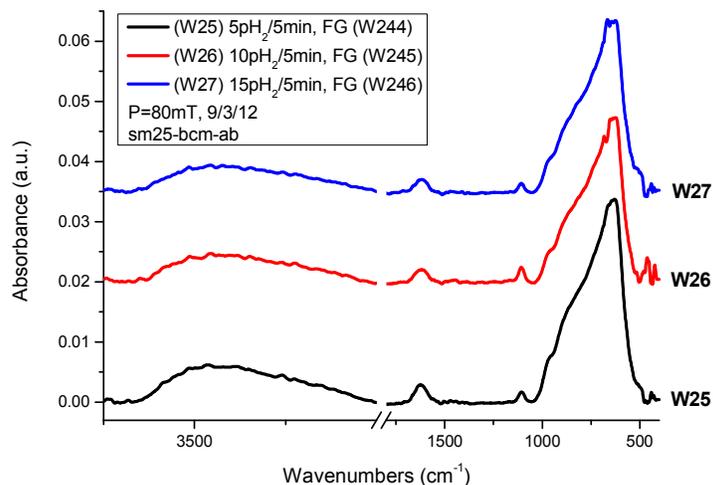
The TEM micrographs shown in S1 and S2 exhibit common characteristics: A granular morphology was shown in all samples with grains sizing between 10 and 15 nm. The dark field TEM images reveal the existence of crystalline regions in samples with dimensions of the order of 2-3 nm probably located at the center of grains and surrounded by a shell of amorphous material. These crystalline regions are distributed randomly and this explains the absence of structure on the XRD patterns. From the XRD spectra and TEM measurements it is concluded that most of the volume of tungsten oxide films is occupied by amorphous material while the small crystalline regions in films are randomly distributed. Therefore, films are characterized as highly disordered-amorphous.



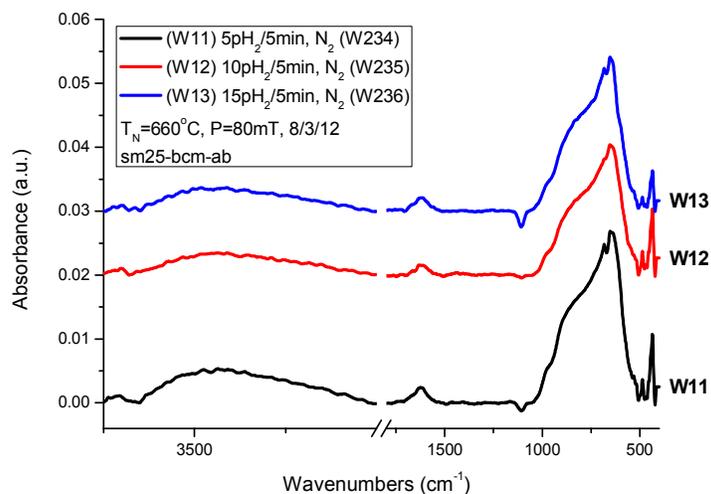
**Figure S3.** FTIR spectra taken on tungsten oxide films grown at different times in  $N_2$  environment. Small peaks superimposed on spectra, the most characteristic of which at  $3612\text{ cm}^{-1}$ , correspond to adsorbed ambient water vapor.<sup>42</sup>



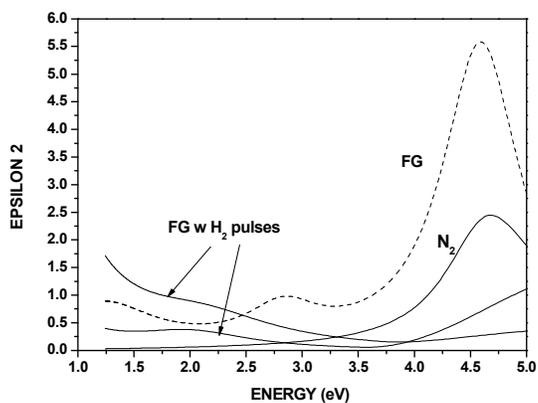
**Figure S4.** FTIR spectra taken on tungsten oxide films grown at different times in FG environment. All peaks exhibited in spectra appear at exactly the same wavenumbers.



**Figure S5.** FTIR spectra taken on tungsten oxide films grown in FG environment at similar deposition times (5 min) with simultaneous pulsed injection of  $\text{H}_2$ . The number of  $\text{H}_2$  pulses was varying between 5 and 15. All spectra appear smoothed out relatively to those taken on samples grown in  $\text{N}_2$  and in FG without  $\text{H}_2$  injection (S3 and S4, respectively).



**Figure S6.** FTIR spectra taken on tungsten oxide films grown in  $N_2$  environment at similar deposition times (5 min) with simultaneous pulsed injection of  $H_2$ . The number of  $H_2$  pulses was varying between 5 and 15. Peaks corresponding to adsorbed water, shown in S3, disappear.



**Figure S7.** Photon energy variation of the imaginary part of dielectric constant,  $\epsilon_2$ , for tungsten oxide samples grown in:  $N_2$ , FG, environments and in FG environment with simultaneous pulsed injection of  $H_2$ . This is a qualitative image of the joint density of states near the gap region.

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