ION FLUX–FILM STRUCTURE RELATIONSHIP DURING REACTIVE MAGNETRON SPUTTERING OF TUNGSTEN.

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Semiconducting metal oxides such as WO_3 are widely used as sensitive layer in gas sensors applications. It has been demonstrated that the sensor performances are strongly dependent on the microstructure of the layer: grain size, phase constitution, material density, ...[1-4] These features can be controlled by varying the energy and flux of the ions impinging the growing films in magnetron processes. [5-8]

In this work, we aim evaluating the effect of ion bombardment during WO_3 thin films growth by reactive magnetron sputtering on the crystallographic and microstructural properties of the material. The ion bombardment was modified by using two distinct strategies: (i) the use of two magnetic configurations (a balanced magnetic field, BM, and a strongly unbalanced one, UBM) of the magnetron using a pulsed magnetron discharge (PDMS).[9] and (ii) the use, for a UBM configuration, of different electrical sources allowing different degree of ionization of the plasma, namely a conventional DC source, a PDMS source, a high power impulse source (HiPIMS) and a modulated plasma source (MPP).

The effects of these different parameters on the chemical, crystallographic and microstructural properties of the deposited films were evaluated by XPS, XRD and TEM/AFM, respectively.

Our results allow the different ion bombardment regimes to be correlated with the structural properties of the films (grains size, texture, etc.). In order to understand our observations, plasma diagnostic through energy-resolved mass spectrometry measurements were performed.

In all cases, depositions without intentional heating of the substrate lead to XRD amorphous thin films. All the depositions were therefore performed at 550°C which was identified as the "ideal" temperature in order to get a sufficient crystallization of the deposited material.

By comparing the two magnetic field configurations (BM and UBM) using the PDMS source, the main observations are that in all cases, the films crystallize in the low temperature stable monoclinic phase of WO_3. Nevertheless, due to the increased ion bombardment enabled by the UBM configuration, the texturation of the films changes from (002) in the BM case to (200) for the UBM configuration. Concerning the grain size, it appears that the UBM conditions lead to significantly smaller grains. These results are correlated with the ion flux towards the growing films which was measured to be at least 2 times higher in the UBM case while the deposition rate and the mean energy of the bombarding ions remains similar.

When comparing different sputtering sources for the UBM case, the situation becomes more complicated. Indeed, for the MPP case, the films features look like those observed when the BM configuration is used with the PDMS source. For the HiPIMS deposited films, we observe a modification of the crystalline structure since the films crystallize in the high temperature orthorhombic phase of WO_3. If the latter situation is expected, we expected a similar situation for MPP which is also a highly ionized physical deposition method (IPVD).

The analysis of the plasma phase during these depositions reveals that both MPP and HiPIMS discharges are effectively IPVD methods.

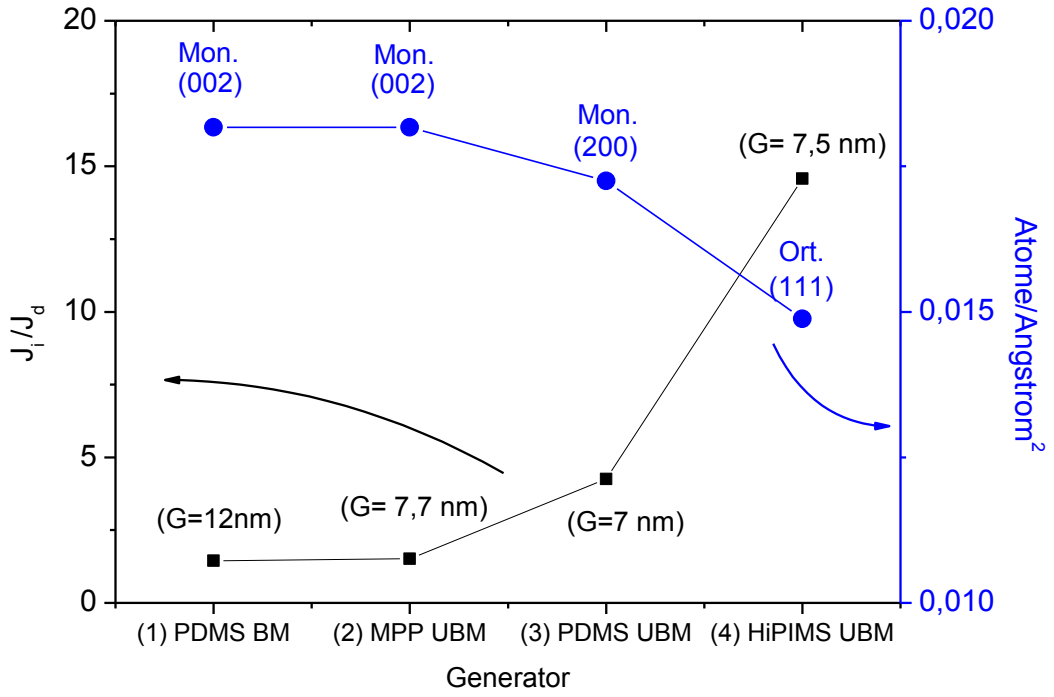

Figure 1: Evolution of J_i/J_d and plane density as a function of the deposition conditions: PDMS (balanced and unbalanced), HiPIMS and MPP discharges. G is the grain size.

In order to understand these data, it has been necessary to consider not only the ion fluxes towards the growing film but also the ratio between the ions and deposition (neutral+ions) fluxes: (J_i/J_d). Indeed, it is accepted that this quantity is a key parameters controlling the diffusion process on the surface during the thin film growth and therefore, the growth mechanism and the phase constitution of the material.[6] In this work, it has been roughly estimated by dividing the ion fluxes measured by mass spectrometry by the deposition rate (expressed as a quantity of matter). **Figure 1** shows the evolution of this parameter as a function of the synthesis method used in this work.

These results show a global view of the energy provided to the growing films during the different processes. It appears that, even if the ion flux is lower in MPP, due to the high deposition rate of the process, the J_i/J_d ratio is significantly lower than in HiPIMS. On the other hand, the PDMS-UBM combination allows a low value of this ratio to be reached.

When looking at the crystallographic properties of the deposited films as a function of the source used (**Fig. 1**), a correlation is observed with, at low J_i/J_d value, the synthesis of the room temperature monoclinic phase with a strong (002) texturation and at high J_i/J_d value, the synthesis of the high temperature orthorhombic phase. In that case, by playing with the pulse length in HiPIMS, it is even possible to modify the texturation from the (001) plane to the (111) plane due to higher energy provided to the films.

Concerning the grain size (G) of the material which is important for the efficiency of thin films based MOS-based gas sensors, we observe a reduction of the latter as the ratio increases as revealed by **Figure 1**. This can be understood by the limited growth of the grains due to the strong bombardment when the ion flux increases.

We have therefore established that it is possible to finely control the crystallographic and microstructural properties of WO_3 thin films deposited by reactive magnetron sputtering by playing either with the magnetic configuration of the magnetron and/or with the electrical source used to sputter the W target. In order to understand the evolution of these data, it is necessary to consider the energy provided per depositing atom. This parameter can be roughly deduced by combining the data provided by energy-resolved mass spectrometry measurements and the deposition rate data.

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