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Deposition of nanocrystalline WO_3 thin film using magnetron sputtered multilayer structure in view of gas sensor applications

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Abstract:

Tungsten trioxide films with nanocrystalline surface were manufactured by deposition of a three layer WO_3/W/WO_3 structure by RF sputtering and successive annealing of the structure in appropriate temperature range. Surface morphology was controlled by the thickness of the metal layer and upper oxide layer. WO_3 sample after annealing was not homogeneous, revealing lower density in the region of upper layer. The obtained samples were sensitive to nitrogen dioxide, exhibiting better stability at lower working temperatures.

Key words: tungsten trioxide, nanocrystalline films, NO_2 sensors

Introduction

Tungsten oxide is frequently considered as a promising material in detection of oxidizing gases as nitrogen oxides (NO and NO_2), ozone or ammonia vapours. It is mostly obtained in a form of a thin film by both physical and chemical deposition methods but recently also as one dimensional structures, e.g. nanowires, nanorods, etc (for a review see e.g. [1]). Its gas sensing properties depend on the conditions and methods applied in the preparation but one of the key factors influencing the sensitivity of thin films is the grain size. The smaller the grain, the higher surface to volume ratio for a gas sensitive material and hence higher the concentration of active surface adsorption centres. The influence of effective surface area on gas sensing properties of WO_3 thin films is frequently observed and investigated [2].

There exists quite rich literature on the technology of gas sensitive metal oxide films. The recent example of interesting technique leading to grain size reduction is the deposition of WO_3 based on interruption of RF sputtering process [3].

The technique used by the authors for the deposition of WO_3 nanocrystalline films is similar to that applied by S. Kumar et al. [4] for preparation of ZnO nano-needles. It is based on fabrication by sputtering of a three layer WO_3/W/WO_3 structure with adequate thickness of metal and upper oxide layers. After annealing at appropriate temperature regime one obtains WO_3 layer with modified surface topography.

Results and discussion

RF magnetron sputtering technique (13.56 MHz) was applied to deposit the layers. XRD, Grazing Incidence Reflectometry (GIR) and AFM techniques were used to determine the phase composition, microstructure and surface topography of manufactured thin films.

XRD experiments suggest that the structure after annealing transforms to the grainy oxide with clear diffraction peaks, Fig.1. No tungsten lines in the annealed film are observed.

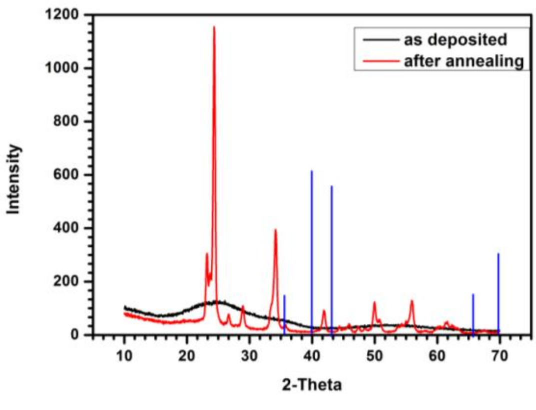

Fig. 1. XRD patterns for the as deposited and annealed structures. Vertical lines indicate the positions of diffraction lines for cubic tungsten.

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GIR experiments approve the assumption that the 3-layer structure (oxide/metal/oxide) after annealing behaves as a single layer of tungsten oxide, Fig.2.,

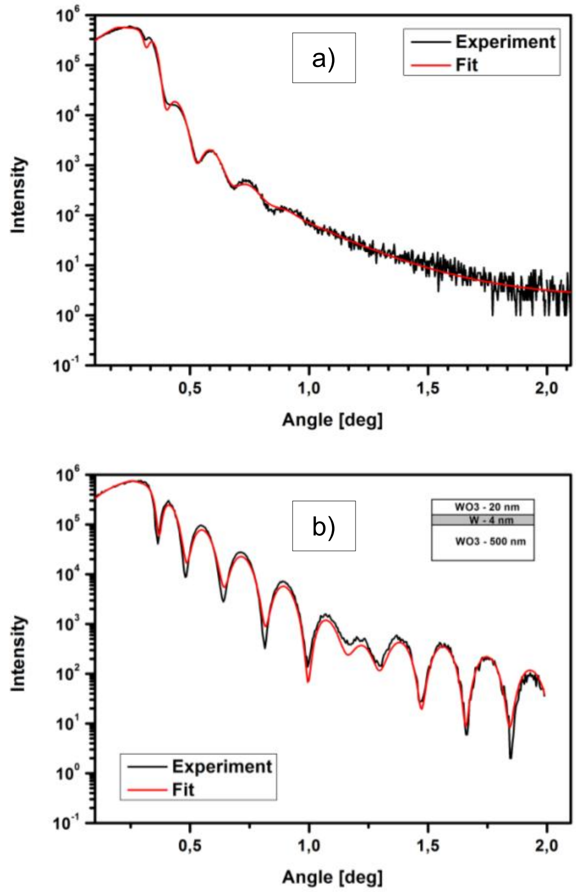

Fig. 2. Grazing incidence x-ray reflectivity for 3-layer structure $WO_3/W/WO_3$ (a) and for the film obtained after annealing of this structure (b).

By appropriate modelling and comparison of experimental data with a fit it was possible to find out that oxide layer after annealing is not homogeneous and exhibits a bit lower density in the upper region of a sample.

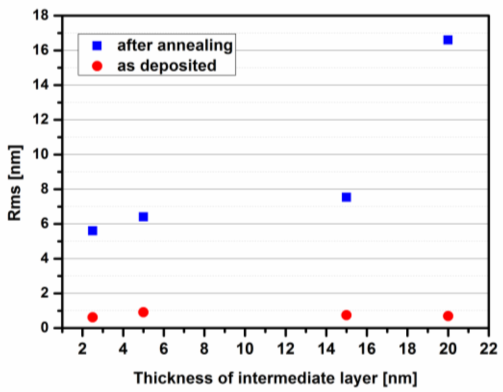

Fig.3. Surface roughness of the films before and after annealing as a function of intermediate layer thickness.

Surface roughness of the sample was also obtained from the fit. The detailed investigations indicate that thickness of the intermediate layer had no influence on the surface roughness before annealing, as could be expected, Fig.3. In contrast, with increasing thickness of this layer the surface roughness after annealing also increased.

Surface topography of the film was determined using AFM technique, Fig.4. From AFM experiments it can be concluded that the surface morphology of the sample is controlled by both the thickness of the metal intermediate layer and upper oxide layer. Also the temperature of annealing influences the shapes and size of surface nanocrystals.

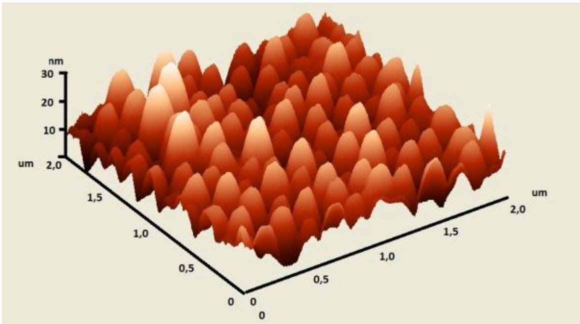

Fig.4. Three dimensional AFM image of WO_3 film obtained after annealing of the multilayer.

The influence of thickness of the intermediate tungsten layer on the average size of surface grains for the sample after annealing is shown in Fig.5. As was expected the intermediate layer had no influence on this topography for the sample before annealing.

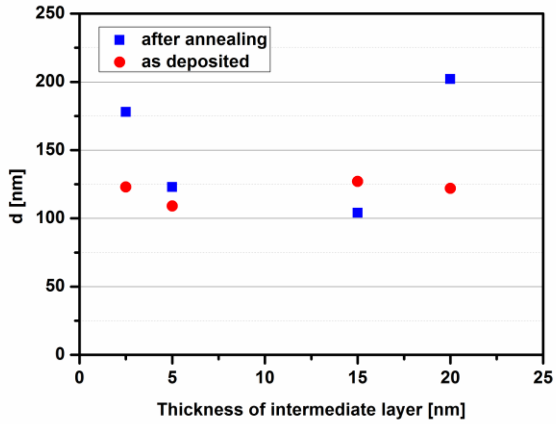

Fig.5. Influence of intermediate tungsten layer thickness on the average size of surface nanocrystals.

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Sensitivity of obtained samples in relation to nitrogen dioxide was investigated as a function of gas concentration at selected working temperatures.

Resistance of the gas sensitive films was measured using electrometer working in the voltage source mode. Very high sensor resistance readings were partially reduced by using the interdigitated electrode configuration. The manufactured films exhibited good sensitivity for NO_2 gas (in a few ppm range), Fig.6. Practical sensor applications require however lowering of the baseline resistance.

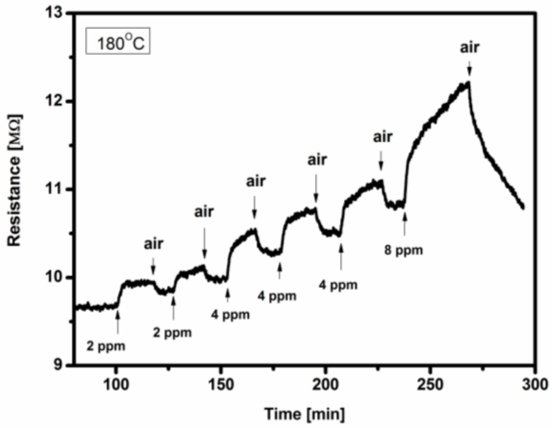

Fig.6. Response to NO_2 measured for the WO_3 film at 180^OC.

From Fig.6 it can be seen that the baseline of the sensing layer exhibits the tendency to increase with time. This phenomenon is even more pronounced at higher working temperatures of the sensor, Fig.7. Such a tendency is a drawback for the sensor which calls for further investigations.

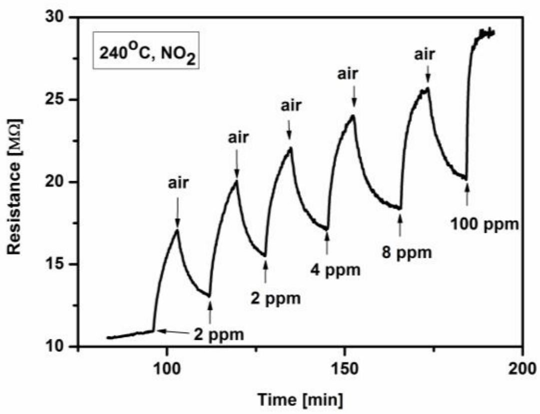

Fig.7. Response to NO_2 measured for the WO_3 film at 240^OC.

Conclusions

The three layer manufacturing procedure is a promising technology in obtaining tungsten trioxide thin films with developed surface. Dimensions of surface grains can be controlled by selecting the thickness of surface layers and adequate annealing procedure. Response of the obtained films to oxidizing NO_2 is within single ppms in a medium working temperature range. The baseline drift observed particularly at higher working temperatures is however a drawback which should be overcome.

Acknowledgements

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