NANOSTRUCTURED ANODIC TUNGSTEN OXIDE FILMS AS A PROMISING MATERIAL FOR GAS SENSOR APPLICATION

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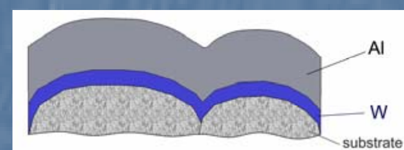
- **Introduction** In the last few years the new ways for preparing gas sensors with improved performance have appeared. Most of these ways are connected with the attempt of finding methods to increase the surface area (or the surface to volume ratio) of any active layer used for chemical sensing. One of these methods consists in employing thin porous layers with enlarged surface areas as support material for semiconductor, metal-oxide gas sensitive films. Particularly, nanoporous alumina resulting from the anodisation of aluminium can be used as a nanotemplate providing a connection between silicon microsystem technology and nano-chemistry. Different methods including sputter-deposition, CVD and electrochemistry can be considered to fill the pores with gas sensitive metal oxides or mesoporous materials. For example, the tungsten oxide gas sensing structures supported by nanoporous alumina templates showed high responsiveness to toxic gases, especially to NO_2 [1]. It is known that the porous tungsten oxide layers can be formed by direct anodization of W in NaF electrolytes [2]. The morphology of the layers depends strongly on the NaF concentration as well as the formation potential.

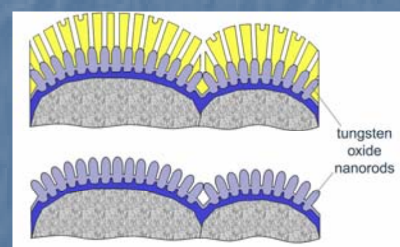
- **The main aims of this work were to develop a new technology for the formation of nanostructured tungsten oxide films and to study the properties of the anodic films formed.**

Preparation of nanostructured tungsten oxide thin films

- Nanostructured tungsten oxide thin films were formed in the several steps.
- **First**, thin tungsten films, up to 300 nm thick, were deposited onto alumina substrates (Rubalite 710) by rf magnetron sputtering of a tungsten target in an Ar atmosphere using an ESM100 Edwards sputtering system. A tungsten target of 99.95% purity was used. The r.f. sputtering power was 100 W. Subsequently, thin aluminum layers, up to 1.2 µm thick, were sputter-deposited onto the tungsten layers to form W-Al bilayer stacks.
- **Second**, the overlying aluminum layer was transformed into its porous anodic oxide in 0.2 M $H_2C_2O_4$ stirred electrolyte at a constant current density of 10 mA/cm2 at 296 K. During the galvanostatic period, the forming voltage rises almost linearly up to about 55 V, before reaching a maximum of 60 V, and then decreases gradually until a steady-state value of 53 V is naturally taken up. Over this period, a porous alumina grows with a constant rate up to the underlying tungsten. According to these current density and film thickness, after 5 min of galvanostatic anodizing the alumina barrier layer reaches the tungsten metal and the voltage begins to increase. Practically, 0.1-0.2 V rise is enough to distinguish this moment and then the process is switched into potentiostatic mode and anodizing is carried out until the current lowered to its leakage value. During this period, oxidation of the underlying tungsten occurred through the pores in the alumina film, and an array of the nanosized tungsten oxide hillocks was formed at the W-Al interface.
- **Third**, after electrochemical treatments, the samples were rinsed with deionized water and dried with N_2 stream.

Schematic sketches of nanostructured film formation

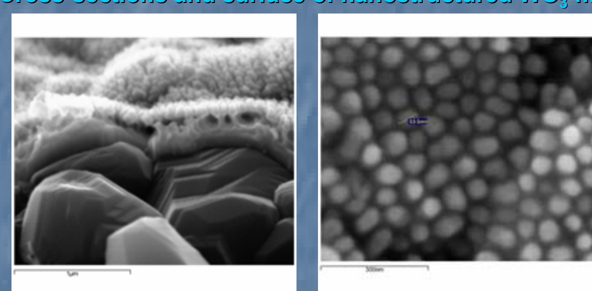




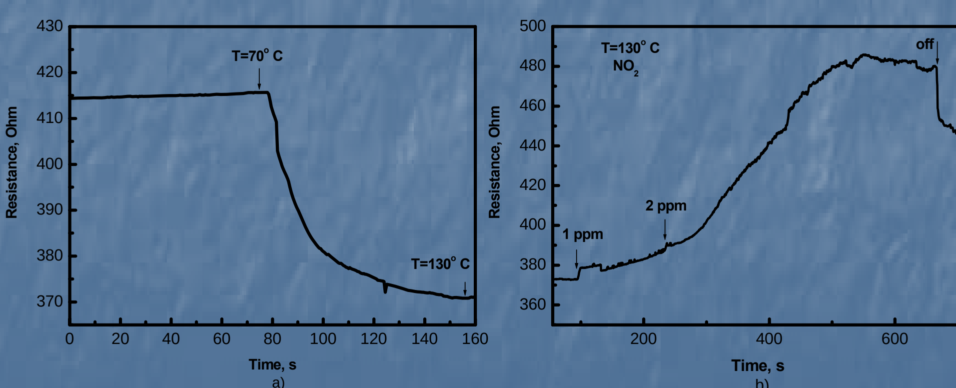
Investigation of sensor structures

The physical properties and chemical response of the tungsten oxide films to nitrogen dioxide were investigated. The films were kept in a temperature and moisture controlled test chamber. The resistance of the films in the presence of either pure air or the different pollutants at the different concentrations was monitored and stored in a PC.

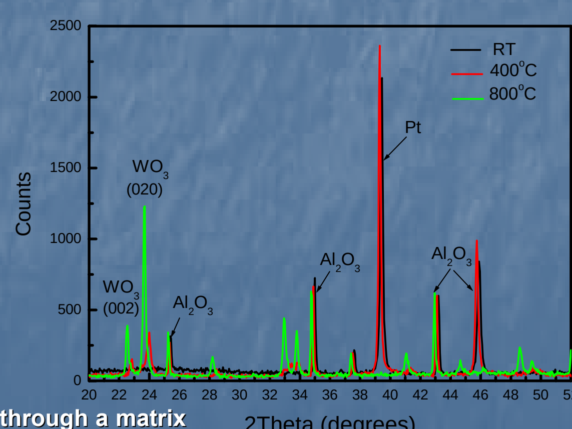
Cross-sections and surface of nanostructured WO_3 film



Temperature (a) and chemical (b) responses of tungsten oxide films



X-ray diffractogram of tungsten oxide film annealed in N_2



- **Conclusiones** After electrochemical processing the tungsten film was fully oxidized through a matrix of alumina. In the result of volumetric growth, the tungsten oxide has filled in the bottom parts of alumina pores and has got the form of hillocks. The tungsten oxide films were low-resistance semiconductors with n-type of the conductivity and had the chemical response to NO_2.

References

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[2] H. Tsuchiya, J. M. Macak, I. Sieber, L. Taveira, A. Ghicov, K. Sirotna, P. Schmuki; *Electrochemistry Communications*, 7 (2005), pp. 295-298.