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Porous-alumina-assisted formation of 3-D nanostructured niobium oxide films for advanced sensing applications

A. Mozalev[a,*], R. M. Vazquez[b], M. Bendova[c], Z. Pytlicek[a], E. Llobet[b], J. Hubalek[a,c]

[a]*Central European Institute of Technology (CEITEC), Brno University of Technology (BUT), Technicka 10, 61600 Brno, Czech Republic*
[b]*MINOS-EMaS, University Rovira i Virgili, Av. Paisos Catalans 26, 43007 Tarragona, Spain*
[c]*Centre of Sensor, Information and Communication Systems, Faculty of Electrical Engineering and Communication, BUT, Brno, Technicka 10, 61600 Brno, Czech Republic*

Abstract

Here we synthesize a 3-D metal/oxide/metal nanostructured film that merges the benefits of advanced nanocomposite inorganic materials with the flexibility of nonlithographic electrochemical technologies based on so-called porous-anodic-alumina-assisted anodizing of a refractory metal and the point electrodeposition of noble metals. The film is composed of a thin niobium oxide layer with spatially-ordered upright-standing niobium oxide nanocolumns, assembled between the two parallel electrodes, which work as long aspect ratio semiconducting nanochannels whose resistivity is greatly impacted by chemisorption reactions when a gas interacts with the film. A laboratory gas sensor employing the film, assembled on a standard TO-8 Metal Can Package, shows superior characteristics for H_2 and especially C_2H_5OH detection.

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Keywords: niobium oxide, anodizing, porous alumina, 3-dimentional nanostructure, hydrogen, ethanol, gas sensor

1. Introduction

Nanostructured niobium oxide semiconductor is attracting growing interest as active layer for chemiresistive gas sensors. Resent reports on the advanced gas sensing properties of 2-D films built up of nanowires or nanotubes *via* direct anodization and thermal oxidation of Nb foils [1] have inspired us to develop an alternative electrochemistry-based technology for well-controlled niobium-oxide columnlike nanostructured sensing films *via* anodizing Al/Nb

*Corresponding author. Tel.: +420 541146194
E-mail address: alexander.mozalev@ceitec.vutbr.cz

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bilayers, which proceeds with the formation of nanoporous anodic alumina film followed by the pore-directed oxidation of the underlying niobium metal [2,3]. However, with the *in-plane* conductivity measurements [4], the benefits of upright-standing nanowires might not have been fully realized.

The making of more complex 3-D nanostructured materials is becoming the most competitive area of research, aiming at future nanomaterials with enhanced or unusual properties and for gas sensing devices with further improved performances. Here we advance the approach described in [2,3] and employ the porous-anodic-alumina-assisted anodizing to develop a *3-D columnlike niobium oxide semiconductor nanofilm*, which serves as the highly sensitive and efficient transducer of surface chemical processes into electrical signals, where a change in the conductivity *along* the columns, assembled between the two parallel patterned metal electrodes, is the controlling factor during chemisorption reactions.

2. Experimental

The film formation begins with sputter-deposition of an Al/Nb (aluminium-on-niobium) layers onto an oxide-coated Si wafer. After the Al layer is converted into nanoporous alumina by anodizing in an aqueous acid solution (Fig. 1a) [3], an array of niobium oxide nanosized protrusions forms of the niobium layer under the pores [2]. Then the sample is re-anodized to a higher potential, so as to achieve the pore-directed growth of long aspect ratio niobium oxide nanocolumns reaching the surface of the alumina film (Fig. 1b). Thus, the film comprises an array of alumina-incorporated niobium oxide nanocolumns anchored to a lower, uniform niobium oxide layer having graded oxygen composition [1]. After selective dissolution of the alumina layer, the sample was annealed at 550ºC in a vacuum atmosphere to achieve crystallization of the nanostructured oxide.

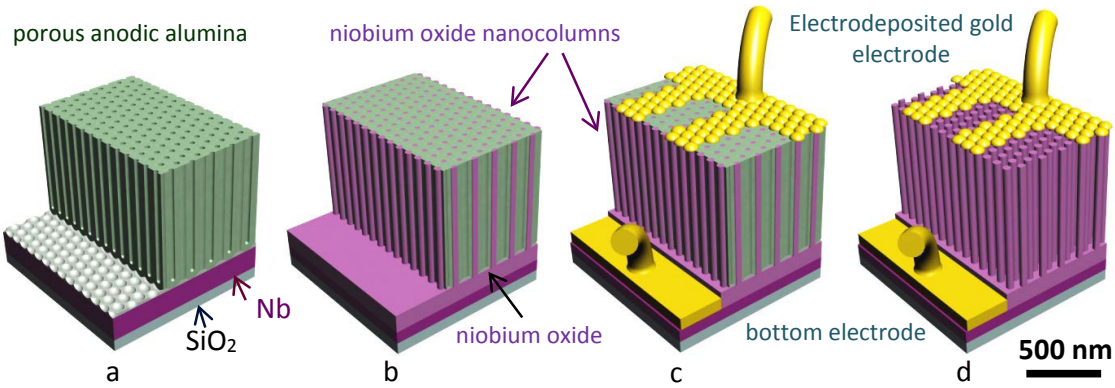

Fig. 1. Schematic for forming a 3-D niobium-oxide-based microsensor: (a) formation of porous alumina by anodizing aluminium layer in an Al/Nb couple sputter-deposited onto an oxide coated Si substrate, (b) anodizing the Nb underlayer through the alumina nanopores to grow niobium oxide nanocolumns in the alumina pores, (c) preparation of top and bottom electrodes *via* the point electrodeposition of Au, (d) selective dissolution of the alumina overlayer

A patterned noble-metal mesh-like electrode was formed on the column tops *via* photolithography and the original point electrodeposition technique (Fig. 1c); then the alumina was selectively dissolved away around and under the top electrodes (Fig. 1d). The formation-morphology-structure relationship for the nanostructured niobium oxide was examined by scanning electron microscopy (SEM) and X-ray diffraction analysis.

The sample was attached to a miniaturized hotplate allowing the operating temperatures up to 350°C and assembled to a standard TO-8 Metal Can Package installed on a printed circuit board set up in an experimental stainless steel chamber for gas sensing experiments, as described elsewhere [3]. Gas sensing tests were performed with a fully automated system by measuring the chemiresistive response of the films to hydrogen gas and ethanol of variable concentrations at various working temperatures. The controlling factor was the resistance measured between the top electrode and the substrate metal; dry air was used as a balance gas.

3. Results

Fig. 2 shows SEM views of the film and a digital photograph of the TO-8 packaged sensors. The length and diameter of nanocolumns may vary, if necessary, in the range of 450-900 nm and 30-80 nm, respectively. The initially amorphous Nb_2O_5 crystallized at 550ºC, while the alumina did not [5], with transformation from dielectric to a semiconductor behavior, as seen in the resistance-temperature curve of (Fig. 3a).

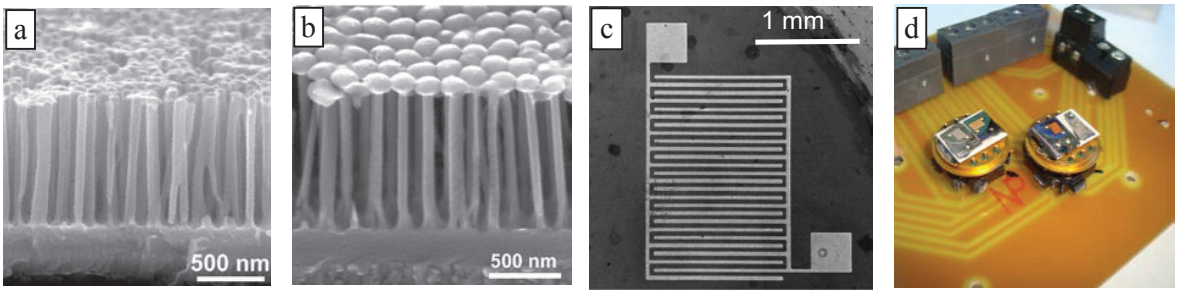

Fig. 2. SEM images of an Al/Nb/SiO_2/Si sample processed to different stages towards making a 3-D metal/oxide/metal nanostructured film as shown schematically in Fig. 1 and laboratory microsensors employing the films as active layers: (a) an array of niobium oxide nanocolumns anchored to a lower niobium oxide layer; (b) a fragment of the array after making a top electrode *via* the point electrodeposition; (c) a top view of the active area of the 3-D nanofilm with the upper Au electrodes. The digital photograph (d) shows test gas microsensors employing the films assembled on standard TO-8 Metal Can Packages mounted on a printed circuit board (before installing in a gas chamber).

As an example, the resistive response to 1000 ppm H_2 at 250ºC and the resistance-concentration dependence are shown in Fig. 4 a and b, respectively. The sensor responded to hydrogen even faster (2 min) at 150ºC but with a longer recovery time. The fastest response measured so far was to 1000 ppm H_2C_5OH (<1 min, not shown). In comparison with the Nb_2O_5 columnlike film tested in the in-plane configuration in our recent works [2, 3], the 3-D Nb_2O_5 nanofilm developed here revealed the extraordinary enhanced thermistor properties, the higher response to H_2 and the greatly improved performance in ethanol detection, that is, incomparably faster response and recovery time. Computer-aided modelling of gas flow through, and interaction with, the film is being in progress to better understand and further advance the sensor performance.

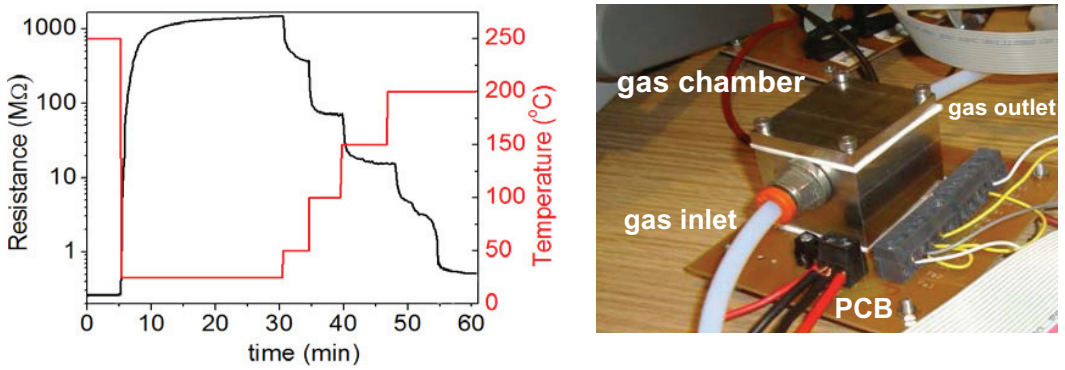

Fig. 3. (a) Resistance-temperature relationship measured for a microsensor employing the 3-D nanofilm, (b) a stainless steel gas chamber hosting a printed circuit board (PCB) with the TO-8 packaged test sensor employing the 3-D nanofilm as active layer.

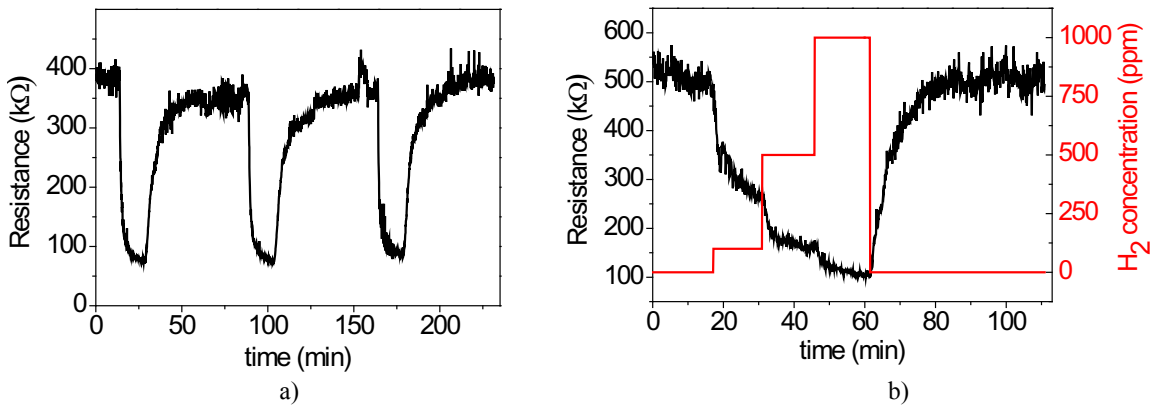

Fig. 4. Resistive response of the 3-D nanofilm (a) to H_2 1000 ppm at operating temperature of 250°C, (b) as a function of hydrogen concentration (0, 100, 500, 1000 ppm) measured at operating temperature of 250°C

4. Conclusions

The porous-alumina-assisted 3-D nanostructured niobium oxide film developed in this work has great potential for use in gas sensing applications. The approach may be applicable to some other refractory valve metals that in principle allow high voltage anodizing, like tungsten or titanium [6]. The technique and materials are potentially compatible with standard Si microtechnologies, which is advantageous for developing low-cost, environmentally friendly solutions for practical micro- and nanodevices [7,8], where the well-defined nano-channels for carriers and surface reactions may bring substantial benefits.

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