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Fast response hydrogen microsensor based on semiconductor niobium-oxide nanostructures via smart anodizing of Al/Nb metal layers

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Abstract

Nanostructured niobium oxide semiconductor is gaining increasing attention as electro-optic and gas sensing material. However, the preparation of stable niobium oxide nanofilm with reproducible morphology and behaviour remains a challenge. Here we describe a rapid and well-controlled approach to synthesize a niobium oxide film with the columnlike nanostructured morphology *via* anodic processing of Al/Nb metal layers sputtered onto an oxide-coated Si wafer. The film is developed due to the growth of a nanoporous anodic alumina layer followed by pore-directed oxidation of the Nb underlayer. The post-anodizing treatment results in the controlled formation of Nb₂O₅ crystal phase, which causes the transformation from dielectric to *n*-type semiconductor behavior of the film. A laboratory gas sensor fabricated by uniting the anodizing approach developed here with standard micromachining technologies shows superior characteristics for hydrogen gas detection, the response-recovery time being among best ever reported.

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1. Introduction

Nanostructured niobium oxide semiconductor is of growing interest as active layer for chemiresistive gas sensing applications [1,2]. Recent reports on the advanced gas sensing properties of nanoporous films *via* direct anodization

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and thermal oxidation of Nb foils [2] inspired us to develop an alternative electrochemistry-based technology for well-controlled niobium oxide nanostructures with tailored morphologies and advanced functional properties in pursuit of fabricating competitive niobium oxide active layers for chemiresistive sensing applications.

2. Experimental

The film formation begins with sputter-deposition of an Al/Nb (aluminium-on-niobium) layers onto an oxidized 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 Nb layer under the pores (Fig. 1b). Then the sample is reanodized to a higher potential [4] so as to achieve pore-directed growth of long aspect ratio niobium oxide nanocolumns (Fig. 1c). After selective dissolution of the alumina layer (Fig. 1d), the columnlike nanofilm is annealed at 650°C to achieve crystallization and phase transition effects in the nanostructured oxide.

The formation-morphology-structure relationship for the film grown was examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. A laboratory scale microsensors fabricated for gas sensing tests comprised pairs of 80- μm spaced interdigitated Pt electrodes placed over the SiO₂/Si-supported niobium oxide nanocolumn array prepared by magnetron sputter-deposition and lift-off photolithography. The sample was cut in several pieces that were then attached to a miniaturized hotplate allowing the operating temperatures up to 350°C (Fig. 1e) and assembled to a TO-8 package (Fig. 2). Gas sensing tests were performed with a fully automated system by measuring the chemiresistive response of the films to hydrogen gas of variable concentrations.

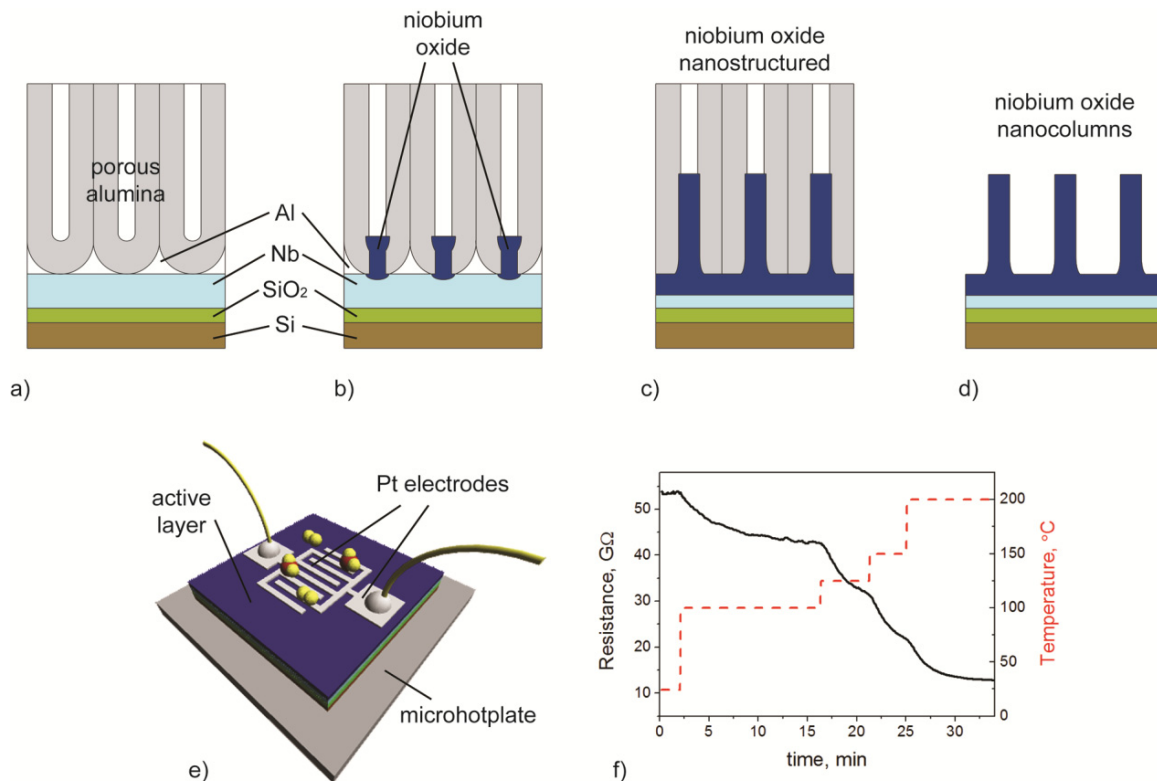


Fig. 1: Schematic for forming a niobium-oxide-based microsensors: (a) formation of porous alumina, (b) anodizing the Nb underlayer, (c) reanodizing the Nb underlayer, (d) dissolution of the alumina overlayer, (e) preparation of a test microsensors and (f) resistance-temperature response of the test microsensors.

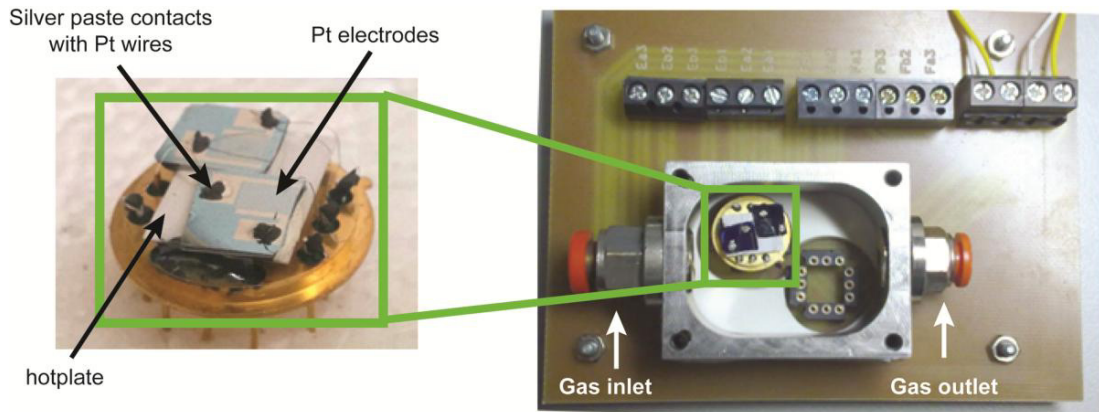


Fig. 2: Digital photographs of samples with the anodic niobium oxide sensing layers mounted on a standard TO-8 package (left) and the TO-8 packaged sensor set up in an experimental stainless steel chamber (the lid is removed for picture taking) installed on a printed circuit board and used for gas sensing tests (right).

3. Results

Typical SEM views of the film surface morphology are shown in Fig. 3. The film is composed of an array of long aspect ratio self-ordered nanocolumns attached to an anodic oxide compact layer. The length and diameter of nanocolumns may vary, if necessary, in the range of 450-600 nm and 30-50 nm respectively.

From the XRD analysis, the initially amorphous niobium oxide film crystallized to orthorhombic Nb_2O_5 phase (space group Pbam) due to the annealing in air, with the transformation to n -type semiconductor behavior (Fig. 3).

The gas sensing properties were carried out by measuring the resistance between the $80\ \mu\text{m}$ interdigitated electrodes formed over the sensing film in the presence of different concentrations of hydrogen gas using dry air as a balance gas. From the measurements, sensor response was calculated as the ratio of the sensor resistance in air (R_{air}) over the resistance in the presence of gas (R_{gas}). The sensor response to 1000 ppm H_2 at operating temperature of $250\ ^\circ\text{C}$ and the response-concentration behaviour are shown in Fig. 4.

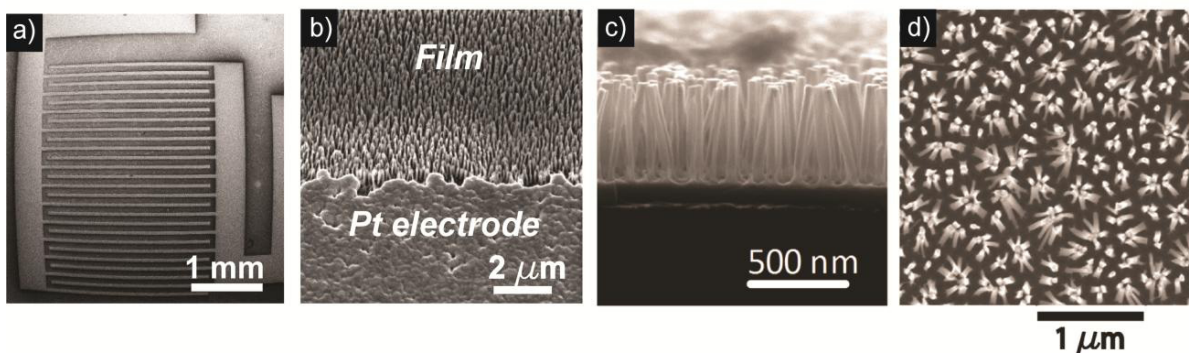


Fig. 3: SEM images of a niobium oxide gas sensing film (a, b) together with interdigitated Pt electrodes and (c, d) between the electrodes. The film was synthesized *via* anodizing of sputter-deposited Al/Nb metal layers at 45 V in 0.9 M $\text{H}_4\text{C}_3\text{O}_4$ aqueous solution followed by reanodizing to 300 V.

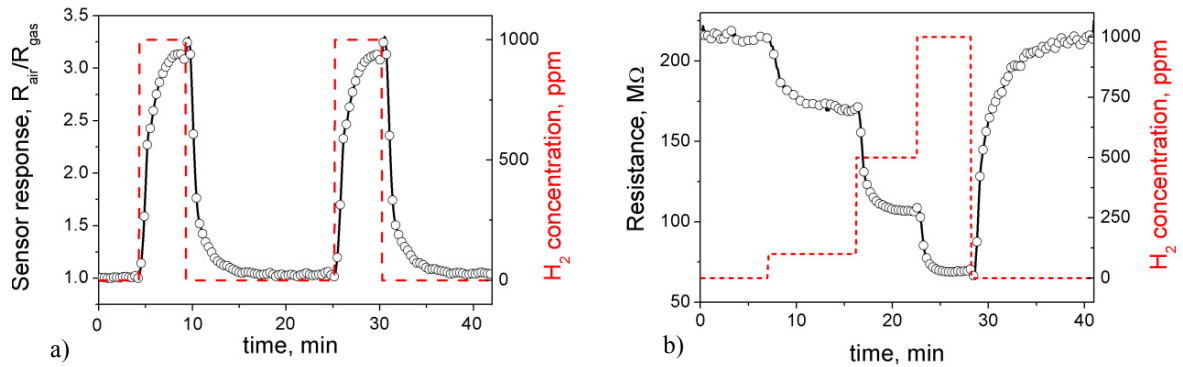


Fig. 4: a) Sensor response to 1000 ppm H₂ at operating temperature of 250°C, defined as the ratio of the sensor resistance in a dry air atmosphere (R_{air}) to the sensor resistance in the presence of H₂ (R_{gas}); b) Sensor resistance as a function of hydrogen concentration (100, 500, 1000 ppm) measured at operating temperature of 250°C.

The fast sensor response (< 1 min), with a rapid recovery and a stable baseline, characterizes the niobium oxide based sensor as one of the fastest among nanostructured metal-oxide H₂-sensing films [1,2]. Further, the sensor resistance appeared to be well-dependent on the hydrogen concentration, with the detection limit not worse than 100 ppm; no measurements have yet been performed in the lower concentration range. The achievement is due to the periodic 2-D nanosized morphology of the niobium oxide film, the nanocrystalline structure and the graded chemical composition, complemented by a substantially enlarged surface-to-volume ratio of the film, all contributing to increasing the rate of adsorption and diffusion processes and enhancing the redox reactions between the oxide and gaseous species and making the whole film volume involved in interaction with hydrogen.

4. Conclusions

In this work, a crystalline self-ordered niobium oxide nanostructured film has been synthesized *via* the smart anodizing of sputter-deposited Al/Nb metal layers combined with the high temperature annealing. A test microsensor employing the film showed fast response and recovery of the initial baseline in a hydrogen atmosphere. The sensor is being tested in more gases to examine the ability of the film to discriminate the different gaseous species, which are present, for instance, in direct-ethanol fuel cells.

Acknowledgements

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