Journal of Physics: Conference Series

PAPER • OPEN ACCESS

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IOP Conf. Series: Journal of Physics: Conf. Series **987** (2018) 012006 doi:10.1088/1742-6596/987/1/012006

Niobium oxide nanocolumns formed via anodic alumina with modulated pore diameters

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Abstract. Niobium oxide nanocolumns with modulated diameters were formed for the first time. An Al/Nb bilayer specimen was prepared by successive sputter-deposition of 300 nm niobium layer and 1200 nm aluminum layer onto silicon wafer. Regular anodic alumina matrix with modulated pore diameters was formed by sequential anodization of initial specimen in tartaric acid at 180 V, and in oxalic acid at 37 V. Further potentiodynamic reanodization of the specimen up to 400 V causes the simultaneous growth of 440 nm continuous niobium oxide layer beneath the alumina film and two types of an array of oxide nanocolumns (thick – with 100 nm width and 630 nm high and thin – with 25 nm width and 170 nm high), which are the filling of the alumina pores. The morphology of the formed anodic niobium oxide nanocolumns with modulated diameters was determined by field emission scanning electron microscopy. The formed nanostructures can be used for perspective devices of nano- and optoelectronics such as photonic crystals.

1. Introduction

The porous anodic alumina (PAA) is characterized by uniform cylindrical pores, which allow it to be used as a matrix for template synthesis of arrays of different nanostructures. Manipulation of the size, position and regularity of the pores allow forming conceptually new structures on its base with a wide range of applications [1]. The most promising are PAA with modulated pore diameters and structures based on it. PAA templates with unusual and complex shape of channels can be synthesized by anodic oxidation of aluminum substrates [2]. Works of the some authors [3, 4] revealed that anodic processing of a niobium layer covered with a relatively thick layer of aluminum in certain electrolytes for PAA formation under appropriate conditions results to the formation of metal oxide "nanocolumns" which represent nanostructured niobium oxide. Such nanostructures have unique properties and can be used for functional applications in devices with improved characteristics [4].

This paper presents the first result of formation of niobium oxide nanocolumns with variable diameters by high-voltage reanodization via PAA matrix with modulated pore diameters. The morphology properties of the synthesized niobium oxide nanostructures are determined by the means of field emission scanning electron microscopy (SEM).

2. Experimental

The initial substrate was double-side polished *n*-type Si wafer, 4" in diameter, 300 µm thick, with (100) crystal orientation and 4-40 Ω/□ resistivity, covered by 200 nm layer of thermally grown SiO_2.

Layers of 300 nm niobium and 1200 nm aluminum were successively deposited on the Si wafer by radio-frequency magnetron sputtering (Figure 1, a). The wafer was cut into pieces of ca. 1×2 cm which were individually anodized in specially designed two electrode cell. The programmable power supply Keysight N5751A was used as the anodization unit. Regular PAA matrix with modulated pore diameters was formed by sequential anodization of the aluminum layer in aqueous solutions of 0.2 mol·dm^{-3} tartaric acid ($C_4H_6O_6$) at 180 V (Figure 1, b) and in 0.4 mol·dm^{-3} oxalic acid ($H_2C_2O_4$) at 37 V (Figure 1, c). Array of niobium oxide nanocolumns was formed by high-voltage reanodization of the niobium layer via PAA matrix in the mixed solution of 0.5 mol·dm^{-3} boracic acid (H_3BO_3) and 0.05 mol·dm^{-3} sodium tetraborate ($Na_2B_4O_7$) in potentiodynamic mode at increase of potential until 400 V (Figure 1, d, e). The temperature of electrolytes was maintaining within ±1°C of the set value during anodization process. After formation of niobium oxide nanocolumns PAA matrix was selective dissolved in aqueous solution of 50% phosphoric acid (H_3PO_4) at 50°C (Figure 1, f).

The main stages of the growth of Nb_2O_5 nanocolumns via PAA matrix, with the relation between the film layers, are depicted in Figure 1.

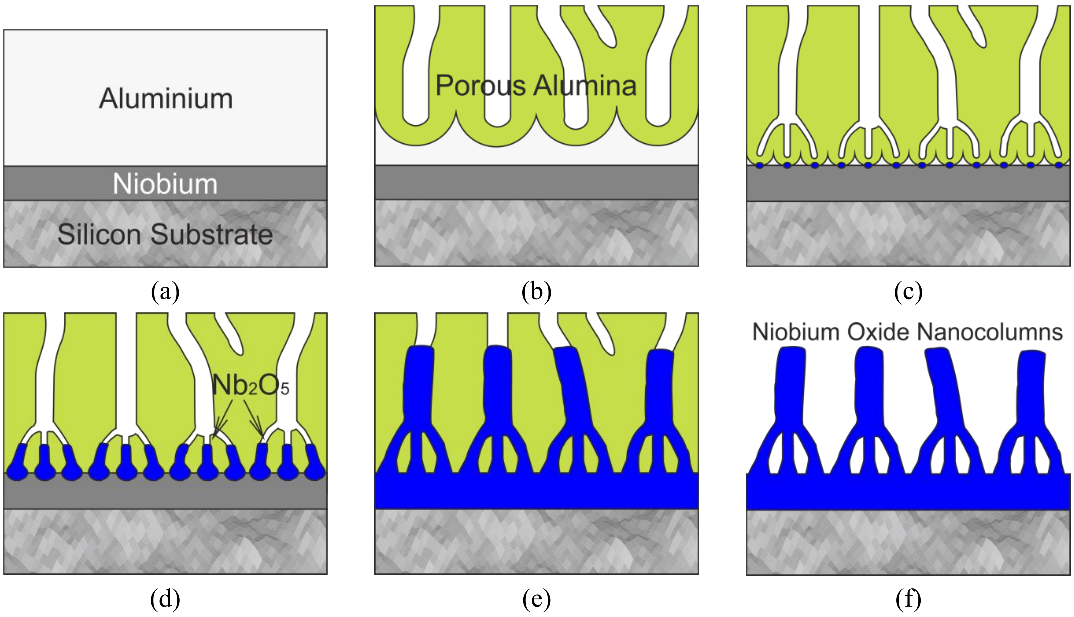

Figure 1. The main phases of the formation process of Nb_2O_5 nanocolumns via anodic alumina matrixes with modulated pore diameters: sputter-deposition of Al/Nb bilayer on SiO_2/Si substrate (a), growth of porous alumina film (b), anodization of the niobium underlayer through the alumina nanopores (c), growth of thin niobium oxide nanocolumns in the alumina pores (d), growth of thick niobium oxide nanocolumns in the alumina pores (e), dissolution of the alumina ("alumina-free" sample) (f).

3. Results and discussion

Figure 2, a–c shows SEM images of the surface and cross-section view of the anodic niobium oxide nanocolumns with modulated diameters which were formed from the initial Al/Nb bilayer sputtered on SiO_2/Si substrate. Three layers can be distinguished on the SEM image. An upper layer comprises the thick nanocolumns of niobium oxide. A middle layer comprises the thin niobium oxide nanocolumns. The lower layer is a strip of continuous niobium oxide, approximately 440 nm in thickness, is lying between the SiO_2/Si substrate and the columnar layers. The material of nanocolumns is about 800 nm in height is pulled out of the band outwards at intervals and generally similar in contrast to the band.

The deposited niobium was completely consumed as a result of the anodization. A schematic view of the array of niobium oxide nanocolumns, which elucidate the layered film structure, is drawn in Figure 2, d. The average diameters (diameters of the equivalent circle) and the height of the niobium oxide nanocolumns were estimated using the electron micrographs in Figure 2 and other numerous images of re-examined samples (not shown). The average diameters of the thick niobium oxide nanocolumns are about 100 nm. The height of the upper layer which comprises these thick nanocolumns is about 630 nm. The average diameter of the thin niobium oxide nanocolumns which is located in the middle layer is about 25 nm and their height is about 170 nm.

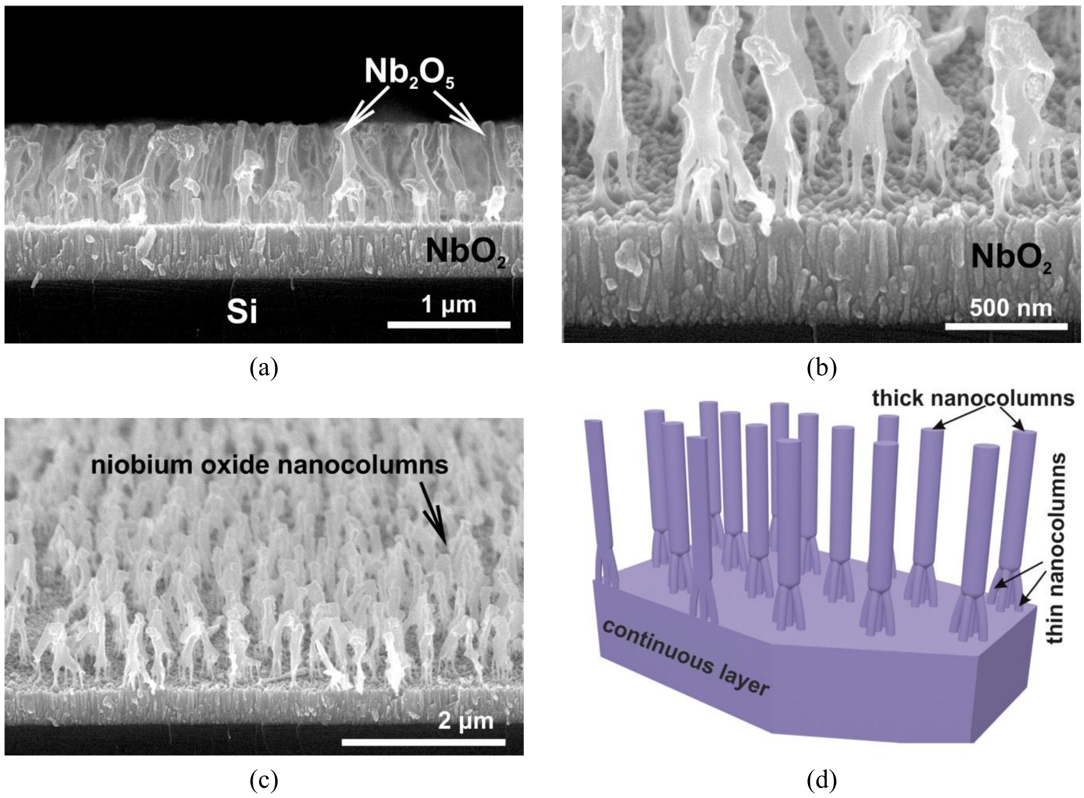

Figure 2. Scanning electron microscope images (a–c) and schematic view (d) of arrays of niobium oxide nanocolumns on Si-substrate formed by sequential anodization at 180 V in 0.2 mol·dm^{-3} $C_4H_6O_6$ and at 37 V in 0.4 mol·dm^{-3} $H_2C_2O_4$ with subsequent reanodization in 0.05 mol·dm^{-3} H_3BO_3+$Na_2B_4O_7$ at 400 V; all images of shown nanostructures were obtained after the alumina layer has been dissolved away ("alumina-free" samples).

Most of the nanocolumns appear to be broken or have an irregular structure and an uneven diameter. The three-step anodizing method, which is generally used in accordance with the procedure set forth in Ref. [5], will improve the regularity of niobium oxide nanocolumns.

4. Conclusions

In our work to date we had successfully formed anodic niobium oxide nanocolumns with modulated diameters by sequential anodization and high-voltage reanodization of the sputter-deposited Al/Nb metal layers via the anodic alumina matrix. The formed nanocolumns have the unordered structure because anodization of aluminum was carried out in one step without preliminary structuring of the surface. The additional ordering of the aluminum layer by the three step anodization will make it possible to form regular matrixes of the anodic aluminum oxide and produce high-ordered nanocolumns on their basis. Such approach to the formation of nanostructures have great practical importance, because used methods are technically simple, well reproducible, cost-effective and environmentally responsible, ecologically-friendly. Shown methods also can be used for the growing of metal-oxide nanostructures on transition metals and their alloys for various potential applications. The formed structures can be used as photonic crystals, autoemission elements and functional applications of perspective devices of nano- and optoelectronics.

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