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Study of metal pillar nanostructure formation with thin porous alumina template

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ABSTRACT

In the present paper, the nickel pillared nanostructure fabrication by electrochemical deposition of Ni into the pores of thin porous anodic alumina is considered. The main characteristics of these structures, obtained by scanning electron microscopy and atomic-force microscopy, are presented. Information on geometrical parameters of porous host and pillar nanostructure elements has been obtained. The influence of the barrier layer thinning at the pore bottom on nucleation and growth of the ordered metal nanopillars is discussed. The process of functional layer formation based on thin aluminum and Al_2O_3 films with incorporated nickel pillars is analyzed. This process may be used for fabrication of advanced high density magnetic memory devices.

1. Introduction

Recently, porous anodic alumina (PAA), produced by electrochemical anodizing, has attracted great interest owing to its potential use as the template under fabrication of nanocomposite materials with ordered structure [1–5] to produce nanostructures and nanoelectronic devices: high density magnetic memory [6,7], single-electron devices [8], nanoemitters in liquid-crystal display [9], etc.

The ordered matrices of porous anodic alumina have been reported firstly by Masuda et al. in 1995 [10]. Earlier, pillar microstructure formation with anodic oxides was reported in 1989 [11] and later in [12,13]. Fabrication of nanostructures using PAA as a mask or as a template is cheaper than for e-beam lithography [14]. When using such templates, the pores are filled, basically, by electrochemical deposition of conducting or semiconducting materials. Despite other deposition methods, like chemical vapor deposition and vacuum deposition, the growth of a nanowire (replicating the pore configuration) during electrochemical deposition starts at the pore bottom and continues to the pore top. However, it is necessary to mean that there is a rather thick barrier layer at every pore bottom (Fig. 1b, c). Its thickness is set by the template fabrication conditions and is proportional to the anodizing constant of aluminum in this specific electrolyte (i.e., 1.0 to 1.3 nm per volt of anodizing potential) [15]. Therefore, the step of local removal of the barrier layer at the pore bottom — i.e., the barrier layer thinning — presents one of critical operations during fabrication of nanostructures by this technique.

Until now, the two different methods have been developed to achieve uniform and complete pore filling by means of electrochemical deposition [16–19]. In the most cases, a direct current deposition (dc-deposition) into the thick porous alumina membrane is used. The membrane is produced by detaching of PAA from aluminum substrate followed by the barrier layer removal using selective chemical etching [20,21]. As a final pre-treatment step before the filling process, a metal contact is vacuum deposited onto one side of free standing alumina membrane. This technique is only applicable for free standing alumina films (membranes) of more than 20 μm thickness (50–80 μm, as a rule) which are stable enough to be handled under subsequent processing. At the same time, for the most of the above mentioned nanostructure applications, a thin porous alumina of few hundred nanometers to some micrometers thickness is required. Such oxide is formed on thin aluminum films vacuum-deposited onto silicon or dielectric substrates [22]. In this case, thin film of porous alumina shall remain on a substrate.

When using the method of alternating current electrochemical deposition (ac-deposition), porous Al_2O_3 remains on the aluminum substrate (foil), and subsequent metal is deposited onto the barrier layer at high cathode potentials [23,24]. However, high cathode potential causes intensive release of hydrogen in aqueous deposition solutions, which inhibits deposition onto the pore walls, especially for the high aspect ratio (the pores' vertical to horizontal dimensions ratio) template.

Later, the methods of pulse electrodeposition [25–27] and pulse electrodeposition with pauses between the pulses of different polarity [28] have been developed which allow deposition into the high aspect ratio templates. The latter method is applied in combination with two-step anodizing process to fabricate hexagonally ordered porous alumina template [29,30]. The barrier layer at the

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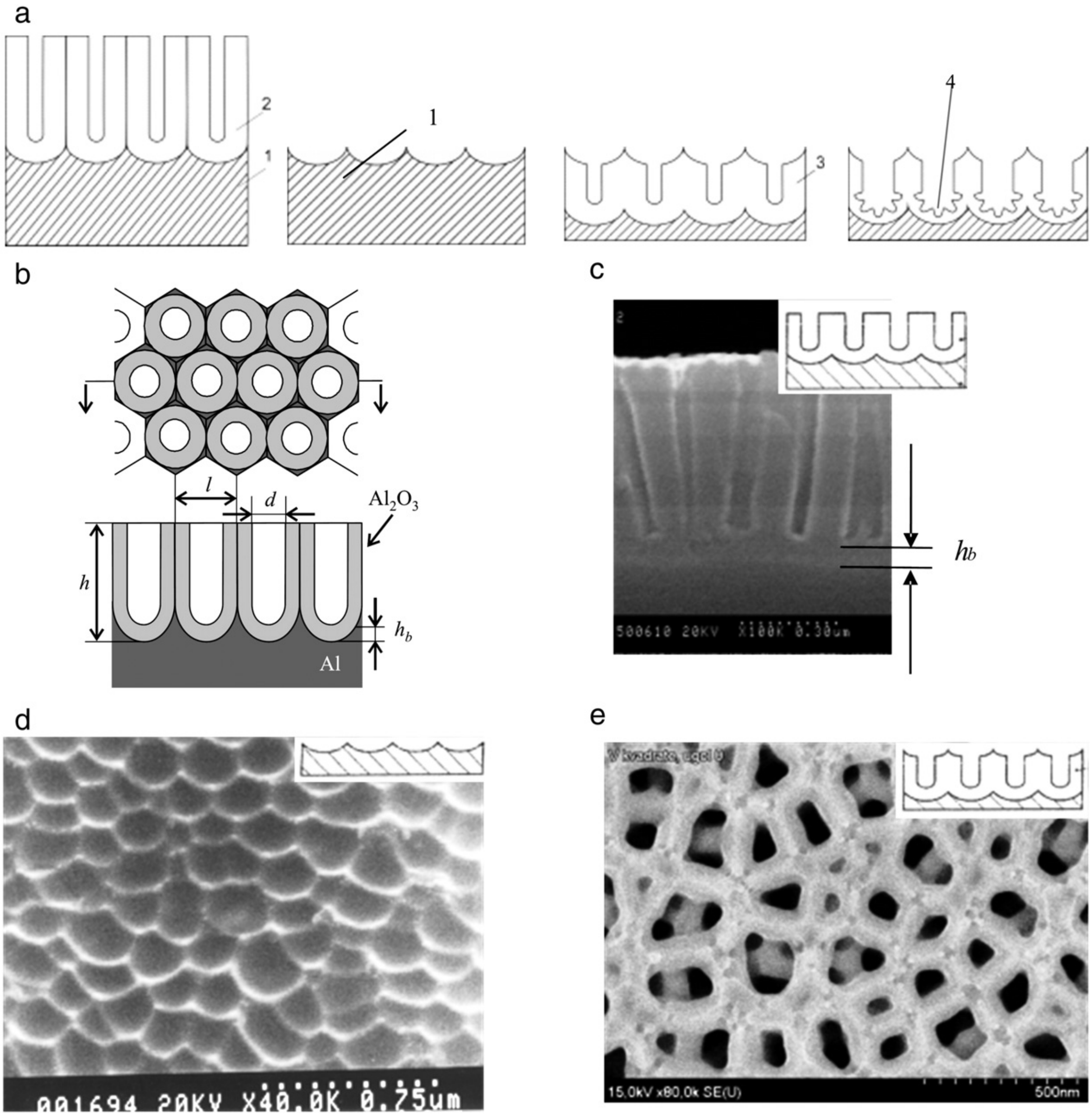

Fig. 1. The scheme of experimental sample fabrication: two-step anodizing of Al thin films (a); schematic image of porous alumina (b); SEM image of PAA chip obtained at the first stage (c); SEM view of the surface of Al film after etching the porous alumina fabricated at the first stage (d); SEM image of porous alumina surface formed by two-step anodizing (e).

pore bottom is thinned by chemical pore widening and subsequent step-by-step reducing of the anodizing current density [28]. The method allows using thin PAA templates without separating them from a substrate.

Publication analysis of various modes of electrochemical deposition into PAA templates non-separated from the substrate has shown that the procedure of the barrier layer thinning at the pore bottom impacts substantially on uniformity of geometrical sizes of the formed pillars and on the deposition process itself.

In the present paper, the method of nickel nanopillar array formation by means of electrochemical deposition of nickel into the thin porous anodic alumina not separated from substrate is considered. Various modes of barrier layer thinning at the pore bottom are compared and their influence on nickel nanopillar formation in the pores is discussed. The latter has been investigated by imaging the nanopillars array with atomic-force microscopy (AFM) after the template removal.

Table 1
The main parameters of the anodizing process for two type specimens.

Electrolyte		10 wt.% aqueous solution of sulfuric acid	3.6 wt.% aqueous solution of oxalic acid
Parameter	Designation	Type I	Type II
Anodizing voltage (step 1 and step 2)	V^1_a, V	12	40
Anodizing duration (step 1)	t^1_a, min	15	15
Anodizing duration (step 2)	t^2_a, min	10	10
Electrolyte temperature	T_a, °C	15	15
Thickness of the oxide (step 1)	h_1, nm	550	450
Thickness of the oxide (step 2)	h_2, nm	500	400
Aspect ratio	β	22	10
Thickness of the barrier layer	h_b, nm	12	40
Average pore diameter[a]	d, nm	20	40

[a] before thinning process.