Applied Surface Science 256 (2010) 7700–7705

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The use of Reactive Ion Etching for obtaining "free" silica nano test tubes

Fatih Buyukserin [a,*], Charles R. Martin [b]

[a] Nanomedicine and Advanced Technologies Research Center, Gazi University, Ankara 06830, Turkey
[b] Department of Chemistry and Center for Research at the Bio/Nano Interface, University of Florida, Gainesville, FL 32611-7200, USA

ARTICLE INFO

Article history:
Received 3 May 2010
Received in revised form 11 June 2010
Accepted 12 June 2010
Available online 19 June 2010

Keywords:
Reactive Ion Etching
Nanoporous alumina
Silica nano test tubes
Ar plasma
Surface sol–gel

ABSTRACT

Silica nano test tubes are one-dimensional inorganic nanostructures with several biotechnological applications including biosensing, magnetic resonance imaging, and targeted cancer therapeutics. They are generally prepared by sol–gel deposition of silica to nanoporous alumina templates. Preparing samples composed of isolated free silica nano test tubes can be a challenging process due to the conformal coating of silica on the template. This causes the formation of a top-surface silica layer which laterally connects the nano test tubes. Herein, we detailed the use of Reactive Ion Etching to remove this top-surface silica layer which yields free silica nano test tubes with template dissolution. Compared with the mechanical polishing approach, Reactive Ion Etching treatment allows a fine manipulation ability of the surface material at the nanoscale level. When used excessively, Reactive Ion Etching causes an orifice closing phenomenon that may be employed to create novel one-dimensional nanocapsules.

1. Introduction

One-dimensional (1D) nanostructures are of great interest in both fundamental and applied sciences due to their unique thermal, electrical, mechanical, and optical properties [1–3]. Several applications that mainly focus on the enhanced electrical and optical properties of these structures have been successfully demonstrated [3,4]. In addition to these unparalleled physical features, recent research is starting to demonstrate the remarkable biological properties of 1D nanostructures. For instance, 1D filomicelles persisted much longer in blood circulation [5], and dextran-coated 1D iron oxide "nanoworm" particles showed increased accumulation and retention at tumor sites compared with their spherical counterparts [6]. Much larger cell internalization rates for 1D polymeric nanorods were also observed when compared with cubical particles [7]. These studies have provided a compelling motivation for the employment of 1D nanostructures in the biomedical research field.

Silica nanotubes and nano test tubes [8–10] are 1D inorganic nanostructures that are typically prepared by the template synthesis method [11,12]. They present various advantages for potential biological applications such as facile surface functionalization, loadable large hollow interior, minimal cytotoxicity, and ease of dispersion [8,10,13]. Moreover, the template synthesis allows the fabrication of multifunctional nanotubes/test tubes by the differential modification [13] of the inner vs. outer surface of the tube walls. Multifunctional silica nanotubes have been successfully employed for biomolecule separation [13] and gene delivery [14]. The latter application, however, is more suited for silica nano test tubes [15,16] which are open at one end and closed at the other (Fig. 1). Various strategies have been developed to cap the open end of the test tube for gene/drug delivery applications. These include capping by self-assembled latex particles via imine bond formation [15], selective Au growth at the open ends of the test tube [17], and mechanical hammering of an evaporated Au layer to fill in the tube opening [18]. Multifunctional silica nano test tubes have also been successfully used for biosensing [19], magnetic cell labeling [20], and selective cancer cell recognition [21].

Majority of these studies utilized the surface sol–gel method [22] in nanoporous alumina membranes [23] to obtain the silica nano test tubes. The surface sol–gel method involves the layer-by-layer deposition of Si with a fine thickness control (~1 nm/deposition cycle), and the alumina membrane provides arrays of monodisperse pores that act as the template. Preparing free silica nano test tubes is not a straight-forward process, however, due to the conformal coating of the silica material on both the template pores as well as the top surface [16,21]. Unless removed, this top silica film causes the formation of joint test tubes with template dissolution (Fig. 1a). Mechanical polishing [16,18,20] is typically applied to remove this surface layer which can be considered as a relatively harsh method considering the μ-scale of the employed alumina beads vs. the nanoscale dimensions of the template as well as the resultant test tubes.

* Corresponding author. Tel.: +90 312 4846270; fax: +90 312 4846271.
E-mail address: fatih.buyukserin@gazi.edu.tr (F. Buyukserin).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.06.040

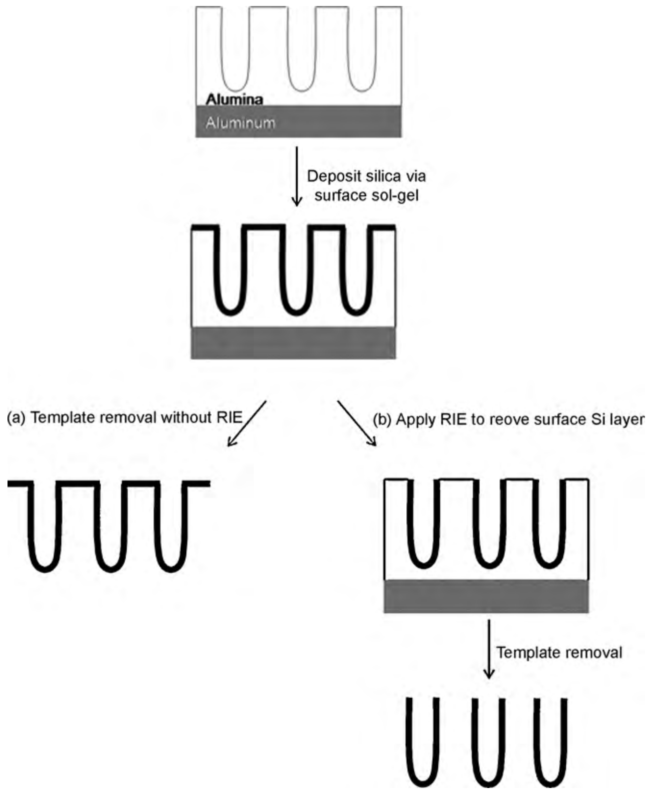

Fig. 1. The rationale for using RIE to obtain "free" silica nano test tubes. (a) After the silica deposition to alumina template, the membrane is dissolved that results in joint silica test tubes. (b) The silica deposited on the template surface is removed by RIE. Subsequent dissolution of the template liberates free silica nano test tubes.

Reactive Ion Etching (RIE) is a powerful method to create anisotropic structures in the integrated circuit industry [24,25] and to form templates for the preparation of organic [26] and inorganic [27] 1D nanostructures. We have recently introduced the use of RIE as an alternative approach to obtain free silica nano test tubes (Fig. 1b) [21]. Ar plasma etching (sputter etching) is used to remove the aforementioned top-surface silica layer via physical etching [24] mainly by Ar^+ ions. In this study, we present the details of Ar plasma use by providing comparative tube release studies with and without plasma treatment, and by demonstrating the formation of independent unconnected test tubes without the total dissolution of the template membrane. The influence of extensive etching has also been investigated which revealed a closing mechanism effective at the test tube orifice.

2. Experimental details

2.1. Preparation of the nanopore alumina template membrane

We have used the two-step electrochemical anodization method [23] to obtain highly ordered nanopores in thin alumina films. It involves the long anodization of high purity polished aluminum films that allows self-organization of pores and homogenization of the pore size within the thick oxide layer. An indentation is created on the Al surface corresponding to each pore. When this alumina layer is dissolved and regrown for a second time under the same anodization conditions, pores nucleate from those indentions, creating highly ordered arrays of monodisperse pores.

Aluminum foil (99.99%) was sanded with 600 grit sand paper, cleaned with purified water and then annealed at 400 °C. After cooling, it was subjected to electropolishing at 15 V for 30 min using a Pb cathode. The electropolishing solution was kept at 70 °C during this process and it was composed of 95 wt% H_3PO_4, 5 wt% H_2SO_4 and

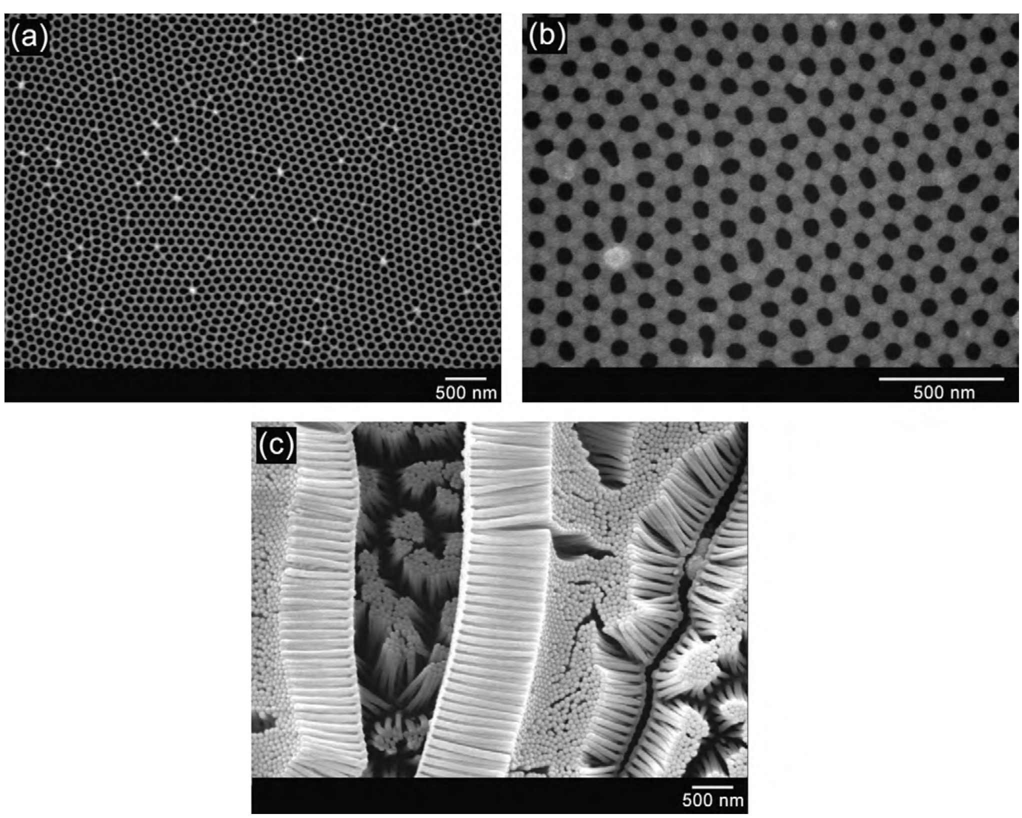

Fig. 2. SEM images of (a) unmodified alumina template, (b) silica-deposited alumina template after 10 deposition cycles, (c) joint silica nano test tubes after complete template dissolution.