Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thin Solid Films 495 (2006) 149 – 153

thin solid films

www.elsevier.com/locate/tsf

Functional nanostructured titanium nitride films obtained by sputtering magnetron

O. Sánchez [a,*], M. Hernández-Vélez [a,b], D. Navas [a], M.A. Auger [c], J.L. Baldonedo [d], R. Sanz [a], K.R. Pirota [a], M. Vázquez [a]

[a] *Instituto de Ciencia de Materiales de Madrid (CSIC), c) Sor Juana Inés de la Cruz n°3, Cantoblanco, 28049 Madrid, Spain*
[b] *Dept. Física Aplicada C-XII, Universidad Autónoma, Cantoblanco 28049 Madrid, Spain*
[c] *Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio, del Amo 8, 28040 Madrid, Spain*
[d] *Centro de Microscopia Electrónica y Citometría de la Universidad Complutense de, Madrid, Spain*

Available online 16 September 2005

Abstract

Development of new methods in the formation of hollow structures, in particular, nanotubes and nanocages are currently generating a great interest as a consequence of the growing relevance of these nanostructures on many technological fields, ranging from optoelectronics to biotechnology. In this work, we report the formation of titanium nitride (TiN) nanotubes and nanohills via reactive sputtering magnetron processes. Anodic Alumina Membranes (AAM) were used as template substrates to grow the TiN nanostructures. The AAM were obtained through electrochemical anodization processes by using oxalic acid solutions as electrolytes. The nanotubes were produced at temperatures below 100 °C, and using a pure titanium (99.995%) sputtering target and nitrogen as reactive gas. The obtained TiN thin films showed surface morphologies adjusted to pore diameter and interpore distance of the substrates, as well as ordered arrays of nanotubes or nanohills depending on the sputtering and template conditions. High Resolution Scanning Electron Microscopy (HRSEM) was used to elucidate both the surface order and morphology of the different grown nanostructures. The crystalline structure of the samples was examined using X-ray Diffraction (XRD) patterns and their qualitative chemical composition by using X-ray Energy Dispersive Spectroscopy (XEDS) in a scanning electron microscopy.

Keywords: Sputtering; Nanostructures; Nanotubes; TiN; AAM

1. Introduction

The development of processes to fabricate functional nanostructured materials with characteristic dimensions in the nanometric scale is one of the main interesting subjects in the current Material Science field. In order to succeed in this goal, numerous Lithographic strategies [1], self-assembly [2] methods, and others have been used. Nevertheless, any of those methods has advantages and disadvantages depending on the feature sizes, the degree of ordering and the material to be used.

Concerning the material type, ceramics and particularly, metal nitrides are characterized by a combination of properties that makes them extremely suitable for manufacturing diverse miniaturised devices, e.g. microelectromechanical systems (MEMS) [3,4]. High thermal stability, hardness, corrosion resistance even in aggressive environments, low chemical reactivity and other functions such as, piezoelectricity, pyroelectricity and catalytic activity make ceramics' advantageous materials respect others for MEMS fabrication [5]. However, in spite of these attractive qualities, there exist many difficulties for sintering and forming pure nitrides mainly due to their covalent bonding, high melting points and, in general, the high impurity content of the products available in the market.

An interesting application of ceramic surfaces is related to its application as stamps in imprinting processes [6] due to its desired hydrophobicity and durability for multiple-use as master molds. Development of new methods in the formation of hollow structures, in particular, nanotubes, nanocages and nanodots are currently generating much interest as a consequence of the growing relevance of these ceramic nanostructures on many technological fields, ranging from optoelectronics to biotechnology [7].

* Corresponding author. Tel.: +34 91 3349078; fax: +34 913720623.
E-mail address: olgas@icmm.csic.es (O. Sánchez).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.08.203

Nowadays, there are very few reproducible techniques for patterning hard ceramic surfaces or building structures under the micron scale and even more under the 100-nm scale. At the beginning the most commonly used approaches for patterning hard material and ceramic surfaces were the hard-lithographic techniques [8–10]. Focused ion beam lithography has been widely used for surface patterning of diamond and diamond-like materials [11] and TiN [12]. Otherwise, laser micro-machining and laser induced CVD have been the chosen techniques for patterning hard ceramics such AlN [13] or TiN [14]. Other approaches are based in arc-discharge and laser ablation methods, in which the main disadvantage are the high temperatures that the substrates are exposed to. Up to the moment, the mentioned techniques in many cases are time-consuming, expensive and/or low resolution techniques.

Reactive magnetron sputtering is a very attractive technique for thin film ceramic materials deposition and has a low substrate temperature, below 100 °C as an advantage, so the substrate degradation is minimized. Other characteristic of the ceramic films grown by reactive sputtering deposition are high deposition rates, high reliability and good control of the film properties. TiN films deposited by this technique using argon and nitrogen gases results in stoichiometric TiN film in cubic phase, known as the hardest and the most stable TiN phase [15].

Recently, the intense research work on Lithographic procedures to improve nanotechnologies associated to the miniaturization of integrated circuits has introduced the Nanoimprint Lithography (NIL) process. It essentially consists in the replication on metals or semiconductor wafer of desired morphological features in the submicrometric scale previously fabricated of hard patterned moulds [16]. In general this novel approach does not mean a significant cost diminution of the process because pattern moulds are made by sophisticated techniques based on electron beam or ion beam lithography. The notable advantage of this technique rests on its enhanced resolution which does not depend on the parameters like wavelengths and numerical aperture as what occurs when traditional photolithographic methods are used.

On the other hand, in the last years a lot of work has been made on nanoporous anodic alumina membranes (AAM) fabrication for functional materials; these materials can be obtained by two successive single anodization processes [17], so that, in general, the final product is characterised by highly ordered nanopores' polycrystalline arrays of hexagonal cells with diameters ranging from tens to few hundreds of nanometers and high aspect ratios depending on the anodization parameters used [18–21]. Based on NIL solution, some authors have obtained cuasi-perfect monodomain AAM, by using previously fabricated moulds, in general, made of SiC or Si_3Ni_4 [22,23] for imprinting alumina or other metallic foils which are then submitted to a single anodization process with qualitative results much better than those obtained by traditional anodization methods mentioned before those. In these works commercial or home-made [24] masks were used. Although the obtained results are really excellent, as it has been said, the masks' fabrication is not an economic issue.

Based on the same ideas, in this work, the fabrication of titanium nitride (TiN) thin films via reactive sputtering magnetron technique using AAM surfaces as substrate templates, is reported. The results essentially consist on hard moulds with surface morphologies of either TiN nanotubes or TiN nanohills depending on the sputtering parameters and the AAM features. The obtained nanohills featured moulds could be used to imprint metal and semiconductor surfaces that can be lately anodized to obtain ordered nanoporous functional materials. The morphology of the TiN surfaces obtained by this method replicates the large range order of the template. Up to our knowledge this is the first time that TiN nanotubes and nanohills obtained by this route i.e., sputtered TiN thin film on anodic alumina membranes, is reported. On the other hand, the higher hardness and lower cost of TiN nanohills' fabrication respect to those that can be made from SiC and Si_3Ni_4 for imprinting applications, makes TiN nanostructured thin films and particularly TiN nanohills, the preferred materials to be used in patterning processes for a wide variety of valve metals and semiconductors.

2. Experimental

In this work, the deposition of stoichiometric TiN films were performed in a balanced dc magnetron sputtering system previously described [15]. Argon and nitrogen gases were introduced into the chamber by separated mass flow controllers. The cathode was placed at three different positions (6.5, 15.5 and 26.5 cm) away from the substrate holder. The vacuum pumping is formed by a turbomolecular pump backed by a mechanical pump, reaching a base pressure lower than 10^{-6} mbar. A titanium target (3″ diam. × 0.1″ thick, 99.995% pure) was used. Prior to the deposition process, the target surface was sputter etched for 15 min in an argon plasma performed using a 100 W cathode power in order to avoid extra impurities incorporation in the layers. The deposition process was also performed at 100 W cathode power. The deposition pressure ($Ar+N_2$ gas) was around 2×10^{-3} mbar, the gases concentrations were 93% Ar and 7% N_2, and the total gas flow was kept constant at 11 sccm. Low substrate temperatures (<70 °C) were maintained during the TiN growth process and the

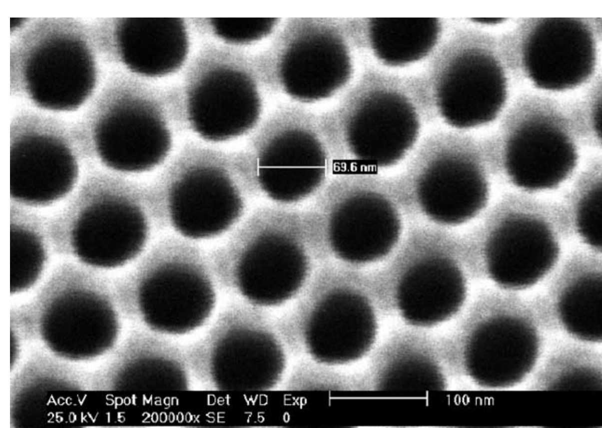

Fig. 1. Typical HRSEM image of an AAM surface.