Materials Letters 172 (2016) 128–131

Contents lists available at ScienceDirect

Materials Letters

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

Architectured columns with a metal-dielectric periodic nanostructure

Nicolas Martin [a,*], Arnaud Cacucci [b], Valérie Potin [b], Luc Imhoff [b], Tomas Nyberg [c]

[a] Institut FEMTO-ST, UMR 6174, Universitéde Franche-Comté, CNRS, ENSMM, UTBM, 15B, Avenue des montboucons, 25030 Besancon Cedex, France
[b] ICB-Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Universitéde Bourgogne, 9, Avenue Alain Savary, BP47870, 21078 Dijon Cedex, France
[c] Solid State Electronics, The Ångström Laboratory, Uppsala University, Box 534, 75121 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 3 February 2016
Received in revised form
28 February 2016
Accepted 29 February 2016
Available online 2 March 2016

Keywords:
Deposition
Sputtering
Multilayer structure
Thin films

ABSTRACT

We engineer a sputter deposited metal/oxide periodic structure based on W and Ta, and corresponding oxides with tuneable alternations from a few nanometers to a few tens nanometers, combined with the preparation of inclined, zigzag and spiral columns. This work shows how bi-component periodic multilayers can be produced within some inclined nano-columns exhibiting oriented, zigzag and helix structures. This unique combination of controlled columnar structure and periodic multilayers enables new opportunities to create some unusual structural designs for functional materials.

1. Introduction

The structuring of thin films on the nanometer scale is currently a material science challenge within the nano-science and technology community. To this aim, different bottom-up strategies based on molecular beam epitaxy, self-assembling polymeric systems, chemical or physical vacuum processes are extensively developed to produce the ordering of thin solid films [1]. In all these advanced techniques, the motivation is to succeed in growing different kinds of periodic structures and architectures with dimensions, which are included between a few tens of nanometers up to a maximum of few hundreds nanometers. Thus numerous biomimetic materials are smartly fabricated with dimensions, which are close to the atomic scale [2] (e.g. clusters, C60, molecules with chiral structures …) and above the microscale [3] (e.g. self-organized colloidal balls, which are stacked, nacre and so on). However, between these two ranges of dimensions, we can argue that there is like a “terra incognita” of structured materials to be explored. Therefore, the development of a toolbox of structuring techniques is highly desirable from a scientific standpoint. The latter is connected to technological challenges to achieve new periodic architectures at these scales, which is also the motivation of this work.

Recently, extensive work has been devoted to the glancing angle deposition (GLAD) since it appears to be an attractive strategy to create nanostructured thin film materials [4]. Brett et al. strongly developed this original approach to fabricate porous films with submicrometer control of the columnar orientation leading to 1D, 2D or 3D structuring [5,6]. Many physical behaviors of such GLAD films have been extended compared to those obtained with conventional processes [7–11]. Similarly, the fabrication of periodic multilayers or superlattices presenting a bi-component nanometric alternation is currently pointed out by means of deposition processes, especially for metal-dielectric stacks [12–14].

Here we present an original structuring of thin films based on the association of the GLAD and the reactive gas pulsing process (RGPP) implemented for the reactive sputter deposition. In GLAD, a flux of vapor-phase atoms strikes a tilted substrate (incident angle α). The latter can be fixed or rotated (rotational speed φ) about its vertical axis (Fig. 1). The columns' growth direction is thus controlled and an appropriate substrate movement leads to the columns' growth into different geometries such as inclined columns, zigzags, helices, vertical posts or even more complex shapes [15]. The RGPP method allows an accurate control of reactive gas injection – oxygen in this study during the reactive sputtering. A rectangular periodic oxygen mass flow vs. time can accurately be generated with adjustable pulses where it is possible to control the periods and injection times of the oxygen gas (Fig. 1). By setting the pulsing parameters, either homogeneously alloyed compounds, or multilayered metal/oxide periodic stacks (a few nanometers of period) can be produced throughout the film [16]. As a result, some unusual structures are achieved by means of

* Corresponding author.
E-mail address: nicolas.martin@femto-st.fr (N. Martin).

http://dx.doi.org/10.1016/j.matlet.2016.02.161
0167-577X/

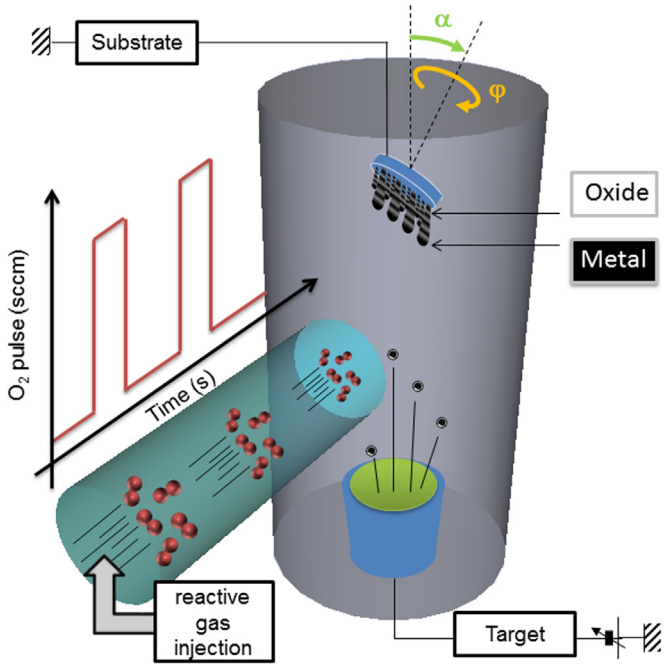

Fig. 1. Schematic illustration of the technique used to growth oriented, zigzag and spiral columns with a metal-dielectric periodic nano-structure. Oxygen gas is periodically injected vs. time with a pulsing period ranging from 10^1 to 10^3 s. During the t_{ON} time, oxygen is supplied in the sputtering chamber whereas it is completely stopped during the t_{OFF} time. Substrate is inclined (angle α) and can be fixed or rotated during deposition (angle φ). The incident angle α of the particle flux can be changed from 0° to 90° and the substrate rotation can be stopped (φ=0°) or mobile (a few revolutions per hour) during the growth.

this unique combination of RGPP and GLAD techniques.

2. Material and methods

Structured films were deposited onto (100) Si and glass substrates by DC reactive magnetron sputtering from a metallic target (W or Ta purity 99.6 at% and 51 mm diameter) in an $Ar+O_2$ gas mixture. The target was sputtered with a constant current density $J=100$ A m^{-2}. The distance between the target and the unheated substrate was fixed at 65 mm. A home made GLAD (GLancing Angle Deposition) substrate-holder allowed the preparation of oriented columnar structures by changing the incidence angle α of the particles flux from $\alpha=0°$ to 90° and/or rotating the substrate holder at various rotating speeds Φ. The gas flow rates were controlled by a home made system. All depositions were carried out with an argon flow rate of 2 sccm and a constant pumping speed of 13.5 L s^{-1}, which produced an argon partial pressure of 0.25 Pa. Oxygen mass flow rate was periodically controlled versus time according to a rectangular signal versus time by the reactive gas pulsing process, namely RGPP [16]. The pulsing period T of the oxygen flow rate was varying from a few hundreds to a thousand seconds. During each period, the flow rate was periodically modulated with a t_{ON} injection time which is a fraction of the total period T. The maximum O_2 flow rate was fixed at 4 sccm during the t_{ON} injection time. This oxygen flow corresponds to a steady-state processing point in compound sputtering mode. Otherwise it was completely stopped (no oxygen injection) during the t_{OFF} time. The multilayer period thickness Λ is expected to be in-between a few nanometers to 50 nm, with $\Lambda=\lambda_{met}+\lambda_{ox}$, where λ_{met} and λ_{ox} correspond to the thickness of the metal and oxide sub-layers, respectively.

Cross-sectional samples for TEM were prepared using the standard sandwich technique. They were mechanically polished, dimpled down to a thickness of 10 μm and Ar^+-ion milled to electron transparency. The structure was examined with a High Resolution Transmission Electron Microscope (HRTEM) JEOL 2100 FEG operating at 200 kV. The shape and dimension of the periodic structures exhibiting inclined, zigzag and spiral architectures were observed in HRTEM and Scanning TEM modes. The scanning technique of TEM (STEM) was used to get local and precise chemical analyses at the nanometric scale (scanning probe of 1 nm). Moreover, dark field imaging was applied to provide a greater contrast between the different phases. The elemental chemical composition was determined by energy-dispersive X-ray spectroscopy (EDX). HRTEM images were acquired with a GATAN Ultrascan camera. Experimental crystallographic structures were compared with simulated ones obtained using Java Electron Microscopy Software.

3. Results and discussion

The first step comprises the growth of oriented columns exhibiting regular metal/oxide periodic alternations based on tungsten and its oxide. Fig. 2 shows high-resolution transmission electron microscopy (HRTEM) images of the films cross-section. The incident angle α was kept constant at 80° whereas the oxygen flow rate was periodically injected vs. time with a pulsing period $T=300$ s and an oxygen injection time of 100 s. The resulting film exhibits a column angle $\beta=40°$ and β-W/a-WO_3 alternations with a thickness period $\Lambda=110$ nm. Sharp interfaces and reproducible stacks of metallic tungsten (β-W phase) and amorphous tungsten trioxide are periodically produced in spite of the inclined particles flux and the nature change of the deposited material. It is further seen that the same columnar growth occurs in β-W and a-WO_3 compounds resulting in the same width of the columns (about 5 nm) throughout the film. Such nanometric width is measured from a few nanometers of the first growing stages and continues into the subsequent metallic and dielectric layers. Thus, the pulsing mode of the oxygen gas does not disturb the growth of the inclined columnar structure. The voids between the nano-columns arise mainly due to shadowing effect, which is specific to the GLAD process. No crystallites have been detected in the tungsten trioxide sub-layers whereas the tungsten ones adopted the crystalline β phase.

In the following steps we involve a rotating substrate during the growth of Ta/Ta_2O_5 alternations using an incident angle of 80° and a suitable oxygen pulsing period to produce zigzag or spiral architectures (Fig. 3). For zigzags (Fig. 3a), the columnar growth is maintained in spite of the pulsing mode of the oxygen gas. As previously observed for inclined columns (Fig. 2), the oxygen injection does not disturb the columnar growth. Similarly, the change of the incident angle α from $+80°$ to $-80°$ leads to an opposite orientation of the columnar growth from $\beta=+40°$ to $-40°$, respectively and a zigzag period of 76 nm is produced. Column diameter is maintained close to a tens nanometers from the first deposition of Ta/Ta_2O_5 period and throughout the whole film. A clear separation between columns can be noticed and a porous structure is produced due to an alternation of the shadowing effect (abrupt 180° periodic rotations of the substrate), which prevents atoms from condensing in the region behind each column. Finally, a controlled and continuous rotation of the substrate allows the growth of helices with tuneable pitches. Steps of 90° rotation lead to squared spirals exhibiting periodic metal/oxide chevrons by means of the pulsing injection of the oxygen (Fig. 3b). Here again, the columnar growth continues despite the 90° change of the incident particles direction combined with the sudden on and off injection of the oxygen gas. Separations between columns are clearly distinguishable and as previously noted