Electrochimica Acta 140 (2014) 366–375

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrochemistry on binary valve metal combinatorial libraries: niobium-tantalum thin films

Andrei Ionut Mardare[a,*], Alfred Ludwig[b], Alan Savan[b], Achim Walter Hassel[a,c]

[a] Institute for chemical technology of inorganic materials Johannes Kepler University Linz, 4040, Linz, Austria
[b] Institut für Werkstoffe Ruhr-Universität Bochum 44780 Bochum, Germany
[c] Christian Doppler Laboratory for combinatorial oxide chemistry at the institute for chemical technology of inorganic materials, Johannes Kepler University Linz, 4040, Linz, Austria

ARTICLE INFO

Article history:
Received 25 December 2013
Received in revised form 24 February 2014
Accepted 24 February 2014
Available online 11 March 2014

Keywords:
Combinatorial libraries
High-throughput experimentation
Scanning droplet cell microscopy
Anodic oxide films

ABSTRACT

A Nb-Ta thin film compositional spread obtained from a co-sputtering process was analysed. The microstructure and crystallographic investigations revealed the presence of a compositional threshold at Nb-60 at.%Ta where the change from tetragonal to cubic symmetry was evidenced by a mixed tetragonal-cubic phase. The electrochemical properties of the anodic oxides were studied via cyclic voltammetry and the oxide formation factors were mapped along the entire compositional spread. Values ranging from 1.8 nm·V^{-1} at the Ta-rich side to 2.6 nm·V^{-1} at the Nb-rich side of the library were measured. All Nb-Ta mixed anodic oxides were found to exhibit a type-n semiconducting behaviour as evidenced by Mott-Schottky analysis. The chemical composition of the surface anodic oxides differed from the composition of the parent metal alloys and no clear trend could be identified regarding their mismatch.

1. Introduction

Tantalum being named after Tantalus and niobium after his daughter Niobe (both from Greek mythology) are typical valve metals exhibiting extremely stable oxides. According to the Pourbaix diagrams they show an extremely large range of stability, e.g. for tantalum a region of relative predominance of the oxide ranges from pH -2 to pH 16 [1]. These oxides are so stable that Ta was thought to be a noble metal until the mid of last century and it was listed as such [2]. These elements are chemically very similar as they are both from the 5th group and ^{73}Ta is heavily influenced by the lanthanoids contraction resulting in an identical atomic radius of 145 pm. Logically, they are often found in identical minerals able to replace each other.

The high dielectric properties make tantalum oxide the prime choice for high performance electrolytic capacitors which can have a breakdown field strength as high as the oxide formation field strength [3]. Addition of W to Ta thin films was recently proven to enhance the capacitance of barrier-type anodic films at low formation potentials [4]. The presence of Ta in various alloys in both bulk and thin films leads toward improved chemical stabilities. Excellent corrosion resistance was recently proven when Ti was alloyed with Ta either by atmospheric high-velocity electron beam cladding of powder materials [5] or by plasma tantalumising in vacuum [6]. The more abundant Nb is cheaper than Ta and therefore a lot of research activities are dedicated to the replacement of Ta or the use of Nb-Ta alloys. Very interesting dielectric properties have been found in bulk Ag perovskite structures containing almost equal amounts of Ta and Nb with applications as high permittivity microwave ceramics [7]. Thick and thin films of Ag perovskite functional materials containing Ta and Nb were reported to have very good electrical properties with low dielectric losses, high permittivities with small frequency dependence and low leakage currents [8]. Ta and Nb additions have been shown to increase the high temperature strength of Pt-based alloys [9] which is of particular interest when such thin film is used as a heating element [10]. Both elements can be added as an alloying element and later during use at higher temperatures in an oxygen containing atmosphere they will be oxidised to form small oxide particles within the platinum. This process is called oxide dispersion strengthening since these small particles hinder direct sliding of crystallographic planes. In combination with Ni, Ta and Nb alloys can form bulk metallic glasses which due to their amorphous structure have shown high fracture strength, high corrosion resistance and high thermal stability [11,12].

Both Nb and Ta belong to the valve metal family (typically represented by Al) which produce barrier-type anodic oxides, usually amorphous, at high current efficiencies. Apart from the bulk applications mentioned before, these metals are also highly interesting

* Corresponding author. Tel.: +4373224688702; fax: +43 732 2468 8905.
E-mail address: andrei.mardare@jku.at (A.I. Mardare).

http://dx.doi.org/10.1016/j.electacta.2014.02.138
0013-4686/

in their thin film form. Recent applications of anodic oxides on valve metal thin films include plastic electronics, when a polymeric flexible substrate is used for fabrication of MIM or MOS-FET structures, thus opening new directions in modern electronics [13]. Studying the mixed Nb-Ta anodic oxide properties is highly relevant especially due to their high dielectric constants, high breakdown fields and interesting photoelectrochemical behaviour under UV irradiation [14]. Recently, field crystallization of anodic oxides grown on Nb-Ta thin film alloys revealed an almost linear dependence between the alloy composition and oxide properties, i.e. oxide formation factor, density and permittivity [15]

High throughput combinatorial methods for recent material properties screening became largely used techniques in latest years. Recent research directions including battery development, electrocatalysis, photocatalysis, corrosion protection, sensor development, photovoltaics and light-emitting materials, etc. are dependent on combinatorial electrochemistry [16–18]. In the current work, a high throughput study of localized anodic oxidation of a wide compositional spread Nb-Ta thin film combinatorial library using a scanning droplet cell microscope is presented.

2. Experimental

2.1. Preparation of Nb-Ta compositional spread

Nb-Ta gradient composition thin films were obtained using co-sputtering in an ultra-high vacuum system (DCA, Finland) using two sputtering targets, 101.6 mm in diameter. Both targets were pure-element sputtering targets (99.995%, Kaistar R&D) and were placed at an angle of 144° to one another while aimed at the centre of the substrates. Both Ta and Nb were sputtered in the RF mode using a power of 200 W which resulted in deposition rates of 0.73 nm·s^{-1} and 0.49 nm·s^{-1}, respectively. Three thermally oxidised Si wafers with an oxide thickness of approximately 1 μm and with diameters of 100 mm were sequentially used as substrates for the combinatorial deposition. Using this co-sputtering method, due to the vapour phase mixing of both sputtered species an overall compositional spread ranging from Nb-5 at.%Ta to Nb-94 at.%Ta was achieved defining the Nb-Ta thin film library. This spread translates into a compositional resolution of 0.3 at.% mm^{-1}. For all depositions, the base pressure of the vacuum chamber was in the range of 2·10^{-6} Pa. The samples were deposited at room temperature in Ar atmosphere with a pressure of 6·10^{-1} Pa. The distances between targets and substrate were kept constant at 190 mm, which resulted in total film thicknesses of about 300 nm at the wafer centre. The actual thickness variation (wedges) would depend on the elements being used, i.e. atomic volumes, adjusted for the measured composition at each point. The wedges mostly compensate each other, so the thickness variation is from somewhat less, to a lot less than the single wedge thickness variation (which was measured as approximately 40% using various targets). The atomic volumes of the Ta (10.9 cm^3 mol^{-1}) and Nb (10.8 cm^3 mol^{-1}) are pretty similar, so one can reasonably assume that the wedges essentially compensate (in a direct line). Additionally, pure Ta and pure Nb thin films were successively deposited on oxidised Si wafers in the same conditions from single targets for serving as reference samples. After the co-deposition of the Nb-Ta compositional spread, energy dispersive X-ray spectroscopy (EDX) was used for mapping the element concentrations across each wafer. The concentration gradient direction is dictated by the co-deposition geometry and the position of the targets. A precise measuring of the concentration gradient allowed an accurate identification of Nb-Ta alloys along the combinatorial library. More details about combinatorial libraries preparation can be found elsewhere [19].

2.2. Microelectrochemical setup

A scanning droplet cell microscope (SDCM) was used for the high throughput growth and characterization of anodic oxides of individual alloys on the surface of the Nb-Ta combinatorial library. The cell was built in an acryl block having a three-electrode configuration [20]. Using a thermal puller (PC-10, Narishige), a borosilicate glass capillary with a 2.5 mm outer diameter was pulled and a tip with a diameter of 200 μm was obtained using a micro-grinder (EG-400, Narishige). This capillary was used as the outer body of the cell. A micro-reference electrode capillary with a 100 μm tip diameter (μ-AuHg/$Hg_2(CH_3COO)_2$/$NaCH_3COO$) was used for the SDCM measurements [21]. The counter electrode was fabricated using a thin Au band which was wrapped around the reference electrode. The reference and counter electrodes were inserted together into the main capillary body. More details regarding the reference electrode and cell fabrication can be found elsewhere [22]. For a precise definition of the wetted area on the investigated surface (working electrode) a silicone gasket was fabricated at the tip of the cell by immersing it into liquid silicone followed by drying in flowing nitrogen. A high reproducibility of this surface was ensured by pressing the tip against the investigated surface with a predefined force (3 mN) for producing only an elastic deformation of the sealing. In the same time, the electrolyte-air contact was avoided during the electrochemical investigations and the wetted area on the surface of the compositional spread had a very high reproducibility, with errors smaller than 1%, as previously demonstrated on pure Hf films [23].

2.3. Hardware description and measurement details

Since the investigated metallic alloys have a spread in composition along the surface of the samples (wafers), an automated, high-throughput measurement approach was necessary. Thus, the SDCM used for the electrochemical investigations on the Nb-Ta thin film library was fully computer controlled. Self-made control and data acquisition programs written with LabView software were used for controlling all the components of the SDCM system:

- a video camera providing live imaging of the sample, for definition of the scanning points/areas
- an XYZ translation stage, for high precision positioning of the SDCM tip on the sample surface
- a force sensor (KD45 2 N, ME-Messsysteme) combined with a lock-in amplifier (EG&G 7265), for the automated control of the applied force while pressing the SDCM tip against the sample
- a micro-syringe pump (Micro 4, World Precision Instruments), combined with a 100 μl syringe, for dosing the electrolyte from the cell in order to wet the investigated spot

The electrical contact to the metallic surface was achieved using a W needle in hard contact with the sample surface. More details about the automation of the SDCM and its software can be found elsewhere [22,23].

Scanning electron microscopy (SEM) was used for the characterisation of the Nb-Ta composition spread microstructure. Grazing incidence X-ray diffraction (GIXRD) performed at 1°, was used for the local crystallographic investigation of the thin film alloys. The irradiated spot had an elliptical shape (3 mm × 7 mm), the small diameter of 3 mm being oriented parallel to the compositional gradient. Due to the compositional resolution measured by EDX (0.3 at.% mm^{-1}) this means that individual alloys can be investigated by XRD with a resolution of 1 at.%. The X-ray diffraction results were correlated with the composition map obtained by EDX in order to obtain a complete description of the Nb-Ta combinatorial library before the electrochemical treatment. The