



Interfacial Oxide Formation during Anodization of Hafnium/Aluminium Superimposed Layers



Christian M. Siket^a, Maria Bendova^{b,c}, Cezarina Cella Mardare^d, Jaromir Hubalek^b, Siegfried Bauer^a, Achim Walter Hassel^{c,d,*}, Andrei Ionut Mardare^{c,d}

^a Soft Matter Physics, Johannes Kepler University Linz, 4040 Linz, Austria

^b Centre of Sensor, Information and Communication Systems, Faculty of Electrical Engineering and Communication, Brno University of Technology, 61600 Brno, Czech Republic

^c Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, 4040 Linz, Austria

^d 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 18 April 2015

Received in revised form 6 July 2015

Accepted 7 July 2015

Available online 9 July 2015

Keywords:

combinatorial libraries

high-throughput experimentation

scanning droplet cell microscopy

anodic oxide film

hafnium oxide

ABSTRACT

The anodization behaviour of Hf/Al stacked thin films, sequentially deposited from vapour phase without breaking vacuum, was investigated using scanning droplet cell microscopy. Surface microstructure and crystallographic analysis revealed the formation of highly textured and compact hexagonal Hf films for thicknesses above 7.5 nm. Cyclic voltammetry suggested the formation of discrete anodic layers starting with pure HfO₂ on the surface, a mixture of HfO₂ and Al₂O₃ as an intermediate layer and pure Al₂O₃ in depth of the films. Coulometric investigations revealed oxide formation factors of 2.2 nm V⁻¹ for HfO₂ while for pure Al₂O₃ a maximum of 1.4 nm V⁻¹ was measured. Electrochemical impedance spectroscopy performed for various Hf thicknesses and different final anodization potentials revealed almost ideal dielectrics formed from mixed HfO₂/Al₂O₃, permittivities up to 26 being measured for the anodized Hf/Al films. Surface analytical investigations and depth profiling as well as high resolution transmission electron microscopy confirmed the discrete anodic layer growth and the mixing of both anodic oxides. The significant thickness values found for the mixed oxide layer must redefine the general expectations for the use of anodized superimposed layers in various applications.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Aluminum is technically the most important metal besides iron and copper. The applicability of this un-noble and thus potentially reactive metal is simply based on its valve metal behavior. A thin oxide layer that forms on the surface is passivating and thus hinders further reaction of this metal. Upon electrochemical treatment this oxide layer can be further increased in thickness due to the high field conditions under which the thickness of the forming barrier layer is directly proportional to the formation voltage. Anodization in acidic and/or complexing solutions opens further possibilities as it allows to create structured porous layers.

Anodization of Al-based multilayered structures is highly relevant for applications focused on their oxides. An enrichment of the alloying element at the metal/oxide interface and its

incorporation into the oxide film were reported during anodization of large numbers of Al-alloys containing e.g. Cr, [1] Fe, [2] Mn, [3] Mg, [4] Cu, [5] Ni [6]. A similar behavior was found for Al alloys containing other valve metals. The presence of W in Al led to a W enrichment in the anodic oxide without distinctly affecting the anodization rates [7] while Ta alloyed with Al produced a pure anodic Al₂O₃ at the surface followed by a mixed oxide layer in depth [8]. A different oxidation dynamics was found in Al-Zr alloys where the top-most oxide layer consists of crystalline ZrO₂ [9]. In all cases the anodic oxide formation is directly influenced by the individual ionic transport numbers of the metals forming the parent alloy. Anodization of superimposed valve metals containing Al is driven by the same mechanism, as evidenced by both theoretical and experimental studies revealing that if the underlying metal forms a lower ionic resistivity oxide as compared to the outer Al₂O₃, “fingers” of the inner metal oxide may penetrate into the outer oxide layer [10–14]. However, even though a correct theoretical prediction describing the formation of a layered anodic oxide when the underlying film has a high ionic resistivity (e.g. Al) was formulated [10], studies on the metals interfacial anodization

* Corresponding author. Fax.: +43 732 2468 8905.

E-mail address: achimwalter.hassel@jku.at (A.W. Hassel).

are scarce in spite of their tremendous importance for the overall anodic oxide properties.

Hafnium is a valve metal like aluminium and forms the chemically extremely stable oxide HfO_2 . Technical application of Hf was long limited to the use as control rod in nuclear power plants until it entered microelectronics technology as high- k material due to its high dielectric constant [15], interfacial stability on Si [16], and large conduction band offsets on III-V semiconductors limiting the leakage currents [17]. Implementation of HfO_2 in conjunction with π -electron organics promises novel applications in unconventional flexible electronic circuits [18]. While various physical and chemical techniques for HfO_2 deposition are used [19–21], great difficulties are encountered in the preparation of smooth films at low processing temperatures. Electrochemical anodization of Hf seems to be an ideal solution for the fabrication of smooth and dense HfO_2 films.

In nature Hf always appears in connection with Zr showing an unprecedented chemical similarity due to their position in the periodic table and the lanthanoid contraction. Production of hafnium is directly linked to zirconium mining and production allowing to estimate an annual world production of about 100 metric tons of Hf per year. It is thus highly desirable to find ways and means for an efficient use of Hf in alloys or thin film layers in which the smallest possible amount of Hf is employed to yield the properties of a high performance mixed oxide. This oxide shall be used in such promising fields like MOSFET, flexible electronics, memristors, metal insulator metal tunnel junctions [22], hot electron emitter and bioelectronics.

This work investigates the anodic oxide formation on Hf ultra-thin films superimposed on thicker Al films. A true metal/metal interface is ensured by sequential vacuum depositions and the oxidation dynamics are discussed with focus on the Hf/Al interfacial oxide. Due to the low processing temperatures involved potential applications arise in micro- and flexible electronics.

2. Experimental Details

2.1. Thin films deposition

Multilayer thin film structures containing stacked Al and Hf layers were obtained via thermal evaporation and electron beam evaporation techniques, respectively. In a first step, Al thin films were deposited on optically flat $40 \times 40 \text{ mm}^2$ borosilicate glass substrates (Marienfeld, Germany). The base pressure of the thermal evaporator chamber was in the range of 10^{-5} Pa and a substrate-source distance of 120 mm together with a fast deposition rate (1 nm s^{-1}) ensured obtaining room temperature high quality Al films 100 nm thick. As evaporation source, high purity Al wire (99.95 %, Goodfellow, United Kingdom) was used in direct contact with a planar W thermal element (evaporation boat, Kurt J. Lesker, United Kingdom).

Without breaking the vacuum, the Al-coated samples were transported into another vacuum chamber for the second and final step of the sample preparation when Hf thin films of various thicknesses were deposited directly on Al. The in-vacuum transport was achieved via a robotic arm holding a forklift built inside of a radial distribution center (Kurt J. Lesker, United Kingdom). In this way, a true metal-metal interface was obtained between Al and Hf thin films. Due to its high evaporation temperature (2523 K @ 10^{-4} Pa) a mini-electron beam evaporator (Tectra, Germany) was used for Hf thin film depositions at room temperature. The electron beam chamber operates in ultra-high vacuum having a base pressure of $5 \times 10^{-7} \text{ Pa}$. A very low Hf deposition rate (0.5 nm min^{-1}) was used for all depositions which allowed an extremely precise thickness control achieved via a built-in flux meter previously calibrated for Hf. As Hf source, a

3 mm in diameter rod with a purity of 99.9 % (exclusive Zr) was used. Final Hf thicknesses of 5, 7.5, 10, 12.5, 15, 20, 25, 30, 50 and 100 nm were obtained on different Al thin films in identical conditions. All Hf/Al samples were exposed to normal atmospheric conditions before electrochemical investigations.

2.2. Scanning droplet cell microscopy

For all electrochemical investigations presented in this work, a scanning droplet cell microscope (SDCM) was used. The idea of bringing a small electrolyte droplet in contact with the investigated surface (rather than dipping an entire sample into electrolyte) defines a scanning droplet cell [23] and recently its capability of mapping or imaging various properties along a surface led to the use of the term microscopy [24].

The microelectrochemical cell was fabricated using borosilicate glass capillaries. The outer body capillary (2.5 mm in diameter) was thermally pulled and the obtained tapered tip was ground open to a final diameter of approximately $500 \mu\text{m}$. A capillary based μ -reference electrode (μ -RE, $\text{AuHg}/\text{Hg}_2(\text{CH}_3\text{COO})_2/\text{NaCH}_3\text{COO}$) was fabricated by electrodepositing $\text{Hg}_2(\text{CH}_3\text{COO})_2$ on an amalgamated Au wire, $100 \mu\text{m}$ in diameter [25]. The reference electrode wire was inserted into a glass capillary (1 mm in diameter) which was prepared in a similar manner as the outer body capillary with a final tip diameter of $100 \mu\text{m}$. Filling the capillary with hot aqueous solution of NaCH_3COO containing 3 wt% agar resulted upon solidification in an improved mechanical stability of the reference electrode. As counter electrode (CE), an Au wire was used ($100 \mu\text{m}$ in diameter) wrapped around the μ -RE glass capillary. Both μ -RE and CE were inserted into the main SDCM outer body capillary and the entire construction was fixed into an acryl block. Channels within the block allowed electrolyte pumping through so that the SDCM tip became the cell outlet. For all experiments, the SDCM was used in contact mode [26]. A soft sealing was formed at the rim of the SDCM tip by dipping it into liquid silicone followed by N_2 flow drying. The cell was brought in hard contact with the investigated surface and a force sensor ensured the use of a constant force (25 mN) for each measurement. Pressing down the SDCM tip in contact mode ensured a high reproducibility of the wetted/addressed area together with avoiding electrolyte evaporation during longer time measurements [27].

2.3. Anodic oxide formation and characterization

The anodic oxide growth on Hf/Al thin films was investigated in several steps on different locations on the film surface. A potentiostat with built-in frequency response analyzer for impedance studies (Autolab PGSTAT204) was used for all measurements. Cyclic voltammetry (CV) between 0 and 10 V vs. SHE was used for studying the overall potentiodynamic anodization behavior. Separate CV series, where the maximum applied potential was step-wise increased between 0 and 10 V vs. SHE, was used for preparing oxides to be investigated by electrochemical impedance spectroscopy (EIS). All potentiodynamic studies were performed using a rate of potential increase of 20 mV s^{-1} . After each oxide step growth, the oxides impedance behavior was measured using a 0 V vs. SHE DC bias and a 50 mV AC perturbation in a wide frequency range from 10^6 Hz down to 10^{-1} Hz . All electrochemical investigations were performed in buffered acetic acid / sodium acetate solution with a fixed pH value of 6.0.

The microstructure and crystallographic particularities of the as-deposited Hf/Al samples were investigated using a field emission SEM (Zeiss Gemini 1540 XB) and an XRD system (PANalytical X'pert Pro) with a $\text{Cu-K}\alpha$ source radiation having a wavelength $\lambda = 154 \text{ pm}$. All XRD patterns were acquired in Bragg-Brentano geometry with 0.0021° 2θ step size and 15 s

Download English Version:

<https://daneshyari.com/en/article/183691>

Download Persian Version:

<https://daneshyari.com/article/183691>

[Daneshyari.com](https://daneshyari.com)