Thin Solid Films xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Nanostructured anodic-alumina-based dielectrics for high-frequency integral capacitors

Alexander Mozalev [a,*], Masatoshi Sakairi [b], Hideaki Takahashi [b,1], Hiroki Habazaki [c], Jaromír Hubálek [a]

[a] Department of Microelectronics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 3058/10, Brno 616 00, Czech Republic
[b] Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
[c] Division of Materials Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:
Received 29 August 2011
Received in revised form 14 February 2012
Accepted 22 February 2012
Available online xxxx

Keywords:
Anodizing
Porous alumina
Tantalum oxide
Nanostructure
Dielectric properties
Electric polarization
Integral capacitors
High-frequency performance

ABSTRACT

Three types of thin solid films with the nanoscale inner structures were synthesized by sputtering-deposition and anodizing of Al layer, Al-1.5 at.% Si alloy layer, and Al/Ta bilayer on Si wafers. All the anodic films comprised 1 μm thick nanoporous alumina layer as the key component. The essential differences were due to the silicon impurities (AlSi alloy) and the array of nanosized tantalum oxide protrusions in the alumina barrier layer (Al/Ta bilayer). The films were examined by scanning and transmission electron microscopy and electrochemical impedance spectroscopy. Integral capacitors utilizing the anodic films as dielectrics combine the small-value capacitance (6.5 nF cm^{-2}) with the excellent properties of high withstand field strength (1.7–2.7 MV cm^{-1}), low leakage current ($(3–20)\times10^{-12}$ A mm^{-2} at 1.0 MV cm^{-1}), and low loss tangent ($tg\delta=(4–6)\times10^{-3}$). The revealed dispersion of dielectric constant, although within 10%, and the presence of loss peaks on the temperature and frequency dependencies of $tg\delta$ denote the influence of ion-relaxation mechanism on dielectrics' polarizability, with the characteristic times ranging from 10 to 145 μs depending on the dielectric type. By selecting appropriate technological and electrolytic conditions, the functionality of the capacitors can be optimized to meet the needs of a specific range, from 1 kHz to about 300 MHz operating frequencies.

1. Introduction

In the microelectronic packaging industry passive components such as resistors, capacitors, inductors, and interconnections are defined as the non-active elements, which do not require an energy source for operation. Integral passives are specified as the functional elements either embedded in, or incorporated on, the surface of an interconnecting substrate. Integral passives offer numerous advantages such as increased silicon efficiency, improved electrical performance, elimination of separate packaging, increased reliability, and efficient circuit design [1–3].

Among the integral passives, integral capacitors, especially those having improved high-frequency (HF) characteristics have been in demand to perform an increased number of functions in semiconductor and hybrid integrated circuits for frequencies up to hundreds megahertz, where low losses and stable frequency-dependent characteristics are crucially important attributes [4].

To address the high capacitance density requirements of HF integral capacitors, a series of organic, inorganic, and mixed materials has been developed. For instance, a capacitance density of ~30 nF cm^{-2} has been achieved in polymer/ceramic nanocomposites through optimization of particle dispersion [5]. For even higher capacitance densities (>200 nF cm^{-2}), hydrothermal synthesis of barium titanate particles and deposition of non-stoichiometric inorganics by metal-organic chemical vapor deposition showed promising results [6]. A number of existing materials, like polymers with low dielectric constant and stable frequency-dependent dielectric losses, filled with ferroelectric powder have been used for embedding small capacitance values, up to 5–10 nF cm^{-2} [1,5]. The small-value capacitors are indispensable for filtering applications (the use of large-value capacitors in filter circuits is discouraged).

At the same time, application of inorganic metal-oxide films as dielectrics in HF integral capacitors, in spite of apparent technological benefits, has been limited by operating frequencies up to about hundred kilohertz, because of unstable behavior of capacitive reactance with increasing frequency, owing to the specificity of polarization phenomena in the metal-oxide dielectrics. However, most recent studies have shown that chemical composition and physical properties of thin metal-oxide films can be influenced and improved in some sense by using modern surface finishing and modification techniques [7–10]. Additionally, some of performance metrics of metal-oxide-

* Corresponding author. Tel.: +420 541146194; fax: +420 541 211309.
E-mail addresses: mozalev@feec.vutbr.cz (A. Mozalev), msakairi@eng.hokudai.ac.jp (M. Sakairi), takahasi@asahikawa-nct.ac.jp (H. Takahashi), habazaki@eng.hokudai.ac.jp (H. Habazaki), hubalek@feec.vutbr.cz (J. Hubálek).
[1] Present address: Asahikawa National College of Technology, Asahikawa 071-8142, Japan.

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.02.077

based capacitors can be improved and even tailored by creating advanced capacitor's designs [11,12] and applying modern technological approaches to synthesis of capacitor dielectrics, based mostly on nanomaterials and cutting-edge nanotechnologies, which have mushroomed in the last few decades [13–15].

From the above consideration, metal-oxide films consisting of self-organized periodic arrays of nanosized pores or tubes, formed via electrochemical anodization of aluminum and some other valve metals are attracting increasing interest as a dielectric platform material for potential HF applications. Such nanoporous materials (e.g. Al_2O_3, Ta_2O_5, TiO_2, Nb_2O_5) offer unprecedented opportunities to precisely modify their chemical composition, crystallographic structure, the size, population density, and configuration of pores and oxide cells by controlling and varying technological, electrical, and electrolytic conditions [16,17]. Therefore, it is envisaged that application of such nanostructured metal-oxide dielectrics to a thin-film capacitor may allow for improved high-frequency behavior of the capacitive reactance due to optimization of HF dielectric losses, shifting or flattening polarization peaks, thus extending the operating range up to radiofrequencies.

In the present work, nanostructured capacitor dielectrics have been synthesized via sputtering-deposition and anodizing of three types of initial thin-film samples: Al (99,99%) metal layer, Al-1.5 at.% Si alloy layer, and Al(99,99%)/Ta(99.95%) metal bilayer. These thin-film samples, all having top aluminum layer, have been selected because they are often used for forming interconnection structures for integrated circuits, including those for HF applications. Pure aluminum metal is known to be a good electron conductor, more sustainable to electromigration than copper, being the only interconnection metal that allows anodizing for forming both dense and porous anodic films with protective, isolating, and planarization purposes. The use of an off-eutectic Al–Si alloy for forming patterned thin-film conductors further improves their resistance to electromigration and, more importantly, suppresses the growth of hillocks (hemispherical protrusions) or whiskers in aluminum films when the films are subjected to temperatures above 573 K, e.g. for forming low ohmic contacts. Thin tantalum metal and tantalum oxide films are used respectively as the barrier, protective, current distribution, and stop layers in anodizing technologies of multilevel interconnection compatible with standard semiconductor and hybrid-integrated-circuit technologies [18,19].

Concerning anodic oxide films prepared in this study, the common structural feature for all the films was the presence of a porous anodic alumina film, having self-organized nanosized pore network [20]. The differences between the films were due to the silicon impurities, which form solid solution with aluminum in the initial Al-1.5 at.% Si alloy layer [21] and due to the nanostructured tantalum oxide that grows in the alumina pores in the case of Al/Ta bilayer [22]. These three types of anodic films were evaluated as dielectrics for the fabrication of metal–insulator–metal (MIM) integral capacitors, whose performance was studied in a wide frequency range, from 1 kHz to 300 MHz, at operating temperatures ranging from 293 to 473 K.

2. Experimental details

2.1. Sample preparation

Polished single-crystal silicon wafers, of 100 and 76 mm in diameter, with (111) crystallographic orientation and n-type conductivity (4.5 Ω cm), were used as the substrates for magnetron sputtering-deposition of the initial films. The specification of the films and further referencing the samples in the text are given in Table 1. For preparation of ultramicrotomed sections for later transmission electron microscopy (TEM), the Al/Ta metal bilayer was also formed onto an electropolished aluminum foil, of about 90 μm thick. In the case of the Al/Ta bilayer, prior to tantalum deposition, an additional layer of aluminum, 600 nm thick, was sputtering-deposited onto the wafer so as to be used as a bottom electrode in later MIM capacitors employing the Al/Ta anodic oxide (AO) dielectric.

Table 1
Configuration of initial sputtering-deposited layers employed for forming nanostructured anodic oxide dielectrics.

Sputtering-deposited layers	Thickness, nm	Called hereafter
Al (99.99%)	2000	Al
Al-1.5 at.% Si alloy	2000	AlSi
Al(99,99%)/Ta(99.95%) bilayer (aluminum-on-tantalum)	700/25	Al/Ta

Anodizing the films on the Si wafers was performed in original cylindrical cells made of polytetrafluoroethylene (PTFE), with two-electrode configurations, filled with aqueous electrolytes, in which the wafers were placed horizontally and fastened by PTFE rings pressed firmly to the face sides of the wafers, thus confining the anodizing areas within circles of 90 and 68 mm diameter for the 100 and 76 mm cells, respectively. Large-surface stainless steel spirals were used as the counter electrodes. A CCP500-505MR regulated DC power supply (Takasago Ltd.) and an Agilent N5752A programmable power supply were employed as the anodizing units.

The Al and AlSi layers were anodized partly such as to grow a layer of aluminum oxide of 1000 nm in thickness and keep a 600 nm aluminum layer unoxidized under the anodic film, which is to be used as the bottom plate in MIM capacitors to be prepared later. The Al and AlSi samples were anodized in 0.2 mol dm^{-3} oxalic acid ($H_2C_2O_4$) solution at a constant current density of 10 mA cm^2 at 296 K over a period of 210 s. During the steady state growth of a porous anodic film on the Al and AlSi alloy layers, the voltage was 51 ± 0.5 V.

In case of the Al/Ta bilayer, the whole thickness of the upper aluminum layer was anodically consumed (oxidized), down to the tantalum layer, so that the thickness of the porous anodic alumina formed was expected to be 1000 nm, the same as in the previous two samples. Anodizing the Al/Ta samples was performed in the same formation electrolyte but in two consecutive steps: First, galvanostatic anodizing was carried out at 10 mA cm^{-2}, with a steady-state voltage of 51 ± 0.5 V, until the aluminum metal was fully oxidized. Then the process was switched into a voltage-stabilization mode, at which the current began to decay. At the selected conditions, the tantalum layer also served a purpose of stop layer, preventing the bottom aluminum from being anodically oxidized. The current was allowed to decrease at least tenfold from its initial value. As a result, the tantalum metal oxidized locally through the alumina pores with the formation of nanosized discrete regions (hillocks) of tantalum oxide penetrating into the barrier layer of the alumina cells. Finally, the samples were rinsed in running distilled water and dried in a hot air stream.

2.2. Film characterization

The surfaces and sections of the anodic films and MIM capacitors were imaged by scanning electron microscopy (SEM) in Hitachi-6300 and S-4800 field-emission instruments operated at 20–30 kV. To reduce charging effect and improve the resolution, a coating of gold, about 5 nm thick, was evaporated onto the sections and surfaces of all samples before SEM observation. Ultramicrotomed sections of the anodic film formed onto the electropolished aluminum foil were prepared using a Reichert-Nissei Ultracuts/FCS ultramicrotome. The specimen, encapsulated in an epoxy resin, was trimmed initially with a glass knife and suitably thin sections, about 30 nm thick, were prepared by sectioning in a direction approximately parallel to the metal-oxide interface with a diamond knife. Ultramicrotomed sections, collected onto copper grids, were examined by TEM in a Hitachi H-700H instrument operated at 200 kV.

Please cite this article as: A. Mozalev, et al., Thin Solid Films (2012), doi:10.1016/j.tsf.2012.02.077