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Atomic layer deposition of tantalum oxide thin films using the precursor *tert*-butylimido-tris-ethylmethylamido-tantalum and water: Process characteristics and film properties

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ABSTRACT

In this work, the precursor *tert*-butylimido-tris-ethylmethylamido-tantalum (TBTEMT) was applied for the atomic layer deposition (ALD) of tantalum oxide (Ta_2O_5) thin films for the first time. Water was used as the second reactant. A self-limiting, and hence, ALD-like film growth was confirmed in the temperature range from 100 to 300 °C. The temperature window of this process extends from 250 to 300 °C and features a growth rate of about 0.56 Å/cycle. For lower temperatures, the growth rate increases gradually up to 0.92 Å/cycle at 100 °C. At a deposition temperature of 200 °C, the process showed perfect layer-by-layer growth with 0.64 Å/cycle and without any noticeable incubation period on both silicon with native oxide and hydrogen-terminated silicon. In addition, the conformal coating of structures with an aspect ratio of 40:1 is demonstrated as well.

According to XPS analyses, the films are oxygen rich (Ta:O ratio around 0.34 ± 0.01 for films grown at 150–300 °C) and contain a significant amount of carbon (6 ± 2 at.%) and some nitrogen (<3 at.%). The film densities, refractive indices and dielectric constants increase with increasing deposition temperature and are as high as 8.0 ± 0.1 g/cm^3, 2.25 and 31, respectively. Films grown at 200 °C are amorphous and smooth. They exhibit a film density of 7.8 ± 0.1 g/cm^3, a refractive index of 2.17 (at 550 nm) and a dielectric constant of 26 ± 1. However, the films suffer from high leakage currents (>10^{-4} A/cm^2). In addition, electrical measurements revealed the formation of an interfacial layer between the Ta_2O_5 films and bare silicon. By using substrates with a thin thermally grown silicon oxide, the leakage could be reduced by three orders of magnitude.

Post-deposition annealing at 800 °C in nitrogen resulted in the crystallization of the Ta_2O_5 films, which is also accompanied by an increase in film density and refractive index. Moreover, the crystallized films exhibit an enhanced dielectric constant of 48 ± 2. Electrical measurements revealed the growth of an interfacial layer with an equivalent oxide thickness of around 2.4 nm due to the 800 °C annealing. While this interfacial layer degrades the effective permittivity of the dielectric (*e.g.* 20.5 ± 0.5 for a 20 nm Ta_2O_5 film), it also causes a reduction of the leakage currents by more than three orders of magnitude (*e.g.* to $1 \cdot 10^{-7}$ A/cm^2 for a 20 nm Ta_2O_5 film).

1. Introduction

Tantalum oxide (Ta_2O_5) is a dielectric material having a high chemical, thermal and mechanical stability, a high refractive index (~2.2) and a wide optical band gap (~4.3 eV), a high dielectric constant (22–28 for amorphous Ta_2O_5), low leakage currents as well as a good dielectric breakdown strength [1–3]. Due to these interesting properties, Ta_2O_5 thin films have been utilized for various applications, for example as corrosion resistant coatings [4,5], protective coating for sensors [6], copper diffusion barrier [7,8], antireflective coating [9], optical waveguides [10,11], ion-sensitive membranes in solid-state ion sensors [12,13], alternative gate dielectric in metal-oxide-semiconductor field-effect transistors [1,14,15] as well as in organic thin-film transistors [16], and as high-k dielectric in dynamic random access memory (DRAM) capacitors [1–3,17,18]. The deposition of Ta_2O_5 thin films has been realized by numerous methods such as sputtering [2,4,6,9,11,17], electro-spray deposition [7], the thermal oxidation of thin tantalum layers [2,12,13], electron-beam evaporation [9,16], chemical vapor deposition (CVD) [15,18–20], photo-CVD [21], and atomic layer deposition (ALD) [7,8,22–44].

ALD is a modified CVD technique in which a substrate surface is alternately exposed to two or more vaporized precursors. Additionally,

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the precursors are separated from each other by inert gas purging or chamber evacuation in order to prevent any gas phase reactions. Due to this pulse sequence, film growth proceeds *via* sequential self-limiting surface reactions and monolayer-by-monolayer. As a result, ALD enables the deposition of thin films with atomic-scale thickness control as well as with excellent uniformity and conformality. Hence, ALD has received considerable attention for, in particular but not limited to, the deposition of thin films in 3D structures such as high aspect ratio DRAM capacitors and through silicon vias (TSV) [45–48].

The ALD of Ta_2O_5 films has been realized with several precursors, whereat the most often used are tantalum pentachloride, $TaCl_5$ [22–26], and tantalum pentaethoxide, $Ta(OEt)_5$ [7,8,26–33]. Besides, the application of the halide precursors TaF_5 [34] and TaI_5 [35,36], the alkylamide precursors $Ta(NMe_2)_5$ [37–40] and $Ta(NEt)(NEt_2)_3$ [37,41], and others like $Ta(N^tBu)$-(3,5-di-tertbutylpyrazolate)$_3$ [42] and $Ta(N^tBu)(^iPrNC(Me)N^iPr)_2(NMe_2)$ [43] has been investigated as well. Recently, Blanquart *et al.* [44] reported the Ta_2O_5-ALD using the precursor (*tert*-butylimido)tris(diethylamido)tantalum ($^tBuN = Ta(NEt_2)_3$, TBTDET) and both water and ozone as the oxidants. These processes yielded ALD growth behavior in a wide temperature range (125–325 °C for the ozone-based process) and growth rates of about 0.5 Å/cycle within the temperature windows. Films grown at 325 °C were amorphous and pure Ta_2O_5, and exhibited a dielectric constant of about 25 as well as low leakage currents after annealing at 700 °C [44].

In this work, we examined the precursor *tert*-butylimido-tris-ethylmethylamido-tantalum ($^tBuN = Ta(NEtMe)_3$, TBTEMT) for the ALD of Ta_2O_5 films for the first time. This compound is liquid at room temperature and highly reactive towards other reactants like water, oxygen and ammonia. The molecular structure of TBTEMT is very similar to that of TBTDET, but here some of the ethyl groups in the alkylamide part of the molecule are substituted by methyl groups (see Fig. 1 in Ref. [49]). Due to this difference, TBTEMT exhibits a smaller molecule size and has a higher vapor pressure (~2 Torr/267 Pa at 100 °C) [50,51] compared to TBTDET, and thus, offers promising properties for its use in ALD. Additionally, TBTEMT is available for a lower price than TBTDET enabling remarkable precursor cost reduction (effective 2016). While new to the ALD of Ta_2O_5, TBTEMT has already been applied in the thermal ALD [49], plasma-enhanced ALD [51,52] and the metal-organic CVD [50,53] of tantalum nitride (TaN) films.

Here, we report about a novel process for the thermal ALD of Ta_2O_5 films using TBTEMT and water (H_2O). The obtained growth characteristics and film properties are presented as a function of the key process parameters and the results are discussed in a comparative manner with data from literature.

2. Experimental details

2.1. Film deposition

Ta_2O_5 film depositions were performed in a warm-wall horizontal cross-flow reactor which is integrated inside the vacuum chamber of a commercial cluster tool (FHR Anlagenbau GmbH). This chamber is pumped by a turbo molecular pump providing a base pressure in the range of 10^{-4} Pa. The deposition reactor is capable to coat substrates with sizes up to 100 mm in diameter. The walls of the reactor can be heated up to 150 °C, while the actual substrate temperature is achieved by heating the substrate carrier from the backside. In this regard, the relation between heater temperature and substrate temperature was determined in advance, and thus, all values given in this work refer to the actual substrate temperatures.

TBTEMT (electronic grade) was purchased from Sigma-Aldrich Co. LLC. The precursor containing bubbler was heated to a temperature of 60 °C to reach a suitable vapor pressure. In order to prevent precursor condensation, the precursor delivery lines between the bubbler and the reactor were maintained at temperatures between 75 and 100 °C. The H_2O was stored in another bubbler kept at room temperature. Argon (Ar, purity >99.9999%) served as carrier and purge gas. A carrier gas flow of 100 sccm was used for both the TBTEMT and the H_2O to enhance their delivery into the reactor. Another 300 sccm of Ar were applied to continuously purge the reaction volume. The resulting process pressure was 150 Pa, but varied between 140 and 180 Pa due to the gas pulsing. The process sequence with repeated ALD cycles, each one comprising the TBTEMT pulse, a first purge, the H_2O pulse, and a second purge, was realized fully automatic by computer controlled ALD valves.

The films were grown on pieces of p-doped (100) silicon (Si) wafers. These substrates had a resistivity of 1–20 Ωcm and were covered by a native silicon oxide (SiO_2) with a thickness of around 1.6 nm. For some experiments, the Si substrates were treated with 0.5% hydrofluoric acid (HF) for 60 s in order to remove the native SiO_2 and to create a hydrogen-terminated surface. Some films were also subjected to a post-deposition annealing in the temperature range of 400–800 °C in nitrogen (N_2) ambient for 1 h.

2.2. Film characterization

Film thicknesses were determined by spectroscopic ellipsometry (SE) using a J. A. Woollam V.A.S.E ellipsometer, a spectral measurement range from 400 to 1000 nm and an incidence angle of 75°. For verification purposes, selected samples were characterized by x-ray reflectivity (XRR) analyses as well utilizing a Bruker D8 Discover XRR tool and Cu-K_α radiation. The growth rate and the growth per cycle (GPC), respectively, were calculated from the determined film thickness and the applied number of process cycles. The deposition uniformity was evaluated by always coating several samples evenly distributed within the ALD reactor. The film conformality was investigated by depositing a film on substrates with deep trenches structures and studying the cross-sections with a Hitachi S-4700 field emission scanning electron microscope (FE-SEM).

The film composition was analyzed by x-ray photoelectron spectroscopy (XPS) using a Multiprobe unit from Omicron NanoTechnology GmbH and non-monochromatic Al-K_α radiation. Prior to the XPS measurements, the samples were treated with a soft sputter cleaning to remove ambient surface contaminations. Atomic force microscopy (AFM) measurements were performed in non-contact mode operation with the same tool. The film densities were determined from XRR analyses. Refractive indexes were derived from multi-angle SE measurements (65–85°) and the evaluation of the obtained data by employing a Cauchy model. The film structure was studied by grazing incidence x-ray diffraction (GI-XRD) utilizing the Bruker D8 Discover tool, Cu-K_α radiation and a grazing angle of 0.45°.

In order to analyze the electrical properties of the Ta_2O_5 films, metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) capacitor structures were fabricated. In this regard, Si with native SiO_2, HF-treated Si as well as Si with a 2.5 nm thermally grown SiO_2 (dry oxidation at 875 °C) were utilized as substrates for MIS structures. On the contrary, 20 nm thick titanium nitride (TiN) films deposited on Si by plasma-enhanced ALD were applied as lower electrodes for the preparation of MIM structures. In each case, circular top electrodes with a diameter of 450 μm were created by e-beam evaporation of 300 nm titanium and 100 nm aluminum onto the Ta_2O_5 films using a shadow mask. Capacitance-voltage (C-V) measurements were performed with a Keithley 4200-SCS semiconductor characterization system at a frequency of 100 kHz, with an AC signal level of 30 mV and in voltage-sweep mode. In order to take into account the impact of high leakage on the C-V measurements, the obtained data were compensated by the series resistance [54]. The dielectric constant and the equivalent oxide thickness (*EOT*), respectively, were calculated from the accumulation capacitance in case of MIS structures and at zero bias in case of MIM capacitors. A Keithley source-measure unit K207 was applied for measuring the current-voltage (I-V) characteristics.