Thin Solid Films 577 (2015) 97–102

Contents lists available at ScienceDirect

Thin Solid Films

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

Characterization of dielectric layers grown at low temperature by atomic layer deposition

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ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 26 January 2015
Accepted 26 January 2015
Available online 30 January 2015

Keywords:
Atomic layer deposition
Dielectric layers
Energy gap
High dielectric constant

ABSTRACT

Dielectric films, such as hafnium dioxide (HfO_2), aluminum oxide (Al_2O_3), zirconium dioxide (ZrO_2), titanium dioxide (TiO_2) and their composite layers are deposited on polycrystalline and amorphous substrates by the atomic layer deposition (ALD) method. We demonstrate that the use of this technology guarantees a uniform and controlled surface coverage in the nanometer scale at low temperatures (in our case, below 100 °C). Modification of the composition of oxide layers allows the deposition of materials with quite different absorption coefficients, refractive indexes and dielectric constants. In particular, we demonstrate structural, electrical and optical properties of dielectric layers and test metal-oxide-semiconductor structures with these oxide materials. Our good quality dielectric layers, obtained at low-temperature ALD, are characterized by a high dielectric constant (above 10), very smooth surface, wide energy gap (above 3 eV), low leakage current (in the range of 10^{-8} A/cm^2 at 1 V), high dielectric strength (even 6 MV/cm) and high refractive indexes (above 1.5 in the visible spectral range).

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1. Introduction

Thin films of high-*k* (i.e. with high dielectric constant) materials are extensively studied due to a wide range of technological applications [1–3]. Most of the studies concentrate on the optimization of their physical characteristics and growth processes. Nowadays, these oxide materials are commonly used as gate dielectrics in silicon-based microelectronics devices [1,3,4]. Due to a wide range of desirable properties, various dielectric oxides can also be applied as gate insulators in transparent devices with low power consumption, resistance switching materials for semiconductor memories, optical coatings in lasers and in microscopes or charge-coupled devices, and barriers and/or active layers in photovoltaic structures [5–10]. Dielectric thin films can be deposited using either RF-magnetron sputtering technology, chemical vapour deposition or atomic layer deposition (ALD) method [11–14], the method originally developed for the fabrication of amorphous Al_2O_3 insulator films for electroluminescent flat panel displays [15].

In fact, a rapidly increasing interest in ALD (observed since the mid-1990s) originates from possible applications in silicon-based microelectronics. In particular, concentrated research was a consequence of the decreasing device dimensions and increasing aspect ratios in integrated circuits [16]. The thickness of isolating films has, in many cases, decreased even to the order of a few nanometers, which required materials with higher dielectric constant values. At the same moment, the main drawback of ALD, its low deposition rate, became less important. What was more important, this technique enables excellent thickness control of thin films at the nanometer scale, enables growth at low temperature, assures a high reproducibility of deposition and of uniformity over large substrates. These properties made ALD an ideal candidate for a low-cost deposition of various transparent dielectrics for electronic and photovoltaic applications [17]. This fact motivated several groups to work on deposition of high-*k* oxides by the ALD method. However, in most cases, these groups reported on growth performed at higher temperatures (110–350 °C) [10–14]. There are some examples of ALD processes working in the range of 100–150 °C; these include the deposition of Al_2O_3, ZrO_2, and HfO_2 [18]. Unfortunately, in some processes, special measures need to be taken to maintain the ALD growth of good quality dielectric layers. Thus, most groups used post-growth annealing (300–900 °C) after the ALD process [11–13]. Furthermore, still lower ALD deposition temperatures (near room temperature) have been demonstrated for only Al_2O_3, in this case, impurity contents of films significantly increase as the deposition temperature is decreased [19]. This restriction of material types is related to the fact that the suitable precursors become fewer as the deposition temperature decreases. This is most often due to the low reactivity of the precursors for ALD leading to increased impurity contents as well as to a decrease in the overall film quality. If deposition temperature is still

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http://dx.doi.org/10.1016/j.tsf.2015.01.059
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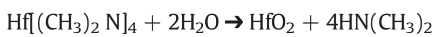
lowered to below 80 °C, insufficient volatility of most solid precursors restricts their use in ALD.

In the present work, we demonstrate the ALD growth processes performed at very low temperature (LT), allowing the deposition of homogeneous thin dielectric films with precisely controlled thicknesses. Use of LT processing is motivated by rapidly increasing interest in electronic devices based on transparent substrates including foils, polymers, and hybrid structures with organic partners. Furthermore, device architectures as well as temperature budget consideration favour the lowering of the deposition temperature well below the actual 200 °C. Consequently, we concentrate on the characterization of high-*k* oxides and test metal-oxide-semiconductor (MOS) structures obtained at temperature below 100 °C. Properties of dielectric layers are described. We analyze their crystal structure, surface roughness, dielectric constant, current-voltage (I-V) characteristics, charge density, band gap and refractive index. Our research leads to the preparation of good quality dielectric films with the properties required for electronic and photovoltaic applications.

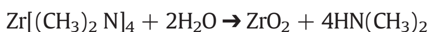
2. Experiment

In the study described below, high-*k* oxides were deposited using either the Savannah-100 ALD reactor of Cambridge NanoTech Company/Ultratech or the TFS 200 ALD reactor of Beneq Company. Glass and *n*-type silicon (*n*-Si) as substrates and tetra-kis(dimethylamido)hafnium, trimethylaluminum, tetrakis(dimethylamido)zirconium, titanium tetrachloride as metal precursors and de-ionized water as an oxygen precursor were used in the present work. The dielectric oxides were deposited at very LT of 85 °C by double-exchange chemical reactions of the type listed below [20]:



$$Hf[(CH_3)_2N]_4 + 2H_2O \rightarrow HfO_2 + 4HN(CH_3)_2$$

$$2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4$$

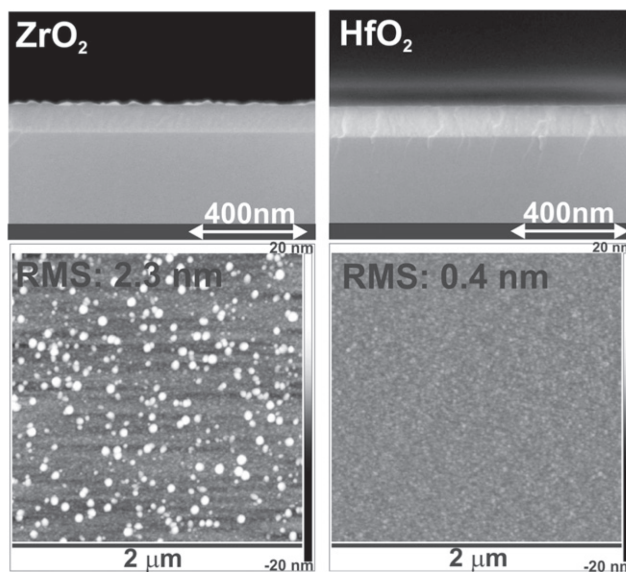


$$Zr[(CH_3)_2N]_4 + 2H_2O \rightarrow ZrO_2 + 4HN(CH_3)_2$$

$$TCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

Precise thickness control was easily achieved as a constant amount of a film material was deposited in each cycle and film thickness scales with the number of the ALD cycles [21]. The growth parameters such as pulse times of the precursors, purging times after precursor pulses and precursor temperatures were the same for all depositions of selected oxides. The films were grown using sequential pulsing of metal precursor and oxygen precursor with purging periods of about 10 s for both precursors. Thus, the duration of a complete ALD cycle was about 20 s. Optimum pulse times of precursors for self-saturated and homogeneous deposition were very short in the range of 10–200 ms. Growth rates at low growth temperatures were about 0.15 nm per cycle for HfO_2, 0.08 nm per cycle—Al_2O_3, 0.13 nm per cycle—ZrO_2 and 0.07 nm per cycle—TiO_2.

The so-obtained oxide layers were characterized with a range of experimental methods—transmission electron microscopy (TEM) investigations (with the use of FEI Titan 80-300 Cubed microscope, at 300 kV accelerating voltage), surface morphology (investigated by an atomic force microscopy, AFM, Bruker in the PeakForce Tapping mode), surface roughness (determined by a root mean square (RMS) roughness of the AFM height measurements from images taken from a $10 \times 10\ \mu m^2$ region), cross-section images (taken using a scanning electron microscopy, SEM, Hitachi SU-70 at 15 kV accelerating voltage), optical properties (using Horiba Jobin-Yvon ellipsometer with the wavelength ranging from 170 to 730 nm, used to determine the band gap values of the investigated oxides), chemical analysis (carried out by an energy-dispersive X-ray spectrometer, EDX, at 5 kV accelerating voltage—as equipment for electron microscopes). The EDX analysis were performed using Thermo Scientific UltraDry silicon drift X-ray detector of SEM and Noran System 7 X-Ray Microanalysis System. Basic electro-physical properties of dielectric layers were determined for MOS type capacitors. Gate dielectrics with thicknesses in the range of 200–20 nm obtained on *n*-Si substrates (10^{-2} Ωcm resistivity). Titanium/gold or aluminum were used as gate electrodes with areas of 0.04–0.09 cm^2 or 0.00049 cm^2, respectively. These gate electrodes were deposited by sputtering. The gate area was 0.09 cm^2 for MOS structures with 100 nm HfO_2 gate dielectrics grown at different temperatures, 0.00049 cm^2—with 20 nm gate dielectrics and 0.04 cm^2 for other MOS structures. Leakage current density values were measured for



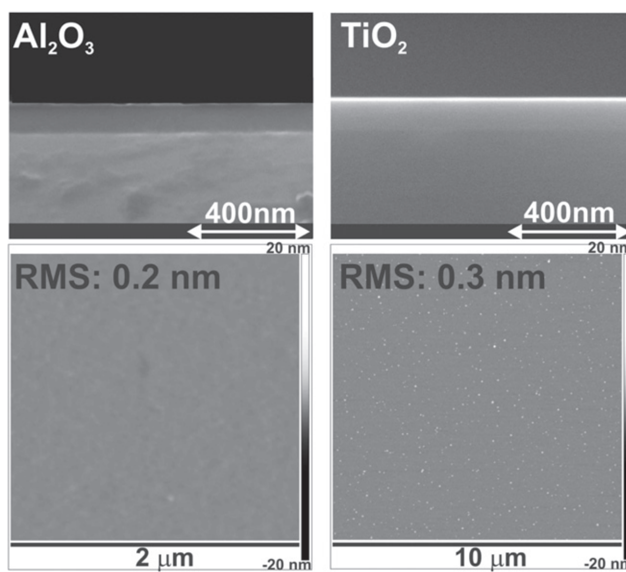


Fig. 1. AFM images of surface morphology and SEM cross-sections for (a) ZrO_2, HfO_2 (b) Al_2O_3, TiO_2 dielectric layers grown at 85 °C on Si with a thickness of 100 nm.

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