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Structural and electrical characterization of multilayer Al_2O_3/ZnO nanolaminates grown by atomic layer deposition

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ABSTRACT

Nanolaminates formed by several bilayers of Al_2O_3 and ZnO (AZA), grown by atomic layer deposition from Trimethyl aluminum, Diethyl zinc and water as co-reactants, were deposited on n-type (100) silicon substrates. A set of 5 nanolaminates with a total thickness of about 100 nm, containing several Al_2O_3/ZnO bilayers with thicknesses of 0.28, 0.38, 2, 10 and 20 nm, were prepared. XRD shows an evolution from amorphous to crystalline structure as a function of bilayer thickness. Capacitance-Voltage (C-V) and Current-Voltage (I-V) electrical characterization was carried out in order to evaluate the potential of the nanolaminates for microelectronic applications. Dielectric constant values between 8.3 and 9.6 were obtained, depending on bilayer thickness. The MOS capacitors exhibited net equivalent oxide thickness values between 44 and 38 nm.

1. Introduction

Nanolaminates are composite films comprised of alternating nanolayers of different materials [1]. Alternatively, composite materials may be homogeneously blended to form alloys. A wide range of physical properties may be achieved by varying the relative proportions of the components. This strategy has been used previously to control various thin film properties, including refractive index, dielectric constant, lattice constant, hardness, charge-storage capacity and surface roughness [2–7].

Atomic layer deposition (ALD) is a useful technique for growing compound films. ALD relies on binary sequence of self-limiting surface chemical reactions. ALD, due to its self-limiting nature, is an almost ideal growing technique [8], for producing high quality thin films of excellent thickness uniformity and resolution down to the sub-nanometric scale. Also, this characteristic makes ALD suitable for managing large surfaces, allowing production of devices of complex geometries [9,10].

Nanolaminates can be applied in microelectronic devices [1,8,11–15], optoelectronics [16], packaging applications [17,18], flexible barriers and conducting films [19]. In CMOS device nanolaminates are used how suppress of the regrowth of the native oxide in the interface between gate and semiconductor [20]. In MOS technology, HFTIO/InGaAs and HFTIO/Al_2O_3/InGaAs nanolaminates have been studied for their application as transistor gates showing a dielectric constant of 18.7 and 21.8 respectively [20–23].

Zinc oxide (ZnO) is a well-known material that is employed in electronic applications because of its low cost and wide availability. It is an n-type semiconductor, characterized by a high dielectric constant (k = 8.6) and with a relatively large band gap of about 3.4 eV [24]. Zinc oxide has applications as semiconductor, luminescent, photoconductor, piezoelectric transductor, gas sensor and transparent electrode for solar cells [24–26]. On the other hand, aluminum oxide (Al_2O_3) is one of the most extensively applied and studied dielectric materials operating very well from room- to high-temperature. It is known for its good chemical stability, extremely high hardness and relatively high thermal conductivity. Al_2O_3 thin films have been used as dielectric gate in electronic devices [27] because of the high-k dielectric constant and their useful physical properties for micro and optoelectronic applications [28]. Nonvolatile memory structures operating at relatively high temperatures were reported as well [29].

The combination of ZnO/Al_2O_3 nanolaminates are important for

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several areas of technology; for example Al_2O_3:ZnO (1:20) is a lower cost and more efficient alternative to indium-tin-oxide (ITO) as transparent electron-selective electrodes for solar cells [30]. Also, as its resistivity is easy to tune, it may improve the reliability of microelectromechanical (MEMS) devices by preventing static charge building [31]. An Al_2O_3/ZnO bilayer coating on polypropylene nonwoven fibers enhances the electrical conductance of ZnO, compared to a pure ZnO coating [32]. Improving the optical and electrical properties of ZnO with Al_2O_3 have promising applications in the field of sensors [33]. ZnO and Al_2O_3 thin films deposited by ALD have been used to synthesize thin films transistors (TFT) [34,35], as well as flexible TFT [35].

Previously, we described the optical properties of nanolaminate films based on bilayers of Al_2O_3/ZnO (AZA) deposited on Si substrates by ALD [36]. In this paper, we report on the electrical and structural properties of this type of nanolaminates.

2. Experimental details

2.1. Synthesis of Al_2O_3/ZnO nanolaminates

Nanolaminates of Al_2O_3/ZnO were deposited on single side polished p-type Si (100) substrates using a Beneq TFS 200 ALD reactor system at a temperature of 200 °C [27,28]. In order to remove organic contaminants from the Si surface, substrates were cleaned in a mixture of equal volumes of acetone, isopropanol, ethanol and methanol using an ultrasonic bath at 50 °C for 15 min. Afterwards, the substrates were cleaned with reagent grade isopropanol and dried with ultra-high purity (UHP, 99.999%) nitrogen. High purity Trimethyl aluminum (TMA) from Strem Chemical and Diethyl zinc (DEZ) from Sigma Aldrich, were used as metalorganic precursors. The oxidant agent was deionized water and for purge and carrier gas UHP nitrogen was used. Average growth per cycle (GPC) for tick pure Al_2O_3 or ZnO films are 0.95 or 1.766 Å/cycle, respectively. For programming approximated thickness of layers, the GPC was rounded up to 0.1 and 0.18 nm/cycle, respectively. Fig. 1 shows the architecture of the samples. The nanolaminate consists of several bilayers of Al_2O_3 and ZnO. A series of samples were prepared varying the programmed thickness of the bilayers from ~ 0.28 nm up to ~ 20 nm, as indicated in Table 1. The thickness of each individual layer was varied systematically from ~ 0.1 to ~ 10 nm for Al_2O_3 and from ~ 0.18 to ~ 10 nm for ZnO, resulting in nominal bilayer thicknesses values between ~ 0.28 and ~ 20 nm (Table 1). The nanolaminate films were prepared by growing alternating layers of Al_2O_3 (A) and ZnO (Z), assembling the structure AZAZ…A, which starts and finishes with Al_2O_3.

For example, the growing process for the sample AZA20 was as follows: first, an Al_2O_3 layer of 100 cycles of TMA/H_2O was grown (~ 9.5 nm); then a ZnO layer of 60 cycles of DEZ/H_2O (~ 10.6 nm) was added; the bulk growth rates are similar to other reports [30,31,37].

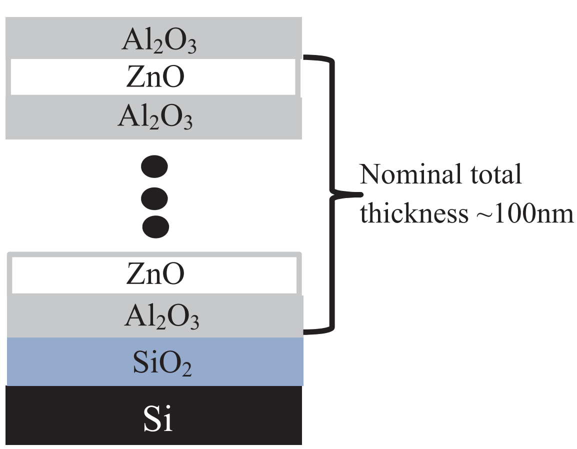

Fig. 1. Architecture of the samples.

Table 1
Deposition sequence for nanolaminates. #: indicate the approximated bilayer thickness in mn.

Sample (AZA#)	Bilayer (ALD cycles)		Bilayers (Amount)	Capping (ALD cycles)
	Al_2O_3	ZnO		Al_2O_3
AZA0.28	1	1	500	1
AZA0.38	2	1	272	2
AZA2	10	5	50	10
AZA10	30	50	10	30
AZA20	100	60	5	100

Table 2
Nanolaminate total thickness values obtained via VASE and SEM.

Total thickness (nm)			
Sample	Nominal	VASE	SEM
AZA0.28	136	86 ± 2	84 ± 2
AZA0.38	100	87 ± 2	85 ± 2
AZA2	93	97 ± 2	95 ± 2
AZA10	105	99 ± 2	97 ± 2
AZA20	110	109 ± 2	107 ± 2

The above procedure describes the deposition of the first bilayer, which was deposited 5 times consecutively. Finally, the nanolaminate was capped with one more layer of Al_2O_3 of the same number of cycles as previous ones; 100 cycles. Total nominal thickness is ~ 110 nm. The reason for depositing this capping layer is to reduce leakage currents and to increase the breakdown voltage of MOS capacitors. A similar procedure was followed to prepare the other samples. Nominal thicknesses are displayed in Table 2.

2.2. Characterization techniques

The ALD deposited nanolaminates were characterized by various techniques. Film thickness was obtained by scanning electron microscopy (SEM) imaging and variable angle spectroscopic ellipsometry (VASE). The AZA nanolaminates were measured in a M2000U J.A. Woollam ellipsometer at four different angles of incidence (45, 55, 65 and 75°) in a wavelength range of 300–1200 nm. The analysis of the measurements and the optical properties of these nanolaminates were reported elsewhere [36]. The applied VASE model for data fitting is a multilayered one, where each layer thickness is considered. That is, the model corresponds exactly to the scheme presented on Fig. 1. For example, for AZA20 the VASE model has 6 Al_2O_3 and 5 ZnO layers, in addition to the native SiO_2 and Si substrate. The estimated thicknesses obtained from ellipsometric data were compared with those from cross-sectional images obtained by means of a JEOL JIB-4500 SEM system at 15 kV. VASE thickness was utilized for calculating the dielectric constant values.

MOS capacitors were fabricated for electrical characterization by evaporating top and bottom gold electrodes. The top electrodes were deposited through a mask with 1 mm diameter holes, whereas the bottom electrode covered the whole back area of the silicon wafer. A JEOL JEE-400 Vacuum Thermal Evaporator was used, in which gold was evaporated for 3 min by heating a tungsten filament with an electrical current of 25 A. The pressure during evaporation was about 1×10^{-3} Pa.

Electrical characterization of the nanolaminate films was carried out by Capacitance/Conductance-Voltage (C/G-V) and Current-Voltage (I-V) measurements using Keithley 4200 SCS instrument. Dielectric constant values were calculated from the C-V curves, while breakdown voltages were determined from the I-V results.

The C/G-V measurements were carried out using a 25 mV a.c. signal