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Investigation of HfO_2 and ZrO_2 for Resistive Random Access Memory applications

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ABSTRACT

This work is focused on the investigation of Au/high k/TiN stacks for Resistive Random Access Memories. A screening of high k oxides, commonly used in advanced metal gates, such as HfO_2 and ZrO_2, is proposed. These oxides were grown on TiN electrodes using Atomic Layer Deposition and Plasma Enhanced Atomic Layer Deposition. The morphological and structural properties of the films were studied as a function of deposition temperature, film thickness and/or annealing using Atomic Force Microscopy, Grazing Incidence X-ray Diffraction and Attenuated Total Reflectance. An amorphous to crystalline transformation was observed with thickness for HfO_2 and ZrO_2, with deposition temperature for HfO_2 from 300 to 350 °C, and with annealing in N_2 for 1 h at 400 °C for ZrO_2. According to density measurements obtained using X-ray Reflectometry, HfO_2 and ZrO_2 are suspected to be stoichiometric whatever the thickness. The film stoichiometry was confirmed using X-ray Spectroscopy. Current–voltage measurements were performed on Au/high k/TiN, where Au and TiN are top and bottom electrodes, respectively. Whatever the high k material, the crystallization increases with thickness or/and temperature without any significant modification of the SET operation. The film annealing, which was proposed as an alternative way to crystallize ZrO_2, may cause a modification of the interfaces, leading to a decrease of the switching performance.

1. Introduction

Flash memory scaling has been continually on-going ever since the appearance of the technology in the market. As physical and cost limitations may appear in the future if is desired to pursue dimension reduction, alternative solutions are being currently investigated. Resistive Random Access Memories (ReRAMs) are considered for next generation non-volatile memories (NVM) due to their promising performance, advantages in terms of integration, as well as material and process availability in the microelectronics industry [1]. Transition metal oxides and metal nitride electrodes are already considered as the most promising materials for ReRAMs as they are already implemented in Metal–Insulator–Metal (MIM) structures and compatible with Complementary Metal Oxide Semiconductor (CMOS) technology. However, critical issues remain to be addressed, such as reliability and retention mechanisms for low power ReRAM. Many oxides – such as TiO_2 [2], NiO [3], TaO_x [4,5] and HfO_2 [6–8] – have already been studied. The mechanisms at the origin of the resistive switching have been recently reviewed [9] but still remain an open issue. In the case of HfO_2, oxygen could be extracted from the oxide at the anode, leaving oxygen vacancies under the anode and oxygen ions within the anode. These vacancies may be drifted by the electric field to the cathode, leading to the growth of conductive filaments from the cathode to the anode. When the filament is in contact with the anode, electrode materials are short-circuited, and the device switches from a high resistance state (HRS) or OFF state to a low resistance state (LRS) or ON state. In the reverse polarity, oxygen vacancies are repelled from the cathode leading to the disruption of the filament [10]. In a previous work, the influence of the bottom electrode (TiN versus Pt) on HfO_2 resistive switching performance was investigated, indicating a good cyclability only using Pt as electrode [11]. TiN has a strong affinity for oxygen, resulting in oxygen depletion in the oxide, and creation of a large amount of oxygen close to the interface. This phenomenon could lead to the formation of stronger filaments that are more difficult to reset. In addition, the presence of an interfacial layer when the oxide is grown on TiN could influence the cycling properties. However Pt is not convenient for microelectronic industry, thus it remains important to avoid its use as bottom electrode in future studies. Another important parameter is the crystalline state of the oxide, for instance HfO_2, often investigated elsewhere but giving different conclusions [12,13]. Nevertheless, the correlation between structure and resistive switching needs to be further studied for other oxides and oxide/electrode couples, in order to be able to establish the right correlation. The present work is focused on the characterization of oxides commonly used as high k dielectrics in advanced metal gates (HfO_2 and ZrO_2) grown on TiN by Atomic Layer Deposition (ALD) and Plasma Enhanced Atomic Layer Deposition (PEALD). The morphological and structural properties of the films are studied as a function of the

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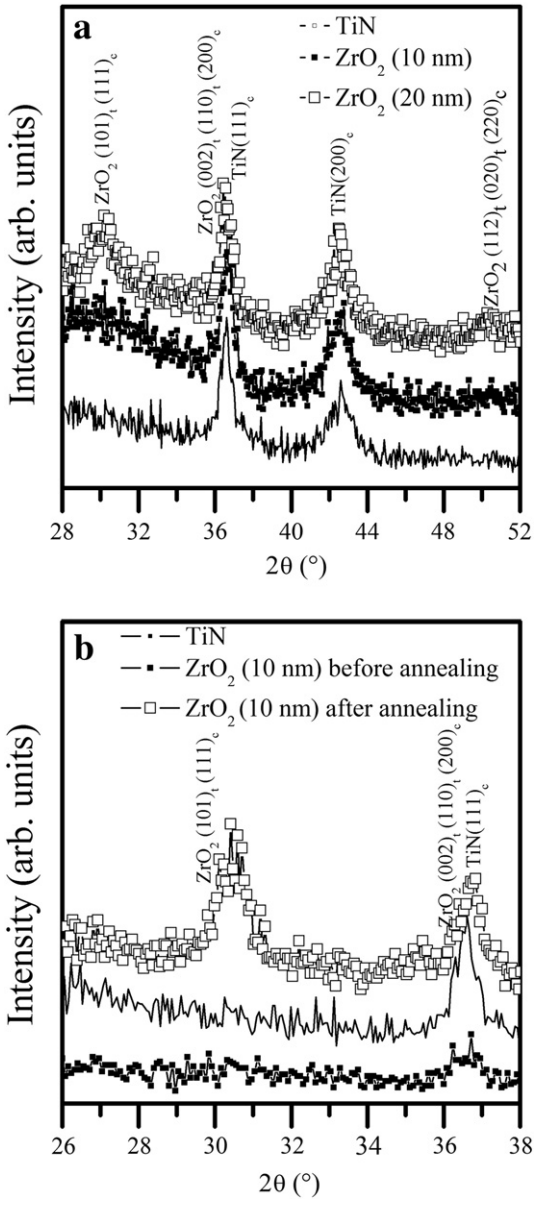

Fig. 1. GI-XRD patterns obtained for ZrO_2 films grown on TiN by PEALD (a) influence of the film thickness (b) influence of an annealing at 400 °C under N_2 for 1 h.

deposition temperature, oxide thickness and annealing conditions. The effect of these parameters on the resistive switching of each stack was investigated for comparison.

2. Experimental procedure

Prior to oxide deposition, TiN (25 nm thickness) was deposited as bottom electrode on SiO_2 by Physical Vapor Deposition at 350 °C. On one hand, HfO_2 films (10 and 20 nm thickness) were grown on TiN in an ALD Pulsar2000 reactor (from ASM) at 300 and 350 °C, using $HfCl_4$ and H_2O as precursor and reactant, respectively. On the other hand, ZrO_2 films (3, 10 and 20 nm thickness) were grown on TiN in a PEALD Emerald reactor (from ASM) maintained at 250 °C, using $(C_5H_5)Zr[N(CH_3)_2]_3$ as precursor [14] and direct O_2 plasma as reactant [15]. Gold top electrodes, with a 2 mm diameter, were fabricated by dc-sputtering, through a shadow mask. Current–Voltage (I–V) measurements (dc modes) were performed in air using a Keithley 2635 Source Meter unit, with a grounded bottom electrode. During the transition from the OFF to the ON state, the current was limited to a compliance current ($I_{compliance}$) of 0.1 mA to avoid irreversible breakdown. The film crystallinity was analyzed by (i) Grazing Incidence (1°) X-ray Diffraction (GI-XRD) using a PanAnalytical X'Pert Pro MPD diffractometer in θ/2θ configuration with a copper anticathode (=1.5418 Å) as the X-ray source, and (ii) Fourier Transformed InfraRed (FTIR) in Attenuated Total Reflectance (ATR) mode to enhance the infrared signature of such thin layers. ATR measurements were acquired between 600 and 4500 cm^{-1} using a home-made setup [16] consisting of a 65° germanium prism in close contact with the sample. A polarized IR beam from a broker IFS55 FTIR spectrometer was directed into the prism base at an angle of incidence of 70° to ensure total reflection. After one reflection, the IR light is directed onto a HgCdTe detector cooled with liquid nitrogen. The prism spectrum was taken as a reference when no sample was coupled to the prism. X-ray Reflectometry (XRR) was used to determine layer thicknesses and densities using a JVX 5200 XRR–XRF combined tool from Jordan Valley. Surface morphology and roughness were observed using Atomic Force Microscopy (AFM) using a Dimension 5 apparatus from Bruker in tapping mode with RTESP phosphorus (n) doped silicon tips from Veeco.

X-ray Spectroscopy (XPS) was performed in order to determine the film composition, using XPS SSI S-Probe equipment from Euroscan Instruments with a monochromatic (AlKa at 1.487 keV) X source. The photoelectrons are collected at a 35° angle with respect to the surface. Ar^+ ion beam etching was performed with an acceleration of 3 keV for 1 min before acquisition. The number of scans was fixed to 30 and 50, respectively, for ZrO_2 and HfO_2 samples.

3. Results

3.1. PEALD ZrO_2 on TiN

3.1.1. Crystallization

The 10 nm thick film deposited at 250 °C was found to be rather amorphous, despite the presence of a slight shoulder at 31° that could correspond to either the $(101)_t$ tetragonal or the $(111)_c$ cubic phase (Fig. 1a), but not intense enough to confirm a beginning of crystallization. Nevertheless, the crystallization was clearly observed with increasing thickness from 10 to 20 nm (Fig. 1a), according to the appearance of ZrO_2 diffraction peaks at 31, 35 and 50°, as shown elsewhere [15]. An annealing of the 10 nm thick film at 400 °C

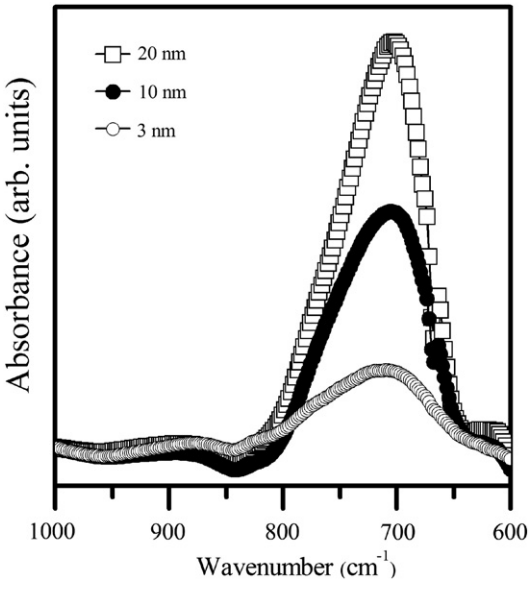

Fig. 2. FTIR-ATR spectra obtained for ZrO_2 films with thicknesses varying between 3 and 20 nm, grown on TiN at 250 °C by PEALD.