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Conduction and stability of holmium titanium oxide thin films grown by atomic layer deposition

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ABSTRACT

Holmium titanium oxide ($HoTiO_x$) thin films of variable chemical composition grown by atomic layer deposition are studied in order to assess their suitability as dielectric materials in metal–insulator–metal electronic devices. The correlation between thermal and electrical stabilities as well as the potential usefulness of $HoTiO_x$ as a resistive switching oxide are also explored. It is shown that the layer thickness and the relative holmium content play important roles in the switching behavior of the devices. Cycled current–voltage measurements showed that the resistive switching is bipolar with a resistance window of up to five orders of magnitude. In addition, it is demonstrated that the post-breakdown current–voltage characteristics in $HoTiO_x$ are well described by a power-law model in a wide voltage and current range which extends from the soft to the hard breakdown regimes.

1. Introduction

Ho_2O_3, like other oxides of the lanthanide series such as Gd_2O_3, has been proposed as a dielectric material for advanced electron devices. This material exhibits a moderate permittivity value ($k \approx 12$) as well as a large band gap (5.3 eV) [1,2]. Ho-doped TiO_2 and $HoTiO_3$ are also high permittivity (high-k) materials and possible candidates to replace SiO_2 in field-effect transistors [3]. Although TiO_2 is considered a good candidate as a dielectric layer in metal–insulator–metal (MIM) capacitors for dynamic random access memories (DRAM) [4] because of its high permittivity value, its major drawback is its small band gap/low barrier height and hence its large leakage current when biased. However, when combined with a larger band gap material, the leakage current reduces significantly: Al-doped TiO_2 MIM capacitors with an equivalent oxide thickness of 0.56 nm with leakage current of around 1×10^{-8} A cm^{-2} have been fabricated [5]. This means a current density decrease of 10^6 times due to Al doping. As it is known, in order to overcome the DRAM limitations, such as the high power consumption and stored charge volatility, new kinds of memories are currently under investigation. In particular, resistive random access memories (RRAMs), which are based on a two-terminal device structure that stores data in the form of a reversible resistance change, seem to be very promising [6,7]. Depending on the particular features of the current–voltage (I–V) characteristic, the switching behavior can be unipolar (the switching direction depends on the magnitude of the applied voltage but not on its polarity) or bipolar (the change of the state can be obtained by applying voltages with specific polarity). Resistive switching (RS) phenomena have been found in various types of binary oxides including TiO_2, ZrO_2, HfO_x, etc. [8–12]. In fact, TiO_2 is one of the most studied materials for RS applications due to its simple fabrication at low process temperature and mass production compatibility. As it has been said before, the insertion of a thin Al_2O_3 barrier layer helps to overcome its high operational currents. B. Hudec, et al. [13] systematically studied the effect of this layer thickness on the RS behavior of stacks with 20 nm of TiO_2 covered with an Al_2O_3 layer. They found that an Al_2O_3 layer of a certain thickness, around 3–4 nm, is essential to stabilize the RS parameters. Moreover, no RS could be observed in the single layer TiO_2 due to its leaky character. Other authors have reported RS behavior in structures such as $Pt/TiO_2/Pt$ [8,14,15], but large fluctuations in the I–V sweep curves exist during the reset operations, which are one of the big hurdles that the RS memory has to overcome to become a viable device [12]. Recently, a model has been proposed to explain these large fluctuations [16], that might have their origin in the stochastic nature of the set processes during the repeated RS via the I–V sweeps.

In this work, holmium titanium oxide thin films of different chemical compositions grown by atomic layer deposition have been electrically characterized. A variety of MIM structures have been fabricated in order to assess the suitability of these dielectric films for microelectronics

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use. Special attention has been paid to the post-breakdown I–V characteristics because of its connection with the resistive switching effect.

2. Experimental details

The films containing Ho were grown in a commercial flow-type hot-wall reactor F120 (ASM Microchemistry, Ltd.) [17]. Table 1 summarizes the samples studied in this work. Ho_2O_3 was grown using $Ho(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) and ozone as holmium and oxygen precursors respectively. TiO_2 films were grown using titanium-isopropoxide, $Ti(OCH(CH_3)_2)_4$ and ozone as precursors. Deposition temperature was 300 °C for both constituent oxides. TiO_2:Ho_2O_3 films were grown as stacks of alternating layers of TiO_2 and Ho_2O_3. The thicknesses of the films were evaluated by X-ray reflectometry. The ratios of the different metals were calculated by an energy dispersive X-ray spectrometer. The growth rate of Ho_2O_3 is lower than that of TiO_2, and it was thus necessary to apply, at least, two Ho_2O_3 cycles for each TiO_2 cycle in order to achieve $HoTiO_3$ or $Ho_2Ti_2O_7$ stoichiometry. Selected samples were annealed under nitrogen atmosphere for 30 min at 600 or 800 °C. More detailed description can be found in an earlier study devoted to the structure and morphology of these samples [18]. Fig. 1 shows grazing incidence diffraction patterns, taken from K. Kukli, et al. [18], corresponding to as-deposited Ho_2O_3 film (Fig. 1(a)), and annealed $HoTiO_x$ films, with Ho:Ti = 0.54 and 0.48 (Fig. 1(b) and (c), respectively). The Ho_2O_3 films became crystallized in the as-deposited state, whereas in the $HoTiO_x$ films the crystallization required annealing. In order to make MIM structures, the TiO_2:Ho_2O_3 films were deposited on low resistivity silicon substrates covered with 10 nm thick TiN layers. Al/Ti top electrodes (>100/30 nm thick) were e-beam evaporated through a shadow mask. After the top electrode deposition, samples were not additionally annealed. The electrical measurements were carried out with two different capacitor sizes (2.04×10^{-3} and 0.52×10^{-3} cm^2). A permittivity value of around 25 was obtained for the annealed 25.1 nm-thick $HoTiO_x$, with Ho:Ti atomic ratio of 1.5 [19]. The permittivity increased after annealing, when the samples became crystallized [18]. The highest permittivity values (around 40), correspond to the lowest Ho:Ti values (0.54 and 0.48).

I–V measurements were carried out using an HP4155B semiconductor parameter analyzer, whereas a Keithley 4200-SCS semiconductor characterization system was used to obtain capacitance–voltage (C–V) data. I–V measurements revealed the existence of reversible bipolar resistive switching in some of the holmium oxide based devices. As it will be shown in the next section, a clear influence of holmium content and annealing on the C–V linearity has been found.

3. Results and discussion

Fig. 2 shows room temperature C–V curves corresponding to $HoTiO_x$-based MIM capacitors with thicknesses of 7.7, 18.7 and 25.1 nm and Ho:Ti atomic ratios of 1.4, 0.9 and 1.5, respectively. As shown in this figure, the C–V curves are asymmetrical. Capacitance increases for positive voltages and decreases for negative ones. This effect which is relatively weak in the as-deposited samples becomes much more pronounced in the annealed ones. C–V curves are linear for the as-deposited samples and the capacitance values scale according to the dielectric film thickness, i.e. a thinner insulator is associated with a higher capacitance value. However, notice that the C–V curves of the annealed samples are not linear at all. Capacitance is at a minimum value for negative voltages (lower than for the as-deposited samples), then strongly increases up to a certain maximum and then again decreases for positive voltages to an even lower value. Two points are worth mentioning: first, the thickest sample reaches capacitance values similar to those at positive voltage values and, second, the thinnest sample does not reach so high values but returns to values similar to those exhibited by the as-deposited sample. Moreover, maximum capacitance occurs at positive voltages (0.3 V) for the 18.7 and 25.1 nm thick samples, and at a negative voltage (−0.4 V) for the 7.7 nm thick sample. Current conduction measurements show parallel trends: the I–V curves for the same samples are plotted in Fig. 3. These curves were measured on fresh devices, i.e. in samples that were not previously biased. The

Table 1
$HoTiO_x$ samples fabricated for this study.

Material	Metal compounds atomic ratio Ho:Ti	d (nm)	Annealing (N_2, 30′)
$HoTiO_x$	0.48	23.8	600 °C
$HoTiO_x$	0.54	27.5	600 °C/800 °C
$HoTiO_x$	0.9	18.7	600 °C/800 °C
$HoTiO_x$	1.4	7.7	800 °C
$HoTiO_x$	1.5	25.1	800 °C
Ho_2O_3	–	22.7	600 °C

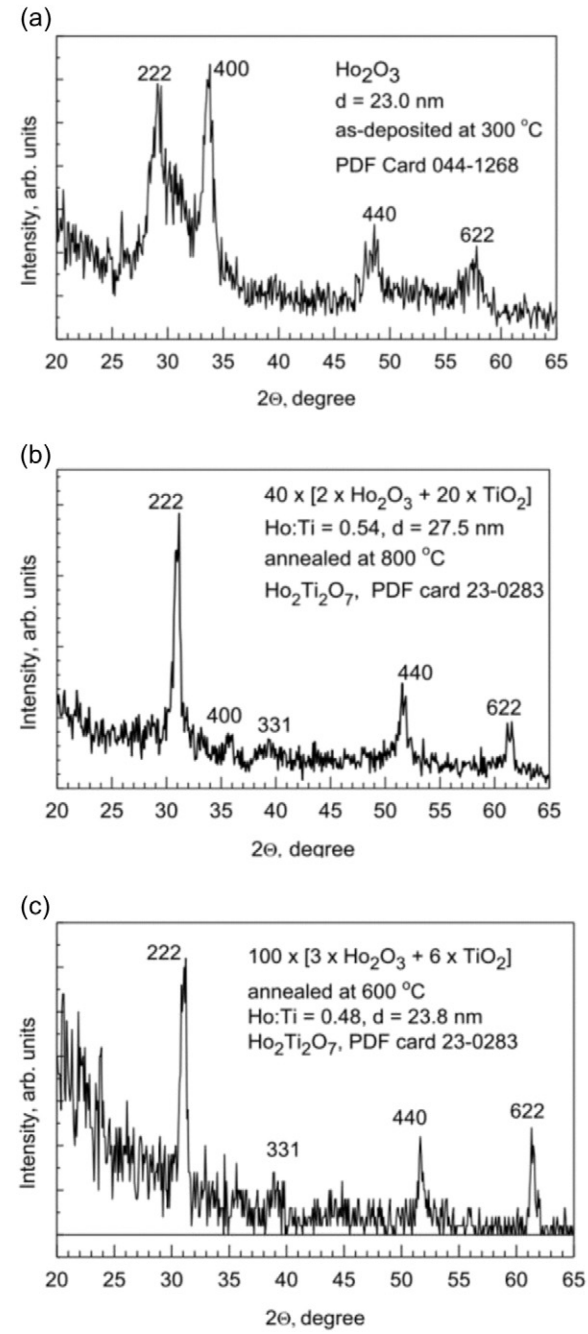

Fig. 1. Grazing incidence diffraction patterns of as-deposited Ho_2O_3 films (a), and annealed $HoTiO_x$ films, with Ho:Ti = 0.54 (b), and 0.48 (c).
(Taken from K. Kukli, et al. [18]).