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X-ray absorption spectroscopy study of Yb_2O_3 and Lu_2O_3 thin films deposited on Si(1 0 0) by atomic layer deposition

M. Malvestuto [a,*], G. Scarel [b], C. Wiemer [b], M. Fanciulli [b], F. D'Acapito [c], F. Boscherini [a]

[a] *Physics Department and INFM, University of Bologna, viale C. Berti Pichat 6/2, 40127 Bologna, Italy*
[b] *Laboratorio Nazionale MDM-INFM, Via C. Olivetti 2, 20041 Agrate Brianza (MI), Italy*
[c] *INFM-OGG, C/o ESRF, BP 220, 38043 Grenoble, France*

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Abstract

Using X-ray absorption spectroscopy we have investigated the local structure of Yb_2O_3 and Lu_2O_3 thin films deposited on Si(1 0 0) by means of atomic layer deposition. These two oxides, as well as those of the other rare earth elements, are considered among the high dielectric constant materials candidates to substitute SiO_2 in ultra-scaled CMOS devices. We find that the films maintain the overall bixbyite structure of the bulk oxides, but exhibit significant distortions of the local structure depending on thickness and thermal treatment.
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1. Introduction

Rare earth (RE) oxides are currently receiving considerable attention in the field of microelectronics as high dielectric constant (κ) materials candidates to substitute SiO_2 [1] in complementary metal oxide semiconductor (CMOS) devices. Indeed, in semiconductor technology there is the need for high transistor density and speed [2], which require scaling down the size of integrated circuit components, so as to increase the capacitance. The latter requirement demands a lower thickness of the conventional SiO_2 gate dielectric layer. However, below about 1 nm, SiO_2 layers become less effective barriers against tunneling currents between transistor channel and metal gate electrodes. An alternative way to increase the gate capacitance is the use of materials with higher κ values than the one of SiO_2 (3.9) [1]. This way, a higher physical thickness of the high-κ layer can match the equivalent oxide thickness of SiO_2, and, consequently, the leakage current can be significantly reduced. Some of the rare earth oxides films under consideration as high-κ oxides are La_2O_3, Pr_2O_3, Gd_2O_3 and Lu_2O_3 [3–7].

In this work we consider two RE oxides, namely Lu_2O_3 and Yb_2O_3. In both cases, the RE element has a completely filled 4f shell, but a different occupation of the 5d shell, and a different behavior as far as variable cation valence is concerned (Lu has only the oxidation state +3, and Yb has oxidation states +3 and +2) [8]. Moreover, Lu_2O_3 and Yb_2O_3 oxides have a large band gap, between 4.8 and 5.8 eV [8–10], and large conduction band offset with respect to silicon [5,10]. For these oxides, the thermodynamic stability on silicon without protective capping layers is however still debated: while some authors predict these oxides to be stable on silicon [11] others predict or detect experimentally silicate formation at the interfacial layer [3,5,12,13]. Furthermore, Lu_2O_3 and Yb_2O_3 have the highest lattice energies among the rare earth oxides, and they are expected to easily crystallize and form polycrystalline films even prior to an annealing process. In the form of thin films, Lu_2O_3 and Yb_2O_3 have a moderate κ: $\kappa\,(Lu_2O_3) = 12$ [3,14] and $\kappa\ (Yb_2O_3) \sim 14$ [15]. The electrical properties

* Corresponding author. Tel.: +39 0512 095805; fax: +39 0512 095153.
E-mail address: marco.malvestuto@unibo.it (M. Malvestuto).

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seem to be related to the details of the deposition technique, to the precursors eventually used, and to the post-deposition annealing processes [3,4]. To better interpret the electrical properties, as well as the structure of bulk and interfacial layers, fine structural investigations of the local atomic and electronic features are needed. Recently, thin Yb_2O_3 and Lu_2O_3 films were deposited using electron beam evaporation as high-κ layers for microelectronic applications [4,15]. In this field, however, atomic layer deposition (ALD) is an affirmed deposition technique because of the good conformality and the promising electrical properties of the thin films [1]. Nevertheless, there is a limited number of investigations on thin rare earth oxide films deposited using this technique [3,6,10,14].

The aim of this work is to study by means of X-ray absorption spectroscopy (XAS) thin Yb_2O_3 and Lu_2O_3 films grown on Si(100) using ALD. Local structure modifications are studied as a function of deposition parameters and annealing processes. XAS has previously been applied to a similar system, Y_2O_3/Si(001) [16,17]. The advantages of XAS in this context are: (1) chemical sensitivity (only the structure around the excited atom is probed), (2) ability to distinguish different back-scattering atoms, (3) a high precision in the determination of interatomic distances (0.01 Å) and of the variance of its distribution (0.001 $Å^2$) and (4) sensitivity to monolayer thickness.

2. Experimental and data analysis

2.1. Growth, structural and morphological characterization

A set of Lu_2O_3 and Yb_2O_3 films were deposited using a F-120 ASM Microchemistry reactor on Si(100) at the growth temperature of 360 °C. Prior to deposition, the Si(100) substrates were covered with a thin chemical oxide layer (RCA for 10 min at 85 °C, dip for 30 s in a diluted HF solution at room temperature, and RCA again for 10 min at 85 °C). The substrate for sample 270H was H-terminated Si(100) (RCA for 10 min at 85 °C, and dip for 30 s in a diluted HF solution). A 1 min long rinse in deionized water followed each cleaning step.

The Lu_2O_3 films were deposited alternating injections of the newly synthesized complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2LuCl]_2$ (11 s) as Lu source [18] and injections of H_2O (11 s) as oxygen source, both carried in the reaction chamber by an N_2 flux. The Lu and O precursors were kept, respectively at 195 °C and 18 °C. An N_2 flux (8 s) purged away the reaction by-products after each step of the ALD cycle. Eighty two and eighteen cycles were applied for the films studied in this work. The Yb_2O_3 films were deposited alternating injections of $Yb(C_5H_5)_3$ (12 s) kept at 100 °C as Yb source (STREM Chemicals), and injections of either H_2O or O_3 (12 s) as oxygen sources. The Yb and O precursors were kept, respectively at 100 °C and 18 °C. O_3 was fed into the reactor in a 400 sccm flux and at a 167 g/cm^3 concentration. Three hundred and ten, and forty one cycles, respectively, were applied for the films studied in this work. Some samples were treated in a rapid thermal annealing furnace at 950 °C for 60 s in N_2. The precursor combinations of both cations with the two mentioned oxygen sources give rise to non-uniform film thickness distributions over the Si substrates.

Prior to XAS measurements, the films were characterized using in-house techniques. The thickness (t) was determined using X-ray reflectivity (XRR) and Rutherford back-scattering (RBS) for the thicker and thinner films,

Table 1
Structural properties of the films studied in this work

Sample	Code	Layer	Oxygen precursor	Treatment	t (Å)	γ (Å/cycle)	ρ ($e^-/Å^3$)	σ_{XRR} (Å)
a	284	Lu_2O_3	H_2O	As grown	25 [RBS]	1.4		
b	284	Lu_2O_3	H_2O	Annealed	30 [RBS]			
c	283	Lu_2O_3	H_2O	As grown	74 (1)	0.90	2.09(5)	4(1)
		IL			9(1)		1.36(5)	3(1)
d	283	Lu_2O_3	H_2O	Annealed	72(1)		2.23(5)	10(1)
		IL			15(1)		1.62(5)	8(1)
e	266	Yb_2O_3	H_2O	As grown	8 [RBS]	0.20		
f	270H	Yb_2O_3	O_3	Annealed	~5			
g	270	Yb_2O_3	O_3	As grown	5 [RBS]	0.11		
h	264	Yb_2O_3	H_2O	As grown	113(1)	0.36	2.22(5)	9(1)
		IL			11(1)		0.85(5)	4(1)
i	264	cap		Annealed	10(1)		1.38(5)	7(1)
		Yb_2O_3	H_2O		82(1)		2.28(5)	6(1)
		IL			51(1)		1.58(5)	19(1)
j	268	Yb_2O_3	O_3	As grown	52(1)	0.24	2.39(5)	6(1)
		IL			19(1)		0.91(5)	4(1)
k	268	Yb_2O_3	O_3	Annealed	90(1)		1.58(5)	4(1)
		IL			8(1)		0.92(5)	4(1)

The errors on the last digits are reported in brackets. As described in the text, in all cases but one the Si substrate was terminated with an oxide layer; for sample 270H the Si substrate was H terminated.

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