

Preface

The technology for complementary metal-oxide-semiconductor (CMOS) is intensely searching for candidates to substitute SiO_2 as gate dielectric enabling the fabrication of small devices with low power consumption and high speed. The suitable candidates must have a high dielectric constant (κ between 15-40), be thermodynamically stable in contact with the semiconductor substrate (Si, Ge, etc.) and with the metal gate, exhibit high conduction band offset with the semiconductor (to minimize leakage currents), and have low defect density both in the bulk and at the interfaces. Rare earth (RE, from La to Lu)-based oxides are among the candidates to replace SiO_2 as gate dielectrics first of all because of their predicted thermodynamical stability on silicon. In addition, high- κ dielectrics, and RE oxides in particular, show potentials also for applications in nano-electronics, opto-electronics, and spintronics. Advantages and disadvantages of RE-based oxides are often related to the intrinsic properties of the RE elements:

1. the increasing $4f$ shell filling level (completely empty in La atoms, and totally filled in Lu ones);
2. the number and the value of the oxidation states (3 for La, Nd, Pm, Gd, Dy, Ho, Er, and Lu; 3 and 4 for Ce, Pr, and Tb; 3 and 2 for Sm, Eu, and Yb);
3. the decreasing ionic radius with increasing atomic number (from 0.123 nm for La to 0.092 nm for Lu), correlated with the decreasing Pauling electronegativity with increasing atomic number (from 2.34 for La to about 2.15 for Lu).

These intrinsic properties of the RE elements affect those of the corresponding oxides, especially in the form of nano-scaled films, and might influence their eligibility as high- κ dielectrics. The main objective of this volume is to address the various properties of RE elements and to understand how to exploit them to obtain proper functionalities of their oxides.

The increasing $4f$ shell filling level could affect the trap density in the RE oxides, as the different energy and occupancy of the d shells do in transition metal oxides. Moreover, it could determine the different reactivity and moisture sensitivity of the RE oxides. It is noteworthy that only four RE elements (i.e. La, Ce, Gd, and Lu, with respectively empty, mono-electron

filled, half-filled and totally filled $4f$ shell) have also one electron in the outer $5d$ shell.

The existence of two oxidation states induces various stoichiometries in half of the RE elements (Ce, Pr, Sm, Eu, Tb, Tm, and Yb). This fact complicates the oxide chemistry and the electronic structure. The consequences of having pure RE_2O_3 oxides or a mixture of RE_2O_3 with REO or REO_2 oxides on the film functional properties might be remarkable and must be fully understood.

The mixed stoichiometries are expected to affect the band alignment. The reason is that the higher the stoichiometric ratio between the RE element and the oxygen in the oxide, the lower the height of the charge neutrality level (CNL) in the band gap and, finally, the higher also the conduction band offset (CBO) with Si, or another semiconductor substrate, e.g. Ge. Therefore, oxidation states of 2 are more favourable than 4. It is not clear, however, what are the consequences when thin films with mixed stoichiometries are produced.

In addition to the band alignment, the mixed stoichiometries might also affect the κ value which is predicted to decrease as the atomic number of the RE decreases. In reality, however, the measured values are scattered, and sometimes anomalously high. Almost all RE elements with two oxidation states generate oxides with low band gaps (≤ 4.0 eV) and very high κ values. On the other hand, most RE elements with oxidation states 3 and 2 (Sm, Tm, and Yb) or with just oxidation state 3 (La, Nd, Gd, Dy, Ho, Er, and Lu) have a band gap around 5 eV, and a medium κ value (about 13).

The decrease of the ionic radius with increasing atomic number of the RE elements accompanies the decrease of their Pauling electronegativity in a range that determines a constant oxygen coordination of 4 on all RE oxides. Such an oxygen coordination correlates with the disruption of the covalent network bonding, and leads to structures that readily crystallize at temperatures of interest in microelectronic processes (500–1000 °C). Ternary compounds based on RE atoms usually should exhibit lower oxygen coordination than the corresponding oxides, thus higher crystallization temperatures. They are therefore suitable alternatives to RE binary oxides. The electronegativity differences in the RE elements might also explain the different hygroscopic behaviour of the corresponding oxides.

The systematic investigation of the previously outlined issues is challenging because in first place good-quality thin films are needed. Several deposition techniques are currently being considered for nano-scale film fabrication, mainly on semiconductors: atomic layer deposition (ALD), electron beam evaporation, molecular beam epitaxy (MBE), metal-organic chemical vapour deposition (MOCVD), and pulsed laser deposition (PLD). Strength and weakness of these techniques are discussed in this volume, with a careful consideration of the growth mechanisms involved. Special attention is devoted to the synthesis and the properties of RE complexes used as precursors

(e.g. for ALD and MOCVD). Methods to handle hygroscopicity in RE oxide films are considered.

In this volume, the structural and compositional properties of both the interface layer and the film are considered in detail, together with the crystalline or amorphous nature of the thin films, their roughness and homogeneity, and the interfacial layer between thin RE oxide layers and the substrate. These factors must be evaluated in order to proceed to a reliable electrical characterization and assess the potential of RE oxides for the various applications. The relationship between micro-structural and electrical properties is also considered. Finally, the real effectiveness of RE oxides in applications as high- κ dielectrics for logic and memory devices, as active materials in laser technology, and in spintronics is discussed.

A significant investigation on RE oxide thin films is only at the beginning and requires expertise in many fields: growth methods, growth modeling and chemistry, physical-chemical characterization, and device technology. The effort naturally calls upon the convergence of many research groups on the same topic, whose attention we hope to catalyze through this volume.

Agrate Brianza (MI)
November 2005

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Acknowledgements

This volume collects most of the contributions given at the European Exploratory Workshop entitled “*Rare earth oxide thin films: growth, characterization, and applications*”, which took place at the Villa Nobel in Sanremo (IM), Italy, from May 11 to May 13, 2005. It is a pleasure to acknowledge and gratefully thank all the people and the institutions that supported the Workshop, and the preparation of this volume. The Workshop was funded by the European Science Foundation (ESF) through the Physics and Engineering Sciences Committee. The Province of Imperia made available for the workshop the beautiful and suggestive Villa Nobel. The staffs of Villa Nobel and of the Sanremo Promotion Agency have been very helpful in handling the logistics related to the Workshop. Sanremo Promotion also financially supported the Workshop. The National Institute for the Physics of Matter (INFM) contributed also to cover some of the expenses related to the Workshop. We also thank the administrative staff of the MDM National Laboratory (in particular Ms. Mara Lanati) for their help in the workshop organization, in the editorial work related to the collection and organization of the contributions for this volume, and in the handling of the financial part.

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