# Zirconia stabilization by metal addition for MIM capacitor applications

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Metal/Insulator/Metal (MIM) capacitors are passive devices commonly integrated in the copper interconnections of microelectronic chips. They are used in several fields such as analog and RF applications, or power supply decoupling capacitors. In order to keep up with the ever-decreasing size of integrated circuits, MIM capacitance density must be increased, which is usually done by reducing the thickness of the dielectric layer. However because of current leakage increase and electrical breakdown field requirements, “high-k” insulators such as $Ta_2O_5$ have replaced the conventional $SiO_2$.

For the next MIM generation, the selected high-k is zirconium dioxide. $ZrO_2$ has a large bandgap, and its dielectric constant is highly linked to its crystalline structure. Indeed, for the monoclinic, cubic and tetragonal phase, the dielectric constant is respectively 17, 37, and 47 [1]. Conventional tetragonal and cubic polycrystalline structure does not fulfill reliability criteria and zirconia must be stabilized.

The aim of this study is to improve both electrical properties and reliability of $ZrO_2$-based MIM by metal elements addition. Ionic radius is the main criteria to find appropriate dopants. Metals with ionic radius smaller than $Zr^{4+}$ radius stabilize the tetragonal phase of zirconia when substituting at zirconium sites [2]. Since trivalent metals lead to oxygen vacancy formation in zirconium oxide, tetravalent and pentavalent elements were chosen.

Thin films (8nm) of $ZrO_2$ alloyed with Tantalum and Germanium oxides have been deposited by Plasma Enhance Atomic Layer (PEALD) at 250°C. As deposited zirconia layers are amorphous. Samples were annealed at 400°C during 30 minutes.

Electron Probe MicroAnalyser (EPMA) with a Wavelength Dispersive X-ray Spectroscopy (WDS) was performed to quantify Ta and Ge concentration. Results for Tantalum samples are presented Figure 1. Targeted Ta/Zr ratio based on number of PEALD cycles varies between 5 and 15% and is proportional to measured ratio.

Grazing Incidence X-Ray Diffraction (GIXRD) measurements were carried out to determine the effect of Ta and Ge incorporation with regard to crystalline structure. Figure 2 shows diffraction diagrams of $ZrO_2$ as function of Tantalum amount. An orthorhombic ternary compound $Ta_2Zr_6O_{17}$ is found when Ta concentration increases because of low solubility of $Ta_2O_5$ solid solution in $ZrO_2$ [3]. Zirconia doped with Germanium crystallizes in the tetragonal phase (Fig. 3) except the 15% Ge/Zr alloy which remains amorphous after annealing. Ge addition induces strain in $ZrO_2$ lattice [4] and increases the energy needed for zirconia crystallization. For the highest Germanium concentration, energy provided by annealing is too weak to generate crystallization.

Integrated MIM capacitors with TiN electrodes deposited by Physical Vapor Deposition (PVD) were made for electrical measurements purposes. Results will be presented. The choice of these two dopants and their consequences on MIM properties will be discussed.

References:

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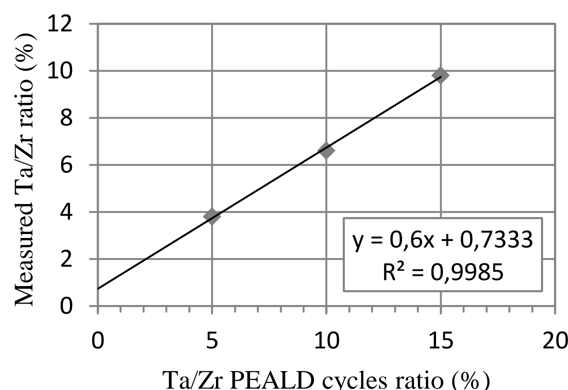


Figure 1: EPMA measured Ta/Zr ratio as function of PEALD cycles ratio

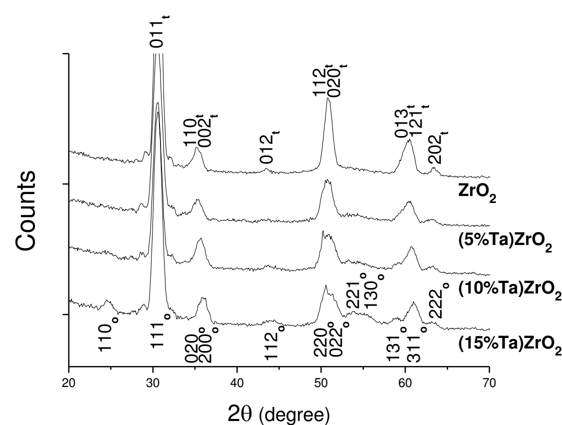


Figure 2: GIXRD diagrams of 8nm $ZrO_2$ thin films with various amount of Tantalum

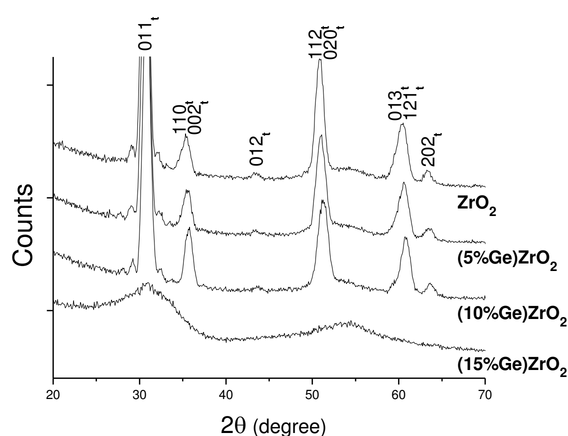


Figure 3: GIXRD diagrams of 8nm $ZrO_2$ thin films with various amount of Germanium