ANALYTICAL CHARACTERIZATION OF PROCESS PARAMETER INFLUENCE ON THE INITIAL GROWTH AND CRYSTALLINITY OF ATOMIC LAYER DEPOSITION HFO_2 THIN FILM

D. Blin[1], N. Rochat[2], G. Rolland[2], P. Holliger[2], F. Martin[2], J.-F. Damlencourt[2], T. Lardin[2], P. Besson[3], S. Haukka[4], M.-N. Séméria[2]

[1]ASM France, 34036 Montpellier Cedex 1, France
E-mail corresponding author: blinde@chartreuse.cea.fr
[2]CEA-LETI, 38054 Grenoble Cedex 9, France
[3]ST Microelectronics, 38926 Crolles Cedex, France
[4]ASM Microchemistry, 02630 Espoo, Finland

Aggressive scaling down of silicon-based microelectronic devices leads to consider HfO_2 as a serious alternative dielectric gate to replace SiO_2. Crystallinity of Atomic Layer Deposition (ALD) ZrO_2 films has been extensively studied (1) but there are only few data about ALD HfO_2 thin films and effect of impurities on their final crystallinity (2). Therefore, this paper deals with thin HfO_2 films deposited on SiO_2 by ALD in a Pulsar 2000^{TM} with $HfCl_4$ and H_2O, as precursors, at different temperatures (250°C to 350°C). Total X-Ray Fluorescence (TXRF) is performed to investigate the early stage of HfO_2 growth by measuring Hf and Cl content after each deposition cycle. Then, influence of process parameters and chlorine contamination brought by $HfCl_4$ on final crystallinity is investigated by Attenuated Total Reflection (ATR).

TXRF displays that the first deposition cycle leads to a high adsorption of Hf (a few 10^{14} at/cm²) whereas during the following cycles a permanent growth with a lower rate of about 4.10^{13} at/cm² is established (Figure 1). Chlorine follows the same trend and exhibits a higher chlorine concentration at the SiO_2/HfO_2 interface (Figures 2 and 3). We also evidence that Hf and Cl adsorptions are well linked and decrease when deposition temperature increases (Figures 1, 2 and 3). This means that chlorine contamination is directly correlated with the hydroxyl group coverage of SiO_2.

The influence of deposition temperature on HfO_2 final crystallinity is shown on ATR spectra of 8 nm HfO_2 oxide films grown on a specific SiO_2 surface (Figure 4): a large peak between 650 and 800 cm^{-1} reveals the presence of amorphous HfO_2 at 300°C whereas two distinct thinner major peaks at 675 cm^{-1} and 775 cm^{-1} stand for crystalline HfO_2 at 350°C. The same 8 nm films grown at 350°C on other SiO_2 surface preparations lead to amorphous HfO_2. Since Cl contamination at the interface and inside HfO_2 film is higher at 300°C, Cl content both at the interface and in the film could have an influence on HfO_2 crystallinity. To refine this study, we anneal at 350°C HfO_2 films deposited at 300°C that have 10 times more chlorine in the HfO_2 volume (Figure 3). As those films remain amorphous after annealing time longer than the deposition time at 350°C, we demonstrate the major effect of chlorine in crystallization (Figure 5).

We conclude that 350°C is a transition temperature that allows to deposit crystallized 8 nm HfO_2 films by careful optimisation of process parameters and SiO_2 surface preparation. Moreover, we demonstrate the inhibition effect of chlorine content on thin HfO_2 film crystallinity.

1. C. Zhao et al., *Microelectronics Reliability*, **41**, 995 (2001)
2. J. Aarik et al., *Thin Solid Films*, **340**, 110 (1999)

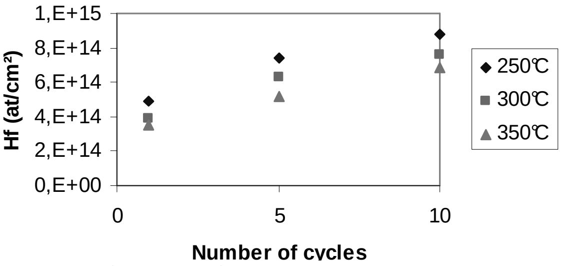

Figure 1. Influence of deposition temperature on Hf adsorption measured by TXRF on SiO_2 surface

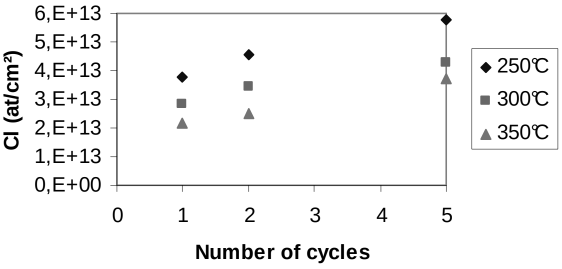

Figure 2. Influence of deposition temperature on Cl adsorption measured by TXRF on SiO_2 surface

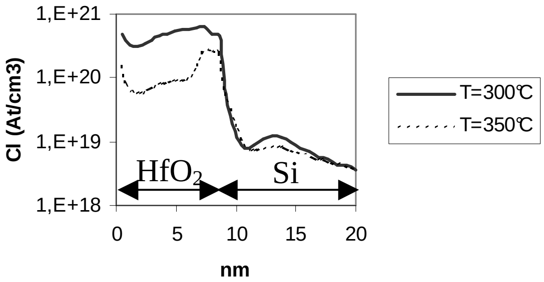

Figure 3. Influence of deposition temperature on Cl content measured by Secondary Ion Mass Spectroscopy (SIMS) for 8 nm HfO_2 layers deposited on SiO_2 surface

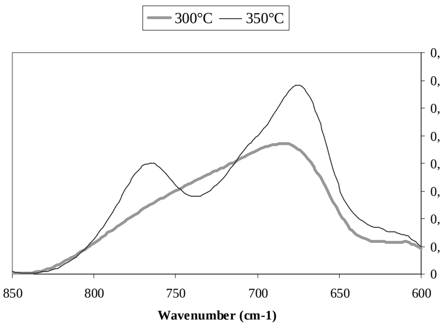

Figure 4. Influence of deposition temperature on HfO_2 crystallinity measured by ATR for 8 nm HfO_2 films deposited on specific SiO_2 surface

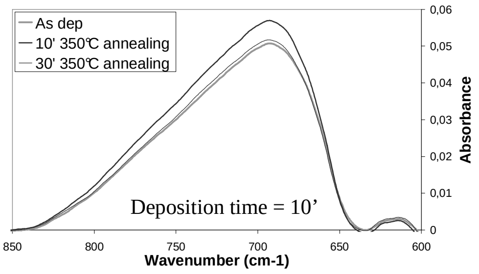

Figure 5. Effect of 350°C annealing on HfO_2 crystallinity measured by ATR for 8 nm films deposited at 300°C