DIRECT INJECTION CHEMICAL VAPOR DEPOSITION OF TEXTURED ZIRCONIUM OXIDE FILMS

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Epitaxial or non-epitaxial zirconia films are already used as thermal barrier, sensors and fuel cells in macro systems and have great potential for these electronic applications. Most of the time, undoped zirconia films are made of monoclinic and tetragonal phases and microstructure and structure are difficult to control. The aim of this study is to realize a monophasic textured undoped zirconia film on a single crystal substrate using a recent injection metal organic chemical vapor deposition technique (MOCVD). It is mainly focused on the microstructural and structural properties of the films.

Zirconia (ZrO_2) thin films were deposited on Si(100) substrates by MOCVD in a cold wall reactor using direct injection process of β-diketonates precursors. Oxide growth was observed over a temperature range from 700 to 900°C and a wide pressure range from 100 to 2000 Pa and deposition time (see table I).

The oxide layers were homogeneous and smooth (AFM) with various grain sizes from one sample to another depending on the total pressure and/or the temperature imposed on the substrate (figure 1). Film thickness and grain size increased with deposition time and a conic shape columnar grain structure was observed by TEM and FEM observations. The film thickness also decreased when the reactor's total pressure or the substrate temperature rose. For low pressure, both kinetic (below 800°C) and diffusion controlled growth (above 800°C) processes could take effect. As epitaxial growth is favored by high temperature (diffusion controlled growth), low pressure and high temperature would promote textured films.

ω–2θ X-ray scans revealed that layer was a polycrystalline tetragonal and monoclinic zirconia that became more and more monoclinic with thickness because of grain size increasing and stress relaxation. High temperature, low pressure and low deposition time enhanced the tetragonal phase quality that became highly textured : $(200)_t$ and $(002)_t$ growing directions were preferred instead of the $(111)_t$ direction (figure 2). However, because of the native silica interlayer, there were no epitaxial relationships between the film and the substrate. These conditions were used to deposit zirconia film on $SrTiO_3$.

Figure 3 confirmed that with appropriate experimental conditions, the monoclinic phase totally disappeared. However, both $(111)_t$ and $(002)_t$ growing directions were identified and showed that comparing to the theoretical intensities, the film was strongly $(002)_t$ textured. This result was confirmed with pole figures. The experiments showed that a part of the film had epitaxial relationship with the STO substrate, $[002]_T$ // $[001]_{STO}$ and $[200]_T$ was turned of 45° to $[100]_{STO}$.

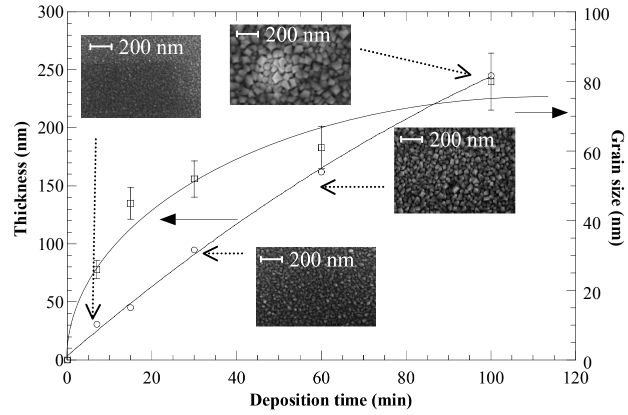

Figure 1 : Thickness, grain size and microstructure of the films as a function of the deposition time.

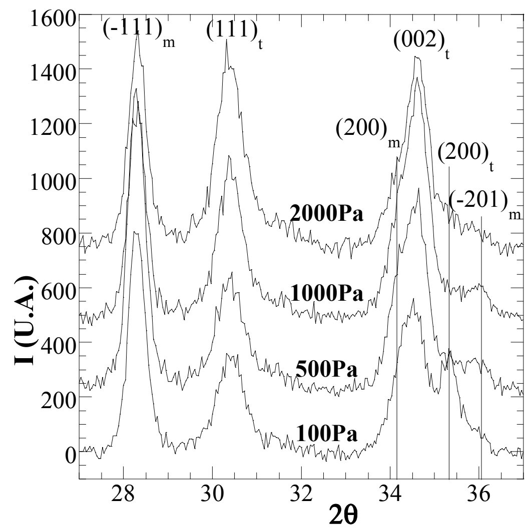

Figure 2 : X Ray scans realised on 110 nm thick films deposited at 700°C as a function of pressure.

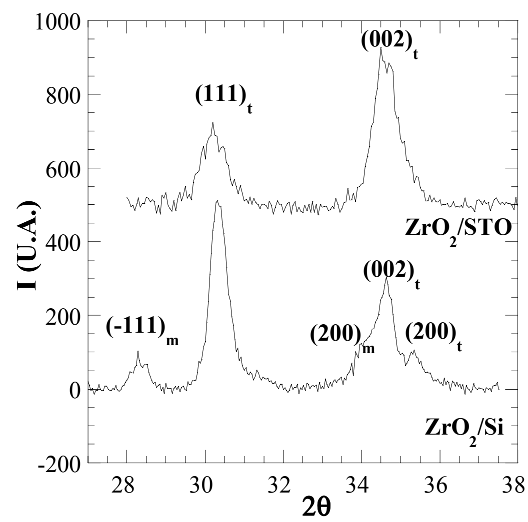

Figure 3 : X Ray scans realised on ZrO2 films (60 nm) deposited at 800°C and 500Pa on Si(100) and STO(100).

Table I : Main investigated deposition parameters.

Substrate temperature (°C)	700-800-900
Total pressure in reactor (Pa)	100-500-1000-2000
Deposition time (min)	7-15-30
Evaporator temperature (°C)	250
Flow rate of N_2 (l/min)	0.5
Flow rate of O_2 (l/min)	0.5
Solution precursor	$Zr(thd)_4$ 0.05mol/l
Solvent	cyclohexane