Sr-Ti-O Dielectric Films Grown by Injection MOCVD for High K Applications

L. Auvray[1], C. Dubourdieu[1], J.P. Sénateur[1], S. Lhostis[1,2], M. Audier[1], P. Chaudouët[1].
[1] Laboratoire des Matériaux et du Génie Physique, UMR CNRS 5628, ENSPG BP 46, 38402 St Martin d'Hères, France.
[2] STMicroelectronics, 38926 Crolles Cedex, France.

Due to its high dielectric constant, $SrTiO_3$ (STO) is a promising candidate for the replacement of SiO_2 as the gate oxide for CMOS technology with equivalent oxide thickness of less than 1.5 nm or for memory applications (DRAMs). We have deposited Sr-Ti-O films on Si(100) substrates by injection MOCVD from a single liquid solution of $Sr(thd)_2$ and $Ti(O^iPr)_2(thd)_2$ mixed together in 1,2-dimethoxyethane. In this growth technique, micro-amounts of the precursors solution are sequentially injected into a vaporization chamber, using a high precision microvalve as those used in conventional thermal motors. The amount of reactive species formed in the gas phase is finely tuned by playing with the opening time of the microvalve or with the precursors dilution. In this presentation, we report on a detailed study of the influence of various deposition parameters on the composition and microstructure of the dielectric films.

The microstructural studies were performed on films with a thickness of about 80 nm in order to have a significant probe volume, especially for X-ray diffraction. A wide range of characterization techniques was used. The structure of the films was investigated by X-ray diffraction (XRD), Fourier Transform Infra red spectroscopy (FTIR) and electron diffraction. Transmission electron microscopy (TEM) was also employed to image the microstructure of the films using planar views. The average composition was determined from wavelength dispersion spectroscopy analysis. The surface morphology was observed by atomic force microscopy.

We first investigated the influence of the composition of the precursors solution on the films composition (Sr/Ti ratio), for a growth temperature of 700°C. A quasi-linear variation was found, but a significant excess of $Sr(thd)_2$ in solution (Sr/Ti ~2.2) was necessary to obtain the desired films stoichiometry (Sr/Ti=1). Partially crystallized STO was formed for Sr/Ti ratios in the film as low as 0.55. For Ti-rich films, the change in films composition was accompanied by a clear change in the lattice parameter (fig. 1a), which was also tracked by FTIR with a shift of the transverse optic band (TO_4) related to the STO compound (fig. 1b). TEM analysis showed that Ti-rich amorphous regions coexist with crystallized STO grains : the proportion of amorphous phase decreases as the Sr/Ti ratio in the film increases. For Sr/Ti=0.9, the amorphous phase is located only at the grain boundaries (fig. 2). Ultrathin films (thickness ~5 nm), independently of their composition, were systematically fully amorphous, which points out difficulties in the nucleation of crystalline STO on the starting SiO_2 surface.

The precursors concentration in solution has also a deep influence on the films characteristics. With increasing concentration (at fixed Sr/Ti ratio and fixed deposition temperature), the Sr/Ti ratio in the films increases and the main diffraction peak changes from 100 to 111, which suggests a change in the films texture. Moreover, the STO grain size decreases and the grain density increases, while the proportion of amorphous phase decreases.

The effect of deposition temperature was studied in the range 500-800°C, starting from a fixed liquid composition. The decrease of growth temperature strongly affects the films composition, inducing a Sr enrichment. The films were partially crystallized for deposition temperatures $T \geq 550$°C. At 500°C, the films were amorphous or nanocrystallized. From the FTIR spectra, it was also shown that a carbonate phase ($SrCO_3$) forms at deposition temperature of 550°C and below.

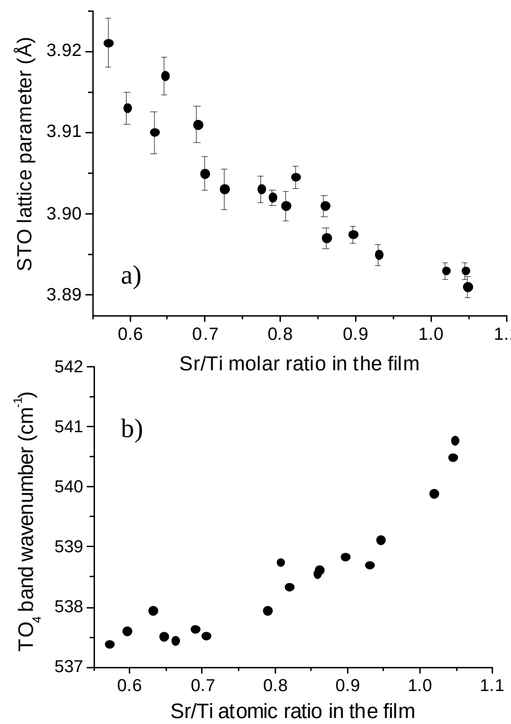

Fig. 1. a) Evolution of the lattice parameter (deduced from 200 XRD peak) versus solution composition and b) related shift of the infra red TO_4 band.

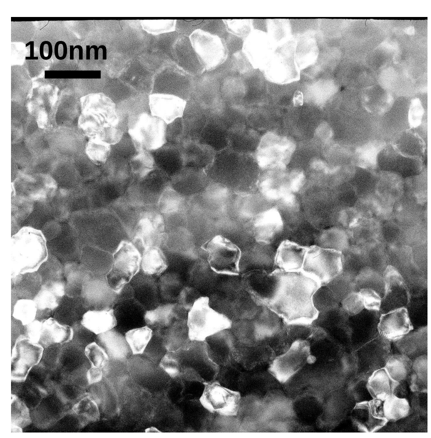

Fig. 2. Dark field TEM plane view of a film with a composition Sr/Ti=0.9, deposited at 700°C. This film is almost completely crystallized. Ti-rich amorphous phase only remains at the $SrTiO_3$ grain boundaries.

This work was carried out within MEDEA+ T201 project and supported by the "Ministère de l'Economie, des Finances et de l'Industrie".