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Characterization of crystalline MOCVD $SrTiO_3$ films on SiO_2/Si(100)

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Abstract

$SrTiO_3$ thin films (STO), were deposited on Si(100) covered by 2 nm of SiO_2, at different temperatures from 450 °C to 850 °C using liquid injection MOCVD, the bimetallic precursor being $Sr_2Ti_2(OiPr)_8(tmhd)_4$. The STO films were analysed by XRD, FTIR, SIMS and TEM. An amorphous layer was observed between STO and SiO_2/Si. The nature and thickness of the interlayer were determined, as well as the most favourable conditions for a good quality crystalline STO film, and a reduced interlayer.

1. Introduction

$SrTiO_3$(STO) is an alternative dielectric material for a broad application area, from its use in high storage capacity devices such as DRAM, to the replacement of SiO_2 as a gate insulator in MOS devices [1–4], due to its high dielectric constant (K_{bulk} = 300). We have shown that an amorphous interlayer between STO and SiO_2/Si is present and that the dielectric properties of the stack decrease consequently.

The aim of this work is to investigate the deposition by metal organic chemical vapor deposition (MOCVD) of STO thin layers with varying substrate temperature, and to define the most favourable conditions in term of microstructure of the STO layers, including the reduction of the interfacial layer thickness.

2. Experiment

2.1. Films deposition

$SrTiO_3$ thin films were deposited by liquid injection MOCVD [5,6]. The CVD injection source offers advantages over conventional bubbler sources such as an accurate control of the precursor delivery and the possibility of using precursors with a low volatility. The layers are grown on p-Si(100) high-resistivity substrates covered by 2 nm thermally grown silicon oxide.

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The source solution is composed of a bimetallic precursor $Sr_2Ti_2(OiPr)_8(tmhd)_4$ [7] solubilized in octane. The global concentration of both the strontium and titanium species was 0.02 mol l^{-1}. 65–75 nm thick $SrTiO_3$ films were deposited under 2 Torr at different substrate temperatures, ranging from 450 to 850 °C.

2.2. Films characterization

Films thickness was measured using a three wavelengths ellipsometer. The structural characterization was carried out using X-ray diffraction (XRD) with CuKα radiation and optical absorption Fourier transform infrared (FTIR) spectroscopy (Nicolet 800, transmission mode 4 cm^{-1} resolution). The depth profile of the samples was performed using secondary ion mass spectrometry (SIMS Cameca 4F). *C*(V) and *I*(V) curves were measured using gold as top electrode. The equivalent oxide thickness (EOT) was extracted from *C*(V) curves in the accumulation mode.

3. Results and discussion

Absorption spectra related to samples with deposition temperatures ranging from 485 to 850 °C were recorded in the mid and far infrared. For a 485 °C sample no STO compound is evidenced; the thin layer obtained corresponds to $SrCO_3$ (C–O bond in CO_3 observed at 1409 and 1455 cm^{-1}, 685 and 867 cm^{-1} (Fig. 1a)) [8].

TO_4 phonon of crystalline STO is present, at 550 cm^{-1}, for a sample grown at 500 °C, together with the C–O bonds of CO_3. For deposition temperatures higher than 500 °C, the TO_4 peak is present at around 538 cm^{-1} [9]; its intensity decreases for temperatures higher than 725 °C. It vanishes and becomes almost null for $T = 850$ °C. The smallest full width at half maximum (FWHM) of this TO_4 band is observed for a deposition temperature of 725 °C. It tends to show that 725 °C is the most favourable temperature to obtain a crystalline layer of STO. For higher temperatures (750 °C and 800 °C) the crystalline quality of the deposited layers decreases.

Far infrared (FIR) spectra (Fig. 1b) display the TO_2 peak at 176 cm^{-1} and the soft mode at 96 cm^{-1} (TO_1) [10]. They also display a rich structure between 50 and 120 cm^{-1}; no definitive conclusion related to this structure is to be drawn.

X-ray diffraction diagrams show that crystallization is evidenced at 550 °C. A (100) preferential orientation appears for $T = 650$ °C. The smallest FWHM of the rocking curve performed on the plane STO (200) is obtained at 725 °C (Fig. 2). For higher temperatures (750 °C and 800 °C), the texturation is less pronounced. This is presumed to be linked to a higher growth rate of

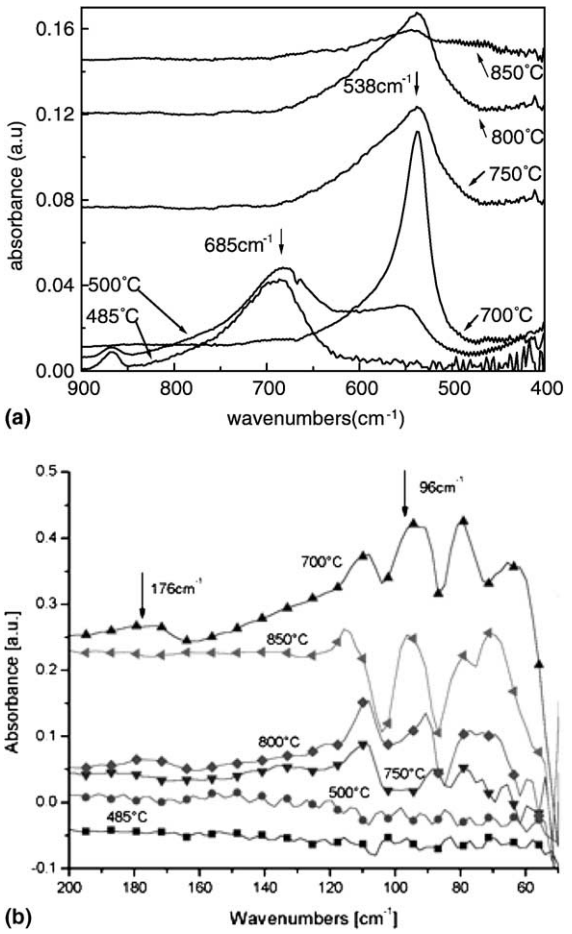

Fig. 1. (a) Mid infrared absorption spectra for STO films grown at different deposition temperatures. (b) Far infrared absorption spectra for films grown at different deposition temperatures.

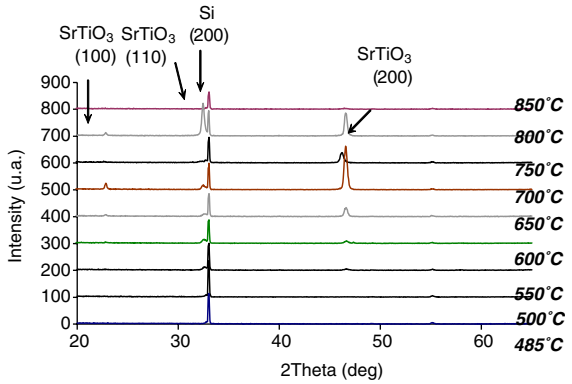

Fig. 2. XRD diagrams for different deposition temperature.

those layers. For T = 850 °C the XRD diagram is flat, hence the deposited layer is no more crystalline. All