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Pulsed laser deposition of $SrZrO_3$ as a buffer layer for ferroelectric thin films

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$SrZrO_3$ (SZO) is a material that has recently received much attention due to properties such as high dielectric constant and switching between resistance states. Our interest was in the possible use of SZO as a buffer layer on various substrates for the epitaxial growth of ferroelectric thin films. SZO was deposited by laser pulses onto $SrTiO_3$ and Si substrates under various deposition conditions. SZO deposited on $SrTiO_3$ substrates exhibits highly oriented c-axis epitaxial growth, as evidenced by X-ray diffraction. A dependence of the crystalline properties of the deposited films on the deposition temperature was observed. In depositing SZO directly onto Si substrates, we paid attention to a possible reaction of Zr with the native amorphous silicon dioxide layer. Unfortunately, no such reaction occurs in the deposition conditions we used, which results in the presence of a thin layer of silicon dioxide, and an amorphous SZO film. When SZO was deposited on the top of YSZ/Si , the silicon dioxide was completely removed from the surface of the silicon substrate, and a-axis orientation growth was possible. This result is very important for the subsequent growth of ferroelectric thin films such as $SrBi_2Ta_2O_9$, which present a large anisotropy of the ferroelectric properties, with much better results for a-axis orientation.

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1. Introduction

$SrZrO_3$ (SZO) is an oxide which presents great interest for applications. Its crystalline structure is orthorhombic Pbnm, with lattice constants a = 5.792 Å; b = 5.813 Å; c = 8.196 Å. Some of its interesting properties are the proton conduction [1], high dielectric constant [2], and the possibility of switching between resistive states [3]. Existing and potential applications of this material include humidity and gas sensors (for hydrogen, due to its proton conduction), and various electronic devices (notably memories) in which it may replace silicon dioxide due to its high dielectric constant.

Our interest was to obtain the epitaxial growth of SZO using laser ablation, using $SrTiO_3$ (STO) and Si substrates (both simple and covered with a buffer layer of Yttria Stabilized Zirconia – YSZ).

2. Experiment

The depositions were made using a Lambda Physik Compex 301 KrF laser. The laser was operated in the present experiments with an energy per pulse between 80 and 130 mJ. Focusing of the beam on the target led to energy densities of 1 – 2 J/cm^2. The pulse repetition rate was 3 Hz. The substrates were heated to temperatures between 400 and 900 °C during the deposition process, and positioned at a distance of 3 or 4 cm from the ablated target. After the deposition, in vacuum (< 10^{-5} mbar) or at various oxygen pressures, the films are slowly cooled to room temperature in an oxygen atmosphere.

3. Deposition of SZO onto STO substrates

The first SZO depositions were made onto STO substrates. The depositions were made at base pressure, at temperatures between 400 and 850 °C. X-ray diffraction analysis of the films indicates c-axis growth of SZO, as can be seen in the θ - 2θ scans of the films, presented in Fig. 1, in which only the (00l) lines are visible. In addition, the high quality of the films obtained is also indicated by the FWHM of the rocking curve of the SZO(002) line, which is smaller than 1 °.

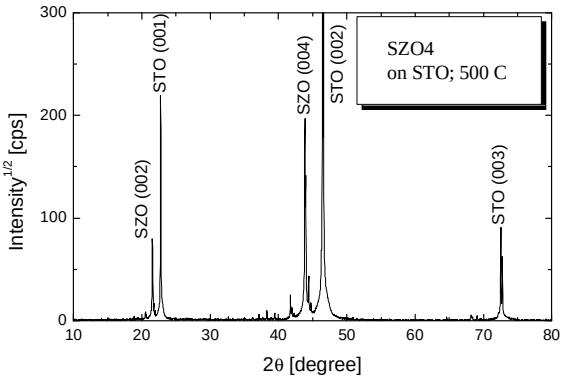

Fig. 1. X-ray diffraction figure for SZO film deposited onto STO substrate at 500 °C deposition temperature. θ - 2θ scan in Bragg-Brentano geometry; $Cu_{K\alpha}$ radiation.

An interesting aspect is the dependence of the position of the (004) line on temperature, as illustrated by Fig. 2. An increase in deposition temperature from 400 to 500 °C leads to a more intense line, since the higher temperature increases the species mobility on the surface of the growing film and improves its crystallinity. A

further increase of the temperature to 800 and 850 °C, however, decreases the intensity of the line, so that temperatures between 500 and 700 °C seem to be optimal. A shift of the position of the (004) line is also observed, which is an indication of the modification of the value of c-axis. The characteristics of SZO films deposited at various deposition temperatures is summarized in the table below. We must mention that, regardless of the deposition temperature and the resulting crystalline quality of the film, a very good film quality is observed.

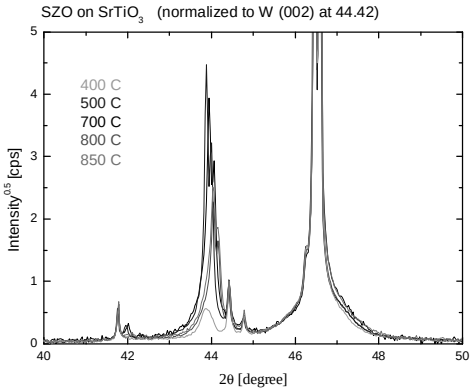

Fig. 2. XRD of SZO films deposited onto STO substrates at various deposition temperatures.

Table 1. Characteristics of SZO films deposited at various deposition temperatures.

Deposition temperature	2θ for (004) peak SZO	c (Å)
400 °C	43.88	8.266
500 °C	43.88	8.266
700 °C	43.94	8.257
800 °C	44.03	8.235
850 °C	44.03	8.235

4. Deposition of SZO directly onto silicon

Silicon substrates are of great interest for technological applications. However, the deposition of epitaxial films onto silicon is difficult due to the amorphous layer of native SiO_2 which is formed on the silicon surface, and which imposes amorphous growth upon the films subsequently deposited on it. We made an attempt to obtain the removal of the native silicon dioxide layer by means of the reaction:

$$Zr + 2SiO_2 \rightarrow ZrO_2 + 2SiO, \quad (1)$$

which occurs in the case of Yttria stabilized zirconia (YSZ) on silicon [4] (the silicon oxide being easily removed at the high deposition temperatures used). We reproduced the conditions which are necessary in order to activate the above reaction in the case of YSZ, namely the deposition of the first few monolayers at base pressure, and the use of relatively high energy densities. The deposition at base pressure is necessary in order to prevent the formation of zirconium dioxide in the gas phase, in the space between target and substrate, and to assure that metallic zirconium is incident on the substrate, and reacts with the silicon dioxide as given above. The high laser energy densities are needed to produce Zr atoms which are energetic enough to produce the reaction. We mention here that the low deposition pressure condition is only kept for the first tens of pulses of the deposition, after which the pressure is raised, allowing the epitaxial growth of the YSZ film.

Unfortunately, reproducing the deposition conditions which allowed to obtain removal of the native silicon dioxide layer using YSZ, and epitaxial growth of YSZ and subsequent layers upon this buffer layer, was not sufficient in the case of SZO deposition onto silicon. We did not find any proof that the reaction occurred in the case of SZO. Grazing incidence X-ray measurements (Laue geometry) indicated the presence of a SiO_2 layer 2 – 8 nm thick and an amorphous SZO layer having 80 – 150 nm on top of it. There is, therefore, no epitaxial growth of SZO. Our attempts to increase the incident particle energy on the substrate by increasing the laser energy density and decreasing the target-substrate distance did not improved the results. In conclusion, the conditions used for SZO/Si deposition did not lead to the SiO_2 reduction reaction. It is, however, possible that in the case of SZO the reaction occurs in conditions somewhat different from the case of YSZ. Further attempts of the optimization of the deposition conditions are therefore necessary.

5. Deposition of SZO onto YSZ/Si

By reproducing the deposition conditions outlined above for the deposition of YZS onto silicon, we sucessfully removed the native silicon dioxide layer from the silicon substrate surface. As shown in Fig. 3, the X-ray diffraction figures for YSZ/Si indicate the presence of only (002) and (004) lines, and therefore the epitaxial c-axis growth of YSZ.

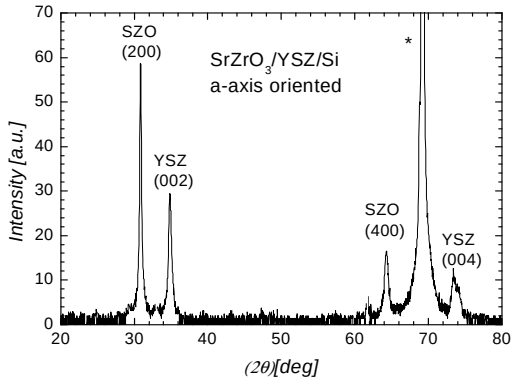

*Fig. 3. X-ray diffraction θ-2θ scan of a typical $SrZrO_3$ film deposited onto a YSZ-buffered silicon substrate. The film was deposited in 5 ×10^{-4} mbar oxygen, at a substrate temperature of 750 °C and a laser energy density of 1 J/cm^2. The line marked with * belongs to the silicon substrate.*

Subsequently, an SZO layer was deposited on top of the YSZ-buffered silicon substrate, using the following

deposition conditions: an oxygen pressure of 5×10^{-4} mbar, a substrate temperature of 750 ^{o}C, and laser energy density 1 – 1.5 J/cm^2. The resulting SZO film is highly a-axis oriented, as seen in Fig. 3. The FWHM of the rocking curve of the SZO(002) line is 1.5- 2 ^{o} indicating good film orientation. Measurements of the SZO film thickness indicated that a typical film, obtained using 1000 pulses, lead to a film 35 nm thick. AFM analysis indicated a surface roughness of 0.21 nm rms. The result is very encouraging, considering that SZO presents a structural anisotropy, having both a and b axis lengths close to 5.8 Å, while the c-axis has a constant of about 8.2 Å [5]. It is quite difficult to grow thin films having such a difference in axis length in the plane of the substrate surface.

6. Conclusions

SZO thin films were laser-deposited onto various substrates. SZO thin films deposited onto STO substrates are c-oriented and have a high crystalline quality. The lattice parameter of the c-axis depends on the deposition temperatures, with higher temperatures (800 and 850 °C) leading to values closer to that for the bulk material. A very good quality of the films is obtained for all temperatures, even those as low as 500 °C.

In the case of SZO deposited directly onto silicon substrates, no epitaxial SZO growth was observed, since no reduction of the native silicon dioxide layer occurred, as in the case of YSZ. It is probable that the deposition conditions are different from those for YSZ, so that further experiments are necessary to completely clarify this aspect.

When the succession SZO/YSZ/Si is used, the YSZ completely removes the SiO_2 on the silicon substrate, and a high-quality c-axis grown YSZ layer is obtained. High quality a-axis growth of SZO onto the YSZ buffer layer is subsequently possible.

This result is of great interest for the growth of ferroelectric thin films of $SrBi_2Ta_2O_9$ (SBT), since the a-axis growth of SZO could induce the a-axis growth of SBT. The pronounced anisotropy of the ferroelectric properties of SBT (whose polarization is practically zero along the c-axis, being large along the a and b axis) makes the growth along a-axis of SBT highly desirable [6]. Moreover, due to other SZO applications of interest, such as its high dielectric constant, the epitaxial growth of SZO is of interest in itself, not just as a buffer layer for the growth of ferroelectric thin films.

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