PULSED LASER DEPOSITION OF $SrZrO_3$ AS A BUFFER LAYER FOR FERROELECTRIC THIN FILMS

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ABSTRACT

$SrZrO_3$ (SZO) is a material that has lately received much attention due to properties such as high dielectric constant and switching between resistance states. Our interest was the possible use of SZO as a buffer layer on various substrates for the epitaxial growth of ferroelectric thin films. SZO was laser deposited onto $SrTiO_3$ and Si substrates under various deposition conditions. SZO deposited on $SrTiO_3$ substrates presented highly oriented c-axis epitaxial growth, as evidenced by X-ray diffraction data. A dependence of the crystalline properties of the deposited films on the deposition temperature was observed.In depositing SZO directly onto Si substrates, a thin layer of silicon dioxide is formed on the Si, and an amorphous SZO film results.When SZO was deposited on top of YSZ/Si, the silicon dioxide is completely removed from the surface of the silicon substrate, and a-axis growth of good quality SZO films is 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 in ferroelectric properties, with much better results for a-axis orientation.

KEYWORDS: *laser deposition, ferroelectric, thin film*

1. INTRODUCTION

Oxides are a class of materials receiving a great amount of attention lately, due to the large variety of properties which they posess. Their electrical properties range from insulator to superconductor, semiconductor or ferroelectric [1-4]. A considerable advantage is the fact that these properties are obtained in materials which are compatible and have similar structures, meaning they can be combined to produce complex devices, when they are obtained in the form of thin films.

One of the oxides whose properties present interest for applications is $SrZrO_3$ (SZO). Initially studied mostly for its proton conducting properties [5], SZO has since been studied for other properties [3, 6].

The present paper describes our research devoted to the epitaxial growth of SZO onto various substrates using laser ablation deposition.

2. EXPERIMENTAL

The depositions were made using a Lambda Physik Compex 301 KrF laser with a maximum output energy of 1 J and a laser pulse duration of about 20 ns. Typical values of the energy of the laser beam incident on the target in our deposition conditions were 80 – 130 mJ. The films were deposited at 3 Hz laser repetition rate. The laser beam is directed onto the target surface using an optical system composed of mirrors, focusing lens and apertures which assures a uniform energy density across the spot and allows variation of the spot size on the target. The energy density on the target can thus be modified by changing the energy or the spot size. The f = 50 cm focusing lens leads to an energy density of $1 – 2$ J/cm^2 on the target.

The target undergoes simultaneous rotation and scanning to eliminate possible modification of its surface morphology and composition during deposition. The multiple target holder allows deposition of successive layers without breaking the vacuum. Prior to deposition, the target surface undergoes pre-

ablation, using 1000 pulses at a repetition rate of 10 Hz, the rest of the irradiation conditions being the same as the ones used for the ablation itself; during pre-ablation, the substrate is shielded, in order to prevent any actual deposition from occuring.

The substrate heater allows reaching of substrate deposition temperatures of up to 1000°C; we used substrate temperatures of 400 – 900 °C. The target-substrate distance was 3 or 4 cm. The depositions were made either at chamber base pressure (10^{-5} mbar or less), or at various oxygen pressures, as indicated below.

Following the actual depositions, the layers were first cooled at the deposition pressure to temperatures of about 300 °C, after which the chamber was vented to atmospheric pressure oxygen and cooled to room temperature. This method of cooling the deposited films was used in order to prevent rapid cooling, which can lead to cracking or even peeling of the film.

Some depositions were made on $SrTiO_3$ substrates (STO). Others were made on Si substrates, either directly or on top of a Yttria-stabilized Zirconia (YSZ) buffer layer. The Si (100) substrate was cleaned using a standard procedure, which included ultrasonic cleaning in acetone, isopropanol, and distilled water. When the depositions are made directly onto the silicon surface, etching in various acid solutions is required in order to remove the native silicon dioxide (SiO_2) layer. This natural SiO_2 layer, having a thickness of several nanometers, is amorphous, thus preventing epitaxial growth on top of it. However, etching to remove the native silicon dioxide layer proved unnecessary when using a YSZ buffer layer. Under proper irradiation conditions (as will be described in a subsequent section), a chemical reaction occurs between the metallic zirconium (released from the YSZ) and the SiO_2 , eliminating the oxide layer and thus allowing epitaxial growth on top of the resulting epitaxial YSZ layer.

3. Deposition of SZO onto STO substrates

The SZO films were deposited onto STO single crystal substrates at base chamber pressure (10^{-5} mbar or less), using a laser pulse energy of 100 mJ. The substrates were positioned 4 cm away from the targets, and 4000 pulses were used for the depositions, after which the cooling procedure described in the prior paragraph was used. Various deposition temperatures, between 400 and 850 °C, were used, in order to ascertain the effect of this temperature on the deposited SZO film.

At the deposition temperatures used, SZO has an orthorhombic Pbnm structure, with lattice constants a=5.792 Å, b=5.813 Å, c=8.196 Å. STO has a cubic structure with a constant of 3.9 Å, giving a mismatch of –4.9% with SZO.

XRD (X-ray diffraction) analysis of the deposited films indicated c-axis growth of SZO, as shown in Figure 1, where only the (002) and (004) lines of SZO appear. The high quality of the films is inferred from the FWHM of the rocking curve of the (002) line, which is 1 ° or less.

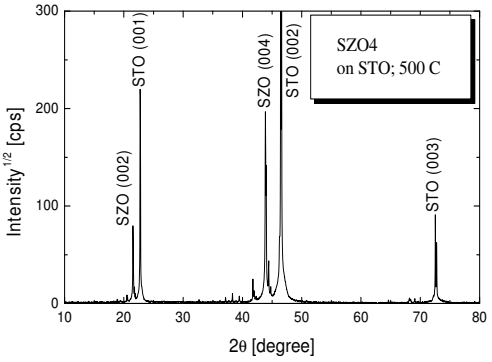

Fig. 1. X-ray diffraction figure for SZO film deposited onto STO substrate at 500°C. θ - 2θ scan in Bragg-Brentano geometry; $Cu_{K\alpha}$ radiation

An interesting dependence of the position of the (004) SZO line on the deposition temperature was found, as illustrated in Figure 2. The 2θ value for which the (004) peak is obtained is correlated with the value of the lattice parameter for the c-axis, as seen in Table 1. The value for the bulk material, as resulting from XRD measurements of the target used in the depositions, is 2θ=44.04, proving that this value is reached at higher deposition temperatures, which allow greater

rearrangement of the arriving species onto the growing film. However, the quality of the films is very good at all temperatures investigated.

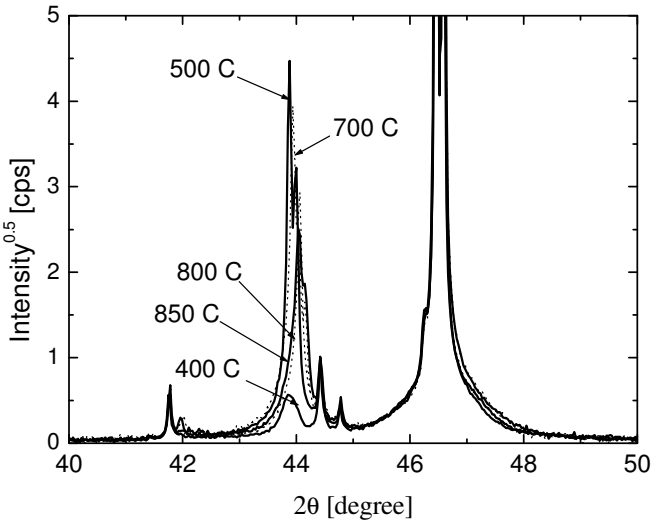

Fig. 2. XRD of SZO films deposited onto STO substrates at various deposition temperatures. Intensity normalized to W(002) at 44.02. Dotted lines are for 700 C and 800 C.

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

Deposition temperature	2 θ 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

Deposition onto Si substrates is of great interest due to the technological importance of silicon. However, deposition of epitaxial films directly onto silicon is difficult due to the native layer of amorphous silicon dioxide formed on the surface, as mentioned in a prior paragraph.

We first attempted to deposit SZO directly onto silicon. The silicon substrates were first ultrasonically cleaned using standard substances (acetone, isopropanol and distilled water), after which they were successively etched using a solution of H_2SO_4 and H_2O_2, and one of 10% HF; the latter has the role of removing the silicon dioxide layer. Depositions were made at base pressure, at substrate temperatures between 500 and 850 °C, similar to those used for deposition onto STO. Most depositions were made using 100 mJ pulses and a target-substrate distance of 4 cm; however, some depositions were made at a larger pulse energy (115 mJ) and smaller target-substrate distance (3 cm), in an attempt to increase the energy of the species arriving onto the growing film. XRD analysis of all films grown in these conditions did not indicate any epitaxial growth. Grazing-incidence X-ray

measurements (Laue) indicated the presence of a thin layer of SiO_2 having 2 – 8 nm, on top of which the amorphous SZO film having a thickness of 80 – 150 nm grows; the higher oxide thicknesses appear for higher deposition temperatures.

In these conditions, we deposited some SZO films directly onto Si, reproducing conditions in which YSZ films were deposited, the YSZ successfully removing the native silicon dioxide layer. Yttria stabilized Zirconia (YSZ) has the property that it can, under proper deposition conditions, ensure the chemical reaction

$$Zr + 2SiO_2 \rightarrow ZrO_2 + 2SiO$$

which removes the native amorphous silicon dioxide layer [7 articol SBT], the resulting silicon oxide being easily removed at the high deposition temperatures used. In order for this reaction to occur, some conditions must be met. The first is that the laser energy density on the YSZ target must be large enough to form metallic Zirconium (as opposed to Zirconium dioxide) during ablation, since it will react on the surface of the substrate with the SiO_2. Additionally, the deposition pressure must be low, to avoid gas-phase formation of Zirconium dioxide from the ablated metallic Zirconium. However, the low pressure condition is only for the first few monolayers, since this is where the reduction reaction for silicon dioxide will occur; the rest of the layer must be deposited at a higher oxygen pressure to insure proper oxygen content and growth of an epitaxial YSZ layer. We reproduced conditions similar to these for the deposition of SZO directly onto Si, hoping that, since SZO also contains Zirconium, a similar reaction with the silicon oxide would occur. Thus, we deposited SZO films at 750 °C, at laser pulse energies of 90 – 100 mJ, using first 50 pulses at base pressure, followed by 950 pulses at a higher pressure of 4×10^{-4} mbar of oxygen. Unfortunately, not even in these conditions were we able to obtain epitaxial growth of SZO directly on silicon, implying that the above reduction reaction of silicon dioxide did not take place. It is, however, possible, that the conditions necessary in the case of SZO be quite different from those for YSZ; this requires more research. The excellent results we obtained by depositing SZO onto a buffer layer of YSZ on silicon interrupted the direction of research described in the present paragraph, and are described below.

5. Deposition of SZO onto YSZ/Si

YSZ buffer layers were sucessfully used to remove the silicon dioxide layer from the silicon substrate surface. In these conditions, etching of the substrate surface was not necessary, standard cleaning procedures being sufficient. As mentioned in the prior paragraph, a large laser energy density is required to produce metallic zirconium; this implied in our case a target energy density over 1.5 J/cm^2. The low deposition pressure for the first few tens of pulses was 6×10^{-6} mbar or less; the rest of the layer was deposited at a higher oxygen pressure of 5×10^{-4} mbar, which was the optimum in our case. A first layer having 1-2 nm deposited at low pressure led to highly oriented c-axis films as observed by X-ray diffraction. The total thickness of the standard YSZ layer is 35 – 40 nm. The deposition temperature for YSZ was 850 ° C. In these conditions, we obtained highly c-oriented YSZ layers, as can be seen in the X-ray diffraction measurements (Bragg-Brentano geometry; $Cu_{K\alpha}$ radiation), where only the (002) and (004) YSZ reflections are present (Figure 3).

The SZO layer was deposited on top of this YSZ buffer layer. The deposition was made at an oxygen pressure of 5×10^{-4} mbar, a temperature of 750 °C, and a laser energy density of 1 ÷ 1.5 J/cm^2. These parameters led to highly oriented a-axis SZO, and no optimization of the deposition conditions was attempted. Using 1000 pulses results in the deposition of a film 35 nm thick, as determined from the oscillations in the grazing incidence X-ray measurements.

In figure 3 we show the results of an X-ray diffraction measurement for a $SrZrO_3$ film deposited on a YSZ-buffered silicon substrate. Only the (200) and (400) SZO reflections are present, indicating growth of the SZO films with the a-axis perpendicular to the substrate surface. The FWHM of the rocking curve for the intense (200) line is 1.5 ÷ 2 ° , indicating good film orientation. A

surface roughness of 0.21 nm rms was determined for these SZO films using AFM.

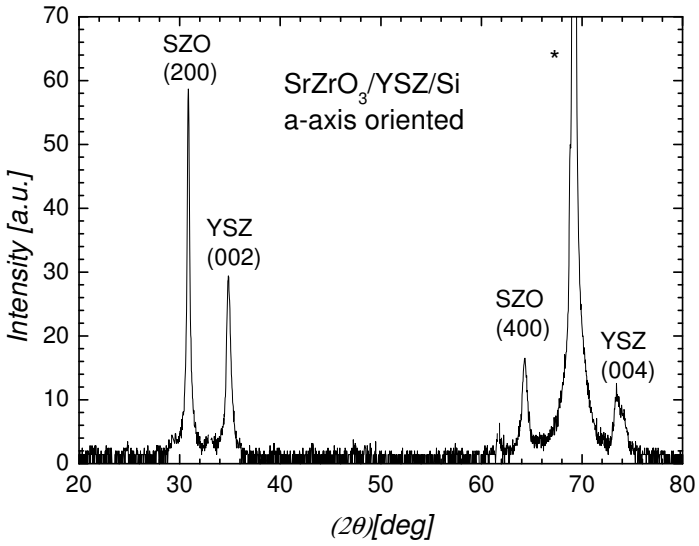

Figure 3. X-ray diffraction θ-2θ scan of a typical $SrZrO_3$ film deposited onto a YSZ-buffered silicon substrate. The film was deposited in 5×10^{-4} mbar oxygen, at a substrate temperature of 750 °C and a laser energy density of 1 J/cm^2. The line marked with * belongs to the silicon substrate.

6. Conclusions

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

We were not able to obtain epitaxial growth of SZO when depositions were made directly onto silicon substrates in any of the irradiation conditions we studied. Etching of the substrate to remove the native silicon dioxide layer apparently either did not completely remove the amorphous layer, or it was reformed during the deposition process. Attempts to reproduce the conditions for reduction of the SiO_2 through reaction with metallic Zr, as it occurs in the case of YSZ, were not successful. We did not, however, deposit SZO films in conditions very different from those used for YSZ. It it thus possible that the reaction may take place, but additional experiments are necessary.

High quality a-axis oriented SZO films were obtained when the depositions were made onto YSZ buffer layers deposited in optimum conditions onto silicon substrates. The YSZ completely removed the silicon dioxide at the surface of the silicon, and epitaxial growth of SZO onto the high-quality c-axis grown YSZ was possible. This result is of great interest for the growth of ferroelectric thin films of $SrBi_2Ta_2O_9$ (SBT), since the anisotropy of ferroelectric properties resulting form this material's structural anisotropy make the "normal" c-axis growth unsuitable for applications. Using the succession of

buffer layers SZO/YSZ/Si, a-axis growth of SBT would be possible, if one takes into account the similarities of the chemical components of the two materials (SZO and SBT) and those of the structural anisotropy.

SZO is not only of interest as a buffer layer, since it has applications itself. For example, SZO has as high dielectric constant [5], materials with high dielectric constant being currently investigated as an alternative to silicon dioxide as insulator in various devices. In addition, SZO was shown [3] to exhibit a reduction of the resistance of several orders of magnitude, becoming conducting instead of insulating, when exposed to an electrical field, which makes it applicable in memory devices. This leads to the successful growth of epitaxial SZO films being of interest in itself.

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