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Ferroelectric properties of compressively strained epitaxial $SrTiO_3$ films on sapphire

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Abstract

Magnetron sputtered and laser deposited $SrTiO_3$ thin films are deposited on CeO_2 buffered sapphire substrates. Their structural and ferroelectric properties are analyzed and possible (mutual) correlations between these properties are investigated. It is shown, that the biaxial compressive strain imposed by the substrate on the ferroelectric films leads to a considerable increase of the Curie temperature, as well as the dielectric constant and the tenability of these films in technically relevant temperature regimes. Generally, the dielectric constant and the tuning decreases with increasing strain. However, the ferroelectric phase transition of the $SrTiO_3$ films is shifted to higher temperatures compared to that of single crystalline $SrTiO_3$. As a consequence, the dielectric constant of the films is larger than that of undistorted $SrTiO_3$ single crystals for small strain ($\Delta a/a < 0.005$) and temperatures above the Curie temperature. Furthermore, a linear dependence of the loss tangent and the tunability on the dielectric constant is observed, which indicates, that all three properties are affected by the same mechanism that itself is affected by the lattice strain.

Keyword: Ferroelectric films; Strained $SrTiO_3$

1. Introduction

Owing to the strong connection between strain and ferroelectricity, large shifts of the Curie temperature T_c are expected[1,2] and have been observed[3,4] in ferroelectric material that is exposed to strain. An ideal method to introduce substantial strain to these materials exists for ferroelectric thin films. Depending on the choice of the substrate, tensile or compressive in-plane strain can be imparted upon epitaxial ferroelectric thin films. It has been speculated,[2] that in both cases (tensile and compressive strain) T_c is shifted to higher temperatures resulting in a more profitable temperature dependence of the dielectric constant ε. This effect has been experimentally demonstrated for tensile in-plain strained $SrTiO_3$ (STO).[3] However, compressive in-plane strained STO on LSAT did not lead to an improvement of the permittivity. In this paper we show, that also in-plane compressive strain induced by CeO_2 buffered sapphire on STO can lead to a significant increase of the dielectric constant at temperatures above T_c. Furthermore, we will show that the ferroelectric properties strongly depend upon the magnitude of strain.

2. Experimental results and discussion

A series of $SrTiO_3$ (STO) films (thickness of 400 nm) is grown on CeO_2 buffered r-cut sapphire (Al_2O_3) at various temperatures (650–870 °C) via on-axis magnetron rf sputtering technique (MST) and pulsed laser deposition (PLD) at various pressures. In order to provide identical growth conditions for the STO layers, all CeO_2 buffer layers are deposited via MST at identical conditions (i.e., rf-power of 130 W on a 6″ cathode, Ar/O_2 gas mixture of ratio 6.6/1 at a pressure of 13 Pa, and a heater temperature of 850 °C resulting in a deposition rate of 0.5 nm/min). Subsequently the STO layers are deposited via MST and PLD. The MST deposition of STO is performed in a gas mixture of Ar/O_2 of 3.3/1 at 4 Pa and a rf power of 260 W on a 6″ magnetron target. The PLD depositions are performed in pure O_2 atmosphere at two different conditions, (i) a pressure of 50 Pa using a laser power of about 2 J/cm^2 at the target and at 10 Hz and (ii) a pressure of 1 Pa, laser power of about 5 J/cm^2 at the target and at 10 Hz.

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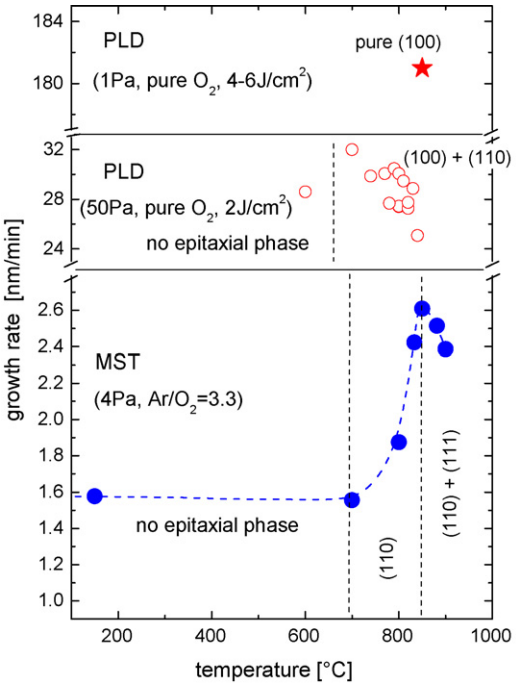

Fig. 1. Growth rates of low-pressure PLD (top), high-pressure PLD (middle) and MST (bottom) deposited STO as function of the heater temperature during deposition. The dashed lines separate different temperature regimes of different STO phase formations.

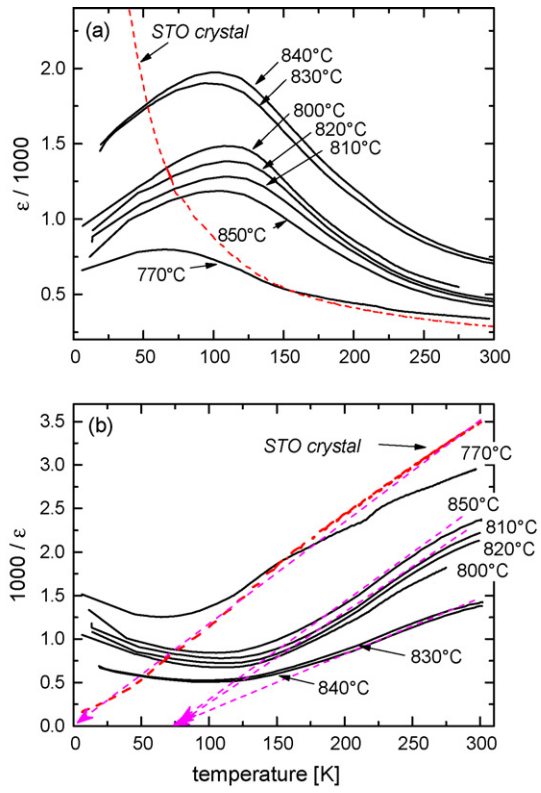

Fig. 2. Temperature dependence of the permittivity (a) and inverse permittivity of STO films deposited via PLD at different heater temperatures. Additionally the data of single crystalline STO is given, which is obtained from measurements of a planar capacitor on a single crystalline STO substrate. All data are recorded a frequency of 1 MHz.

The growth rates, phase formation and ferroelectric properties of the STO layers strongly depend upon the preparation method and preparation parameters. The STO growth rates are (1.6–2.6) nm/min, (25–32) nm/min, and 180 nm/min for MST, high-pressure PLD, and low-pressure PLD deposition, respectively. Furthermore, depending on the technology and the deposition parameters different structural orientations are obtained. Fig. 1 shows the dependence of the STO growth rate and orientation of the epitaxial STO phases on the heater temperature for MST, high-pressure PLD and low-pressure PLD. Generally, the growth of the different STO phases depends (i) on the choice of the substrate and (ii) the particle energy during the nucleation and growth. The first is mainly given by the lattice mismatch between substrate and STO, whereas the latter is mainly defined by the particle energy at the target, the pressure during deposition and the substrate temperature. Depending on the particle energy the deposition rate, the phase and the resulting strain in the film is changed. With increasing particle energy the deposition rate increases (Fig. 1), the phase changes from polycrystalline, via (1 1 0), (1 1 0) + (1 1 1), (1 0 0)+ small amounts of (1 1 0), to finally pure (1 0 0) oriented STO (Fig. 1). This modification is accompanied by a decrease of the strain of the STO film. The strain has been analyzed by XRD experiments.

The dielectric properties of the films are determined by capacitance measurements of planar capacitors at 1 MHz and 2–4 GHz. Fig. 2 shows the temperature dependence of the permittivity of the high-pressure PLD deposited STO layers and, for comparison, the permittivity of a STO single crystal. In pure, unstressed form, STO is an incipient ferroelectric. It remains paraelectric down to about 0 K. This is among others visible in the perfect Curie-Weiss behavior:

$$\varepsilon \propto \frac{1}{(T - T_c)} \tag{1}$$

with an experimentally determined Curie temperatures $T_c \approx 4$–7 K (Fig. 2). In contrast to the single crystal, the films show a Curie-Weiss like behavior only at high temperatures $T > 150$ K. From the linear dependence of ε^{-1}, Curie-temperatures of $T_c \approx 50$–75 K are obtained for all films. However, the temperature dependence of the permittivity of all films shows a pronounce maximum. The position of the maximum depends upon the preparation parameter, it is observed for temperatures around 80–120 K our samples. This maximum can also be associated with a Curie temperature.[5] Moreover, measurements of the hysteretic behavior of our films indicate, that ferroelectricity persist even up to 180–220 K in our films.

This indicates that the Curie temperature is clearly enhanced in the compressively strained films. An unambiguous determination of T_c is not possible. Possible ranges for T_c are given in Fig. 3 together with theoretical predictions[2] and experimental values for STO films on other substrates. The increase of T_c has been demonstrated for STO films on $DyScO_3$ with tensile in-plane strained STO.[4,6] However, due to experimental results of STO films on LSAT it has been speculated, that for compressively strained STO the Curie temperature is not increased.

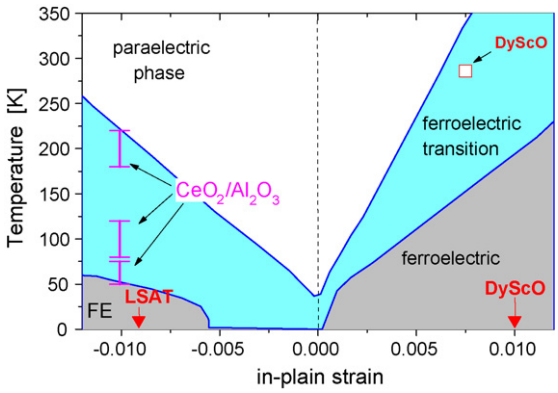

Fig. 3. Curie temperature of STO films on CeO_2 buffered sapphire, LSAT[4] and DyScO[4] and theoretical predictions[2] as function of lattice mismatch between the substrate and film. The T_c values for our films are obtained from different definitions.

However, although the determination of T_c obtained by (i) Curie-Weiss behavior, (ii) maxima in the temperature dependence of the permittivity or (iii) the hysteretic behavior of ε are quite different, they agree with the theoretical predictions. Furthermore, our experiments clearly demonstrate, that a substantial increase of T_c is possible not only for tensile stain, but for compressive strained STO, too.

In order to discuss and compare the different data, let us consider the structural dependence of the ferroelectric properties. Fig. 4 shows the permittivity, losses, and tunability $n = [\varepsilon(0)/\varepsilon(E)] - 1$ of the films as function of the normal lattice distortion normal to the film surface. E represents the applied dc electric field. All three properties decrease in a similar way with increasing lattice distortion. The distortion represents an expansion of the lattice constant $a_\perp$ normal to the film surface. Since the volume of the unit cell should be conserved, the in-plane STO lattice constant $a_\parallel$ will be compressed by up to 1.6%. This is consistent with the structural restrains from the nearly undistorted CeO_2 buffer layer that defines the starting condition for the epitaxial STO phase.

It is known, that strain is one of the important factors affecting the ferroelectric properties since it is directly related to the ionic polarization in ferroelectrics.[7–10] It has been demonstrated, that strain modifies the ferroelectric phase transition, the dielectric constant, and the dielectric tuning.[4,11–17] Generally it is assumed, that with increasing stain (tensional as well as compressive) the permittivity and ferroelectric tuning will decrease.[3] However, due to the demonstrated increase of the Curie temperature, the dielectric constant and, as a consequence, the dielectric tenability is increased at elevated temperature.

On the one hand, we do observe the general tendency, that ε and n decreases with increasing strain for the STO films on CeO_2 buffered sapphire (see Fig. 4). On the other hand, the shift of T_c to higher temperatures leads to a strong increase of ε for $\Delta a/a < 0.005$ and n compared to the values recorded for the undistorted STO single crystal.

Finally, we consider the mutual dependence of the different properties of the ferroelectric layers. Fig. 5 indicates, that the dielectric constant, the loss tangent, and the tunability seem to be correlated. We observe a linear dependence of the loss tangent and the tunability on the dielectric constant. The Kramers-Kronig integral relation is often used to describe the relation between the real and imaginary part of the dielectric susceptibility. The linear correlation between the different parameters might be taken as an indication, that all three parameters are affected by the same mechanism that itself is affected by the lattice strain.

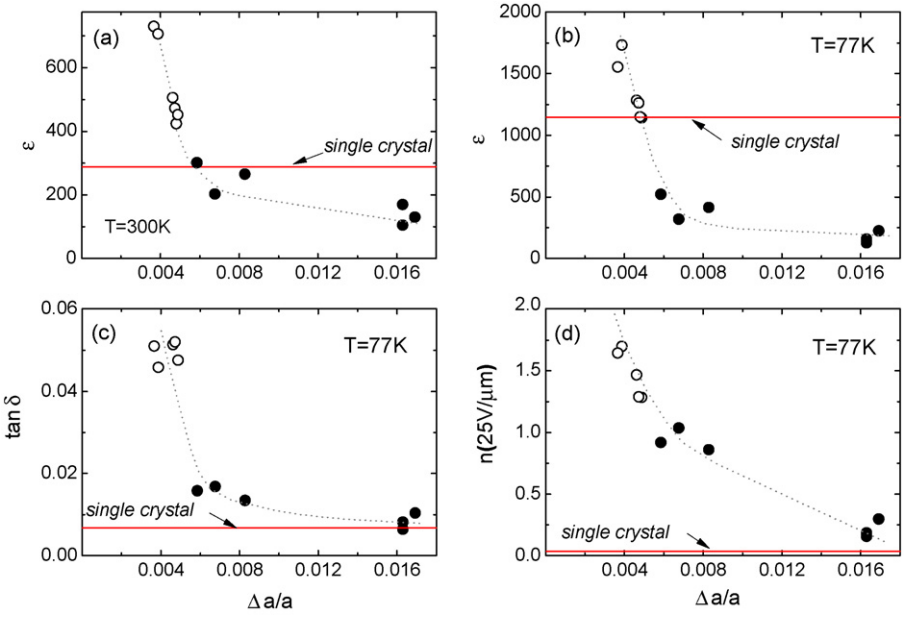

Fig. 4. Dielectric constant ((a) and (b)), loss tangent (c), and tunability (d) at 77 K (and 300 K in (a)) as function of the normalized lattice distortion normal to the substrate surface for high-pressure PLD (open circles) and MST (solid circles) STO films measured at 1 MHz.

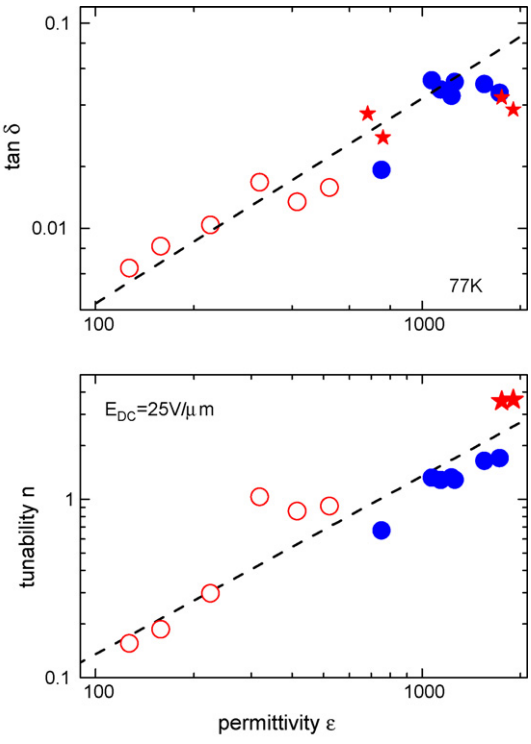

Fig. 5. Double logarithmic plot of the dielectric losses and tunability of the MST (open circles), high-pressure PLD (solid circles), and low-pressure PLD (stars) STO films at 77 K as function of the permittivity. The dashed lines indicate the linear dependence between the different properties.

3. Conclusions

Magnetron sputtered and laser deposited $SrTiO_3$ thin films were fabricated on CeO_2 buffered sapphire substrates. The structural properties and, especially, the strain are investigated and correlated to the dielectric properties of the films.

In agreement with the theoretical predictions,[2] the Curie temperature of the biaxial compressively strained STO films is shifted to higher temperatures (50–220 K, depending of the strain and definition of T_c) compared to that of single crystalline STO (T_c <7 K). As a consequence, the dielectric constant of the films is larger than that of the undistorted STO single crystal for small strain ($\Delta a/a < 0.005$) and temperatures above the Curie temperature. Furthermore, we observe a linear dependence of the loss tangent and the tunability of the dielectric constant. This correlation between the different parameters might be taken as an indication, that all three parameters are affected by the same mechanism that itself is affected by the lattice strain.

It seems that not only biaxial tensile strain, but also biaxial compressive strain can lead to a considerable increase of the dielectric constant and tuning of $SrTiO_3$ thin films in technically relevant temperature regimes. Considering the advantage of the use of sapphire as a low-loss technical substrate, this makes this system – $SrTiO_3$ on CeO_2 buffered sapphire – an interesting system for rf applications like rf tunable devices or phase shifters.

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