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Structural Study of $SrTiO_3$ Single Crystal using High Resolution X-ray Diffraction

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Abstract:

Strontium titanate, $SrTiO_3$ is one of the perovskite – type crystal that commonly used as a substrate for epitaxial growth of multifunctional oxide films and well-defined TiO_2-terminated surface is crucial for the fabrication of oxide hetero-interfaces. Structural properties have a strong effect on thin films characteristics and their applications. Proceeding from this fact, the lattice defects of as-grown or as-annealed $SrTiO_3$ single crystals with a nondestructive technique have been investigated. The structural imperfection and dislocation density (screw and edge types) of STO single crystals with 10x10x1 mm dimension (from crysTec GmbH- Berlin) have been studied using omega scan from high-resolution x-ray diffraction technique, as well as, the symmetric (002) and the skew-symmetric (101) rocking curves (which are sensitive to the structural perfection) also reported. In order to prove the sample quality, the experimental full widths at half maximum (FWHM) of the X-ray rocking curves have been shown. From the FWHMs, the dislocation density (screw and edge types) and the total dislocation density have been calculated.

Keywords: High resolution x-ray diffraction, Rocking curve, FWHM, Dislocation density

Introduction:

Strontium titanate, $SrTiO_3$, is a model example of a perovskite-structured oxide [1, 2]. It can be described as Sr^{2+} and O^{2-} ions with Ti^{4+} ions occupying the octahedral holes created by the oxygen. It has a three dimensional net of corner sharing $[TiO_6]$ octahedral with Sr^{2+} ions in the twelve fold cavities in between the polyhedral (see Figure 1). The lattice constant of STO at room temperature (*a* =3. 905Å) [3-5],

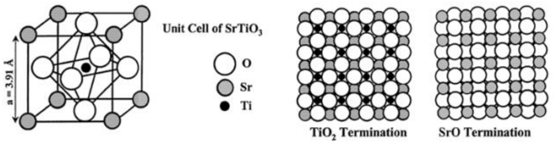

Fig. 1 Schematic drawing of the $SrTiO_3$ unit cell and the Ti-O and Sr- O (001) termination planes [6]

Due to STO multifunctional properties and importances for many applications in various sectors of technologies such as gas sensors superconducting thin film growth, and memory storage devices [7-9], due to the strong relationship between these properties and applications, for example the effect of the dislocation on the lifetime and the mobility of carriers will degenerate the performance of STO devices, the study of $SrTiO_3$ crystal imperfection and its quality has gained a wide interesting and primary importance. Defects and imperfections in oxide films are of particular interest since they can alter or even fundamentally change their ferroelectric, ferromagnetic and superconducting properties [10-15]. Furthermore, STO single crystals are widely used as substrates for thin film growth. Since the quality of the thin film can be strongly dependent on that of the substrate, the optimal film properties will only be fully conceived if the substrate is well characterized in advance [16-18].

There are a lot of techniques which have been widely used to determine the quality of raw single crystal (crystallinity, perfection, dislocation, orientation and surface preparation) such as atomic force microscopy, transmission electron microscopy (TEM) and Etch pit density (EPD). But because of the destructivity of these methods they are not possible for the quality check of the samples which will be used to fabricate thin films and the devices.

It's well known that High-resolution X-ray diffraction (HRXRD) is the corresponding technique with many properties for investigating the structural property of $SrTiO_3$ single crystals and measuring it's dislocation density based on their effects on the x-ray rocking curves [19-22].

Experimental:

The commercially available $SrTiO_3$ single crystals substrate of 10x10x1 mm^3 dimension purchased from crystal Technology GmbH–Berlin were grown by the Verneuil technique [23]. To obtain well-defined single- terminated surface STO (001) single crystals, Pre-treated have been done by immersing the STO substrate in buffered NH4F-HF (BHF) solution with PH 4. 5 for 30 seconds in a special lab coat, special gloves and glasses, to prevented direct contact with the skin and or eyes with the dangerous of HF-buffer, then, the substrate rinsed with distilled water and ethanol, later dried using nitrogen N_2-gas. To reach the desired crystalline perfection of the substrate surface and giving the opportunity to the surface to arrange itself, a heat treatment around 1000 °C were performed for two hours under Oxygen pressure of 700 mbar and the cooling down to room temperature (Which is suitable for such type of samples to obtain fewer holes, open areas and almost single terminated) [18, 24-25]. In order to evaluate the quality of samples, the rocking curve [26] profiles (ω-scan) for symmetric (002) and the skew-symmetric (101) diffraction were performed using analytical materials research diffractometer (Philips X'pert HRXRD) as shown in Fig. (2) equipped with four-crystal Bartel monochromator in symmetric Ge (220) mode to collimate the beam, delivering a pure $CuK_{\alpha 1}$ line of wavelength λ= 0.15406 nm. The incident x-ray beam was produced at 35mA and 45kV settings (1. 6 kW) of the generator [27].

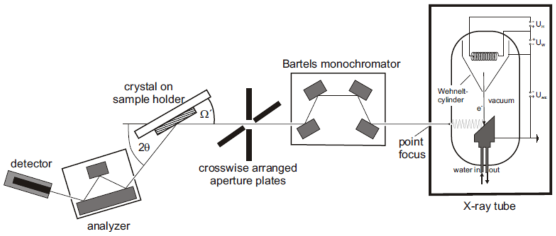

Fig. 2 Schematic diagram of the optical path of the x-ray beam in the commercially available analytical Materials Research Diffractometer (Philips X'pert HRXRD) .

Result and discussion:

Figure (3) shows the representative rocking curves of symmetric, skew symmetric peaks for the investigated STO11, STO12, STO13, and STO14 samples.

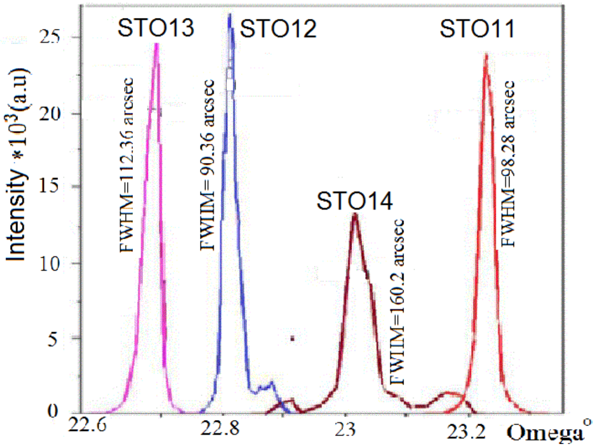

Fig. 3 Comparison of the rocking curves of the STO samples**.**

The influence of the structural imperfection on the X-ray diffraction spectra has been recorded. Table (1) and Table (2) show an overview of the (002) and (101) substrates parameters such as Intensity rate, FWHM value of STO's substrates respectively.

Table 1: An overview of (002) peak for substrates STO.

Sample	Omega (deg.)	Intensity (accounts)	FWHM (arc sec.)
STO11	23, 2312	23150	98. 28
STO12	22, 8095	26189, 4	90. 36
STO13	22, 6898	23355, 7	112. 68
STO14	23, 0157	12682	160. 2

Table 2: An overview of (101) peak for substrates STO.

Sample	Omega (deg.)	Intensity (accounts)	FWHM (arc sec.)
STO11	16. 2195	3677. 7	110. 16
STO12	16. 2043	7492	75. 96
STO13	16. 1965	5075. 3	88. 56
STO14	16. 2046	3287. 3	62. 64

The Variation of the intensity of the STO substrates as a function of FWHM of (002) peaks shown in Fig. 4.

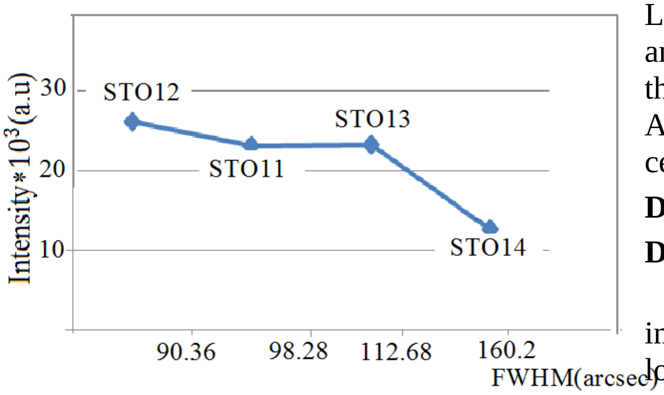

Fig. 4 Intensity of Substrates the samples (STO11- STO14) versus FWHM of (002) peaks.

As shown in Figure 4, the intensity corresponds with high quality of the sample (narrow FWHM) or in another word: inversely with FWHM of rocking curves (Because the peak intensities reflect the total scattering from each plane in the phase's crystal structure, and they are directly depend on the distribution of particular atoms in the structure. Therefore the detector indicates different nonlinear output for each sample. [28].

The peak intensity I*hkl* for a given (*hkl*) can measured by

$$I_{hkl} = I^{o} (\lambda^{3} / \omega) (V_{x} L p A/V^{2}) \ |F_{hkl}|^{2} \ [29]$$

Where, I^{o}= incident beam intensity; λ= wavelength of radiation; ω= rotation velocity of crystal; V_x= volume of the crystal; L= Lorentz factor, which depends on the relative amount of time the peak takes to pass through the Ewald sphere; p= the polarization factor; A=absorption factor; V= volume of the unit cell; and |F*hkl*|= the observed structure factor.

Dislocation density measuring

Dislocations:

Dislocations are defined as abrupt changes in the regular ordering of atoms along a dislocation line. They are characterized by the Burgers vector b, which describes the unit slip distance in terms of magnitude and direction. The dislocations are classified as follows [30-33]:

1. Edge dislocation;
2. Screw dislocation; or
3. Mixed dislocation, which contains both edge and screw dislocation components.

The dislocation will effect and broaden the FWHM of the rocking curves by the following processes:

1. The dislocation induces distortion of the crystal lattice, thus it has a direct effect on the rocking curves broadness.
2. A strain field around the dislocation will be formed, which results in the Bragg angle of the crystal non-uniform [34].

The types and concentration of the dislocation can be analyzed based on the shape and FWHM of rocking curves and calculated.

In principle the screw and edge Components can correspond to the tilt and twist, respect-ively and in another side the screw dis-location density has a correlation with rocking curve of symmetric (002) peak (which is sensitive to the tilt) and the edge dislocation density correlated with the rocking curve of skew- symmetric (101) peak (which is sensitive to the twist) [35-39]. By measuring a set of the rocking curves at different diffraction planes, the dislocation densities can be calculated by using the following expression proposed by Gay and Dunn [32].

From this, when we assume that the broadening of the rocking curves results only from tilt and twist, it will be possible to calculate the dislocation densities from the FWHMs of (002) peak and (101) by using the following relations:

$$\rho_{\mathrm{screw}} = \frac{[\mathrm{FWHM}\ (002)]^2}{[4.35(\mathrm{b}_{\mathrm{screw}})^2]} \qquad (1)$$

$$\rho_{\mathrm{edge}} = \frac{[\mathrm{FWHM}\ (101)]^2}{[4.35(\mathrm{b}_{\mathrm{edge}})^2]} \qquad (2)$$

here b is the Burger's vector, ρ_{screw} is screw dislocation and ρ_{edge} is edge dislocation, $\Delta\Omega$ is (FWHM).

FWHM multiplied by Π/180 to change degree to radian.

$$b_{screw} = \frac{1}{\sqrt{2}}\, a\left(\sqrt{h^2+k^2+l^2}\right)$$

$$b_{screw} = \frac{1}{\sqrt{2}}\, a\left(\sqrt{0^2+0^2+2^2}\right) = 0.552\ nm$$

$$b_{edge} = \frac{1}{\sqrt{2}}\, a\left(\sqrt{h^2+k^2+l^2}\right)$$

$$b_{edge} = \frac{1}{\sqrt{2}}\, a\left(\sqrt{1^2+0^2+1^2}\right) = a = 0.3905\ nm$$

$$\rho_{\mathrm{screw}} = \frac{[\mathrm{FWHM}\ (002)]^2}{[4.35(\mathrm{b}_{\mathrm{screw}})^2]}$$

$$\rho_{\mathrm{edge}} = \frac{[\mathrm{FWHM}\ (101)]^2}{[4.35(\mathrm{b}_{\mathrm{edge}})^2]}$$

$$\rho_{total} = \sqrt{\rho_{screw}{}^2 + \rho_{edge}{}^2}$$

Table (3): Dislocation density of substrates.

Substrate	FWHM (002) (°)	ρ_{screw} cm^{-2} x10^7	FWHM (101) (°)	ρ_{edge} cm^{-2} x10^7	ρ_{total} cm^{-2} X10^7
STO11	0. 0273	1. 7	0. 0321	4. 6	4. 9
STO12	0. 0251	1. 4	0. 0211	2	2. 44
STO13	0. 0313	2. 2	0. 0246	2. 7	3. 48
STO14	0. 0436	4. 3	0. 0174	1. 3	4. 49

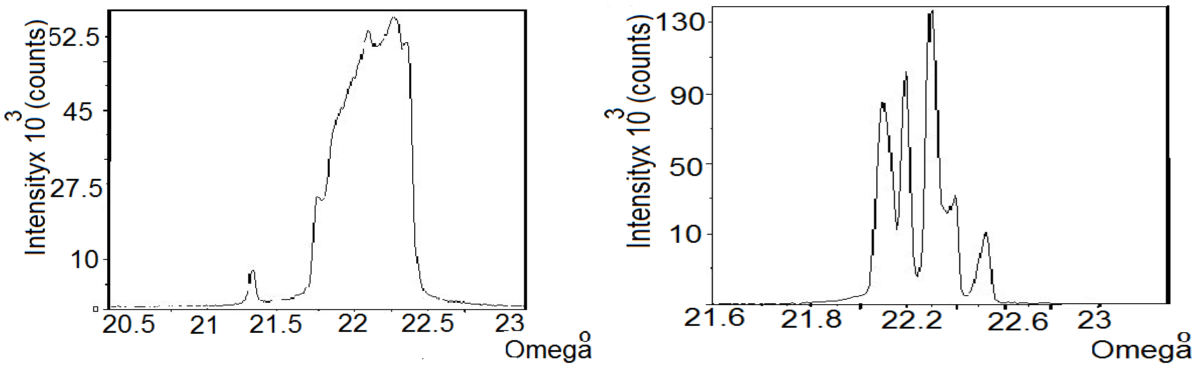

Fig. 5. The out-of-plane (002) STO rocking curves of two as-grown samples from Crys Tec GmbH (Before treatment procedure).

Concluding remarks:

Obviously, Clear effect of annealing on sample quality process {because of decreasing the amount of holes [40]} have been observed through comparison of rocking curves of the treated samples of STO (Fig. 3) with as-grown samples from Crys Tec GmbH (Fig. 4) in one hand. On the other hand we observed the limited ability of this treatment procedure. For example; we have observed that the samples which were from the same batch and they had the same treatment procedure appeared with different (FWHM) s and dislocation densities. We conclude that the batch treatment of the samples does not automatically produces the same results. Since the perovskite-type oxides ABO_3 often exhibit vacancies on the A and the O site these differences might be caused by intrinsic defects in the crystals or caused during the preparing procedure effects (inhomogeneity for example) and extrinsic defects such as cutting for desire samples. Finally we conclude that the rocking curve of Ω scan gives information on the quality of the single crystal. The higher width of the diffraction line indicate poor crystallinity and vice versa.

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