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Top-seeded solution growth of $SrTiO_3$ single crystals virtually free of mosaicity

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ABSTRACT

Strontium titanate ($SrTiO_3$), a well-established traditional perovskite substrate as well as a promising substrate crystal for the epitaxy of new advanced perovskite-type thin films, suffers from the unavailability in adequate quality for the latter. To improve the situation attempts have been made to grow $SrTiO_3$ at moderate temperatures (< 1535 °C) well below the melting temperature and under low temperature gradients by the top-seeded solution growth method. Based on very special modifications of the growth conditions, virtually mosaicity-free $SrTiO_3$ single crystals in the 1–2 cm range were obtained. High crystalline quality was verified by defect selective etching, rocking curve measurements, energy dispersive Laue mappings and by synchrotron X-Ray diffraction topography. The production of virtually subgrain- and dislocation free substrate crystals is essential to considerably improve characteristics of $SrTiO_3$ based SQUIDs, transistors or memory devices and to allow an in-depth analysis of intrinsic and extrinsic factors influencing the properties of epitaxially grown oxide heterostructures.

1. Introduction

Strontium titanate is a widely used substrate material in the field of thin film growth. It has a wide range of useful physical and electronic properties and it is the only known substrate material which can be used for the implementation of oxidic two-dimensional electron liquids (2DELs). So far, oxidic 2DELs could be only realized with $SrTiO_3$ substrates on which, for example, the following layers were deposited: $LaTiO_3$ [1], $LaAlO_3$ [2], $LaVO_3$ [3], $LaGaO_3$ [4], $GdTiO_3$ [5] and $KTaO_3$ [6]. They also have been found in $SrTiO_3/SrTi_{0.8}Nb_{0.2}O_3$ superlattices [7]. For this application high perfection $SrTiO_3$ crystals are needed since the conductivity of the active layer is reduced by dislocations [8]. The commercially available Verneuil bulk crystal quality (etch pit density (EPD) > 10^6 cm^{-2} and mosaicity between 5 and 8′ [9,10]) impedes the progress for modern applications and the detailed understanding of intrinsic and extrinsic properties of the grown oxide heterostructures. It also hampers the development of sensitivity improved $SrTiO_3$-based superconducting quantum interference devices (SQUIDs, used to measure magnetic fields) and the enhancements of transistors and memory devices. For all these applications the reduction or better the elimination of dislocations and subgrain boundaries is of tremendous importance. At the same time, alternative crystal growth approaches should ideally supply crystal volumes comparable to the Verneuil method (≥15 cm^3) if commercial use is pursued.

2. Background

During the last years improvements in bulk crystal quality of $SrTiO_3$ were demonstrated by the following crystal growth methods: (1) optical floating zone (OFZ, EPD: $1–5\times10^5$ cm^{-2}) [11], (2) edge-defined film-fed growth (EFG, EPD: $(1.7 \pm 0.7)\times10^5$ cm^{-2}) [12], (3) top-seeded solution growth (TSSG at temperatures below 1740 °C, EPD: $2\times10^4–2\times10^5$ cm^{-2}) [13] and (4) Czochralski (Cz, EPD: $(4.3 \pm 1.1)\times10^5$ cm^{-2}) [12]. These crystals exhibit lower dislocation densities than commercial Verneuil material and meet relevant crystal volumes (≥9 cm^3) but they are also not entirely free of mosaicity. The lowest reported mosaicity values for bulk EFG and OFZ crystals were below 2.6′ [12] and 3′ [11]. Mosaicity-free crystal regions up to the cm-range were achieved for crystals grown by the TSSG [13] and EFG [12] methods.

It is known from the literature that $SrTiO_3$ crystals with the highest structural perfection can be grown from self-fluxes under very low thermal gradients and at comparably low temperatures below 1560 °C which is much lower than the melting point of $SrTiO_3$ (2080 °C [14]). Due to the necessity of using low growth rates at such conditions and limitations given by the eutectic temperature of 1449 °C [14], the increased quality is at the expense of substantially reduced crystal

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yields. For crystal volumes in the range between 0.5 and 3 cm^3, top-seeded solution grown crystals typically exhibit etch pit density values between 10^2 and 10^3 cm^{-2} [15,16]. Very good mosaicity values of 1.5′ (90″) were reported by Sidoruk and Rytz [17] for crystals grown at FEE (Idar-Oberstein, Germany) under similar conditions described by Rytz et al. [16]. Belruss et al. [18] first applied the TSSG method for $SrTiO_3$ and so far these crystals with volumes of approximately 1 cm^3 exhibit the lowest dislocation density values (below 10 cm^{-2}). Such low dislocation densities indicate a very high structural perfection but these crystals were probably not entirely free of subgrains, since mosaicity values between 2 and 3′ were reported for these crystals by Scheel and Lytvynov [10]. Typical growth times for such TSSG crystals are about one week [10]. Growth from borate fluxes is an option to grow crystals with similar crystal volume, but with 2 months growth time [10]. These borate flux grown crystals usually have flux inclusions, but inclusion-free regions can also be found. For (002) rocking curve reflexes, FWHM values below 1′ were measured and only traces of mosaicity were present. Etch pit density values between 0 and 10^2 cm^{-2} were reported for these samples.

Our approach presented in this work was to grow $SrTiO_3$ crystals by the TSSG method under further improved growth conditions. This was done by careful consideration of (1) the thermal conditions to achieve stress-free long-term cylindrical growth [13,14] and (2) by change of the pulling direction from < 100 > [15,16,18] or < 110 > [16] to < 111 > with 8° off-orientation.

3. Experimental

3.1. Crystal growth and preparation

A melt solution composition of 75 mol% TiO_2 and 25 mol% SrO was used for the self-flux growth experiments. As starting material, dried and mixed powders of $SrCO_3$ and TiO_2 with purities of 99.999% and 99.99%, respectively, were calcined in platinum crucibles at 1300 °C using $MoSi_2$ muffle furnaces. Subsequently, to optimize the crucible filling process cylindrical bars were made by isostatic cold pressing at 2000 bar. Top-seeded solution growth was performed in an rf-heated Czochralski setup in air at atmospheric pressure and at temperatures below 1535 °C. Crystal growth conditions were suitable for the application of automatic diameter control.

To obtain seed crystals, initial growth experiments were performed using Pt tips as seeds. From such subgrain-containing heterogeneous nucleated crystals, dislocation- and mosaicity-free < 111 > seeds with 8° off-orientation were selected and prepared for subsequent growth experiments. The growth runs were carried out in air with the use of a platinum crucible embedded in ZrO_2 and Al_2O_3 insulation [14]. Growth rates were between 0.2 and 0.3 mm h^{-1}. An actively heated platinum afterheater was used to achieve moderate axial temperature gradients (about ≥20 K/cm) along the growing crystal and low radial temperature gradients at the surface of the melt solution (about 10 K/cm).

Samples from a heterogeneously nucleated crystal, from which a high quality seed was prepared, as well as from a crystal grown on such seed were cut perpendicular to the growth direction and chemo-mechanically polished to obtain wafers with a high surface quality for investigations by rocking curve measurements, energy dispersive Laue mapping [19], defect selective etching and synchrotron X-ray topography. Extensive and detailed characterization of several wafers evidenced that nearly defect-free crystals can be grown from high quality seeds by using the TSSG method.

3.2. Crystal characterization methods

Rocking curve X-ray diffraction measurements were conducted with a high resolution diffractometer (General Electric) using Cu $K\alpha_1$ radiation (λ=1.5406 Å). The scans were measured on a $SrTiO_3$ (111) Bragg peak. The collimated beam had a divergence of 11″ and the measurement spot covered approximately 10 mm in length, i.e. the full diameter of the sample. Primary beam slit apertures of 0.2 and 2 mm were used.

Synchrotron radiation X-ray topography (SR-XRT) measurements were performed at the TopoTomo beamline of the 2.5 GeV synchrotron source ANKA, at Karlsruhe Institute of Technology. The topographs were recorded in both back reflection and transmission geometries on high resolution Slavich holographic films.

Energy dispersive Laue mappings (EDLM) were performed at low vacuum conditions (1 mbar) using the μ-XRF spectrometer M4 Tornado (Bruker) for polished wafers prepared from (1) a heterogeneously nucleated crystal and (2) from a high quality crystal grown from a dislocation-free seed. The method was used for the nondestructive identification of small-angle boundaries in the grown crystals. Subgrain misorientations with a lower limit in the range between 40 and 100" can be reliably identified by the method [19]. The measurement system was equipped with a Rh X-ray source operated at 50 kV and 600 μA. Polycapillary X-ray optics with a cone angle of 34° were used to focus the non-polarized bremsstrahlung at the surface of the sample which enables a high spatial resolution of about 25 μm. The bremsstrahlung of the excitation source interacts with the crystals and due to the instrument geometry it is possible to detect Bragg reflections. These reflections can be found at specific energies and can be displayed in two dimensional diffraction intensity maps. These maps were used for the qualitative analysis of crystal domains. The signals were detected using a circular silicon drift detector (SDD) with a high energy resolution (< 145 eV). The detection area of 30 mm^2 allowed the collection of radiation in a wide angular range. The principle of the new XRD surface mapping technique, the measurement procedure and the measurement setup are described elsewhere [19]. Virtually full sample area coverage was achieved by using spot distances of 20 μm. The measurement time per point was set to 40 ms (identical to the measurements performed in [19]) and all spots were measured twice to increase count statistics, i.e. two passes of the scans were performed.

For etch pit density (EPD) measurements the wafers were etched for several minutes in a mixture of $HF - HNO_3 - H_2O$ in the ratio 1:2:2 [20]. EPD values were measured using an optical microscope by counting pointed etch pits per unit area on the etched surfaces.

4. Growth factors affecting crystal quality

4.1. Growth instability

Large temperature oscillations at a growth interface during automatic diameter control, high temperature gradients, the change of an interface shape as the growth proceeds including its inversion, and irregularities in crystal shape have a direct impact on crystal quality due to generation of strain-induced dislocations, misoriented subgrains (mosaicity) and possible cracks. Keeping a stable growth with a smooth diameter control is therefore a crucial factor in growing high-quality $SrTiO_3$ crystals.

Strontium titanate shows an increased tendency to foot formation and spiralling at high growth temperatures [12,13]. This behaviour was observed for crystals pulled from stoichiometric melt by the Czochralski method and can be explained by the optical and thermal properties of the material. The red shift of the optical absorption edge and the rising free carrier absorption strongly narrow the spectral range of transmission and impede radiative heat transport through the crystal [21,22]. The very low thermal conductivity of strontium titanate (thermal conductivity < 2.2 W $(m\,K)^{-1}$ at temperatures > 1700 °C) [13] contributes to a poor heat transport through the growing crystal.

To eliminate the risk of growth instabilities (foot formation and spiralling) [23] due to very limited radiative and conductive heat transfer through the growing crystal, one possible solution is to grow the crystals at comparably low temperatures, i.e., from non-stoichiometric melts by the top-seeded solution growth method (e.g. below