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Indentation size effect and dislocation structure evolution in (001) oriented $SrTiO_3$ Berkovich indentations: HR-EBSD and etch-pit analysis

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In the present work, the dislocation structure evolution and indentation size effect in (001) oriented STO have been studied by using sequential polishing, chemical etch-pit technique and high-resolution electron backscattered diffraction (HR-EBSD) analysis via Berkovich nanoindentation experiments. Nanoindentation load-displacement curves show multiple pop-in events, which relate to nucleation and extension of dislocation pile-ups around the residual impression. Sequential polishing and etching revealed the three-dimensional dislocation etch-pit structure at various sub-surface depths. The dislocation densities are determined for a 5 mN and 10 mN indentation below the surface via HR-EBSD and etch-pit analysis. With HR-EBSD, the lattice rotation and thereby GND densities are determined, while the etch-pit technique revealed the total dislocation density. Based on the independently measured dislocation densities, we clearly show a depth dependent dislocation density, where both total and GND densities increase with decreasing indentation depths. The higher dislocation densities below smaller indents explain the observed size dependency of the hardness in STO, which also sheds light on the extraordinary combination of high indentation hardness and low yield strength in STO.

1. Introduction

Strontium titanate (STO) is an optically transparent perovskite oxide ceramic material, which has been studied extensively because of its remarkable properties like stable cubic symmetry above 105.5 K, large dielectric constant, high thermal and chemical stability [1–4]. Due to such noteworthy properties, STO is a prime candidate for different applications, e.g., as a substrate for a wide range of coating materials including high temperature superconductors, dielectric materials in capacitors, for producing different microelectronic heterostructures and as anode in fuel cells [3,5,6]. Recently, it has been demonstrated that dislocations can act as nanoscale filamentary paths to transport oxygen ions more rapidly than the regular STO lattice, which makes STO a potential material to use as resistive switching memory [7–10]. However, to exploit such effects for technological applications, a comprehensive understanding of the dislocation behavior at all length scales is required.

In literature, the bulk behavior of STO has been studied via uniaxial compression testing for a wide range of temperatures [11–14]. Recently, Patterson et al. [15] studied the temperature dependence of the dislocation density for 1% deformed (001) STO single crystal using uniaxial compression testing and observed higher dislocation density at 300 °C compared to 25 °C. In contrast to other ceramic materials, single crystalline STO can be plastically deformed at room temperature (up to a maximum plastic strain of 9%) and undergoes an unusual ductile-to-brittle-to-ductile (DBDT) transition [11,12,14]. At ambient conditions, slip along $<110>\{110\}$ systems has been reported consistently by several authors for (001) STO single crystals [11–16].

Despite of the comprehensive studies on the bulk single crystal plasticity behavior of STO, rather little is known about the small-scale deformation behavior in this perovskite material. Yang et al. [17] performed Vickers micro-indentations on STO (001) single crystal and reported slip along $<110>\left\{1\bar{1}0\right\}$ and $<110>\{001\}$ systems using Transmission Electron Microscopy (TEM). However, Matsunaga et al. [18] and Kondo et al. [19] in their TEM analysis reported only $<110>\left\{1\bar{1}0\right\}$ type slip systems. Recently, Javaid et al. [20] conducted spherical nano-indentation experiments on

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(001) STO and also verified the presence of only $<110>\{1\bar{1}0\}$ type slip systems using Molecular Dynamics (MD) simulations and etch-pit analysis. Bernard et al. [3] measured the hardness of STO single crystal to be 9.5 ± 1.3 GPa using nanoindentation and observed multiple pop-in events in the load-displacement curve, which they relate to the occurrence of cracking. At lower indentation depths, where cracks are absent, these multiple pop-ins are still observed and can be related to other dislocation phenomena, which still need to be studied in more detail. The high macroscopic indentation hardness of 9.5 GPa is also unexpected for a material having a yield strength of only ~120 MPa [15]. The reason of such a large discrepancy is still an open question. Since STO is considered as a model system to study extended defect structures in perovskite materials and their effect on the ionic and electronic transport properties [20,21], a comprehensive analysis of dislocation structure at the local-scale is necessary. Such analyses are potentially interesting for tailoring the local ionic conductivity, to study the hardness – yield strength discrepancy in STO and the indentation size effect (ISE), which is more pronounced at the local-scale and not addressed in previous indentation studies on STO.

The model presented by Nix and Gao [22] which is built on the concept of Geometrically Necessary Dislocations (GNDs) has been widely used in the literature to interpret the ISE. However, the physical significance of the Nix-Gao model is still under debate [23] and validation further requires direct experimental evidence based on dislocation structures at various length scales. Therefore, the present work aims at a direct observation of the dislocation structure at different length scales to analyze the dislocation mechanism being responsible for the ISE and to understand the hardness-yield strength discrepancy in STO.

The indentation along with electron back-scattered diffraction (EBSD) has been used to study the local deformation mechanisms in a wide range of materials [24–26]. These conventional EBSD techniques used the Nye's framework based on a Hough transform analysis with an angular resolution of around 1°, which is not very sensitive for the determination of GND densities [27]. Demir et al. [28] used Conventional EBSD Hough based analysis to measure the GNDs densities and investigate the ISE using a 1 μm spherical indenter tip. They reported that the GND density does not increase with decreasing indentation depth, but rather drops. Qiao et al. [29] modified the Nix-Gao model including tip rounding effects and showed that indenter tip bluntness can cause a reduction in dislocation densities at lower indentation depths, which could explain a drop in GND density at lower indentation depth as observed by Demir et al. [28]. Recently, Wilkinson et al. have developed the cross-correlation-based analysis of EBSD patterns (named as HR-EBSD), which allows to measure elastic strains and lattice rotations at a sensitivity of about 10^{-4} [30]. In contrast to conventional Hough-based analysis of EBSD, GND densities measured from HR-EBSD have a much lower noise level [31]. The details of elastic strain field and GND density distribution calculations can be found in the work of Wilkinson and Randman [32].

Along with EBSD, the chemical etching technique complemented with Atomic Force Microscopy (AFM) or Scanning Electron Microscopy (SEM) proved to be a powerful tool for analyzing the dislocation structure at different length scales and studying the ISE behavior. For example, Sadrabadi et al. [33] quantified dislocation etch-pits for different indentation loads and revealed the ISE behavior in (111) oriented single crystalline CaF_2. They found a higher dislocation density at lower indentation depth. Montagne et al. [34] used a similar etching technique to study the dislocation structure and effect of pre-existing dislocations on pop-in effects in a (001) MgO single crystal.

In the present work, both chemical etching and HR-EBSD techniques are combined to reveal the dislocation structure around/underneath Berkovich nanoindentations. This unique combination can provide further insights into the ISE and hardness-yield strength discrepancy in STO, since the total dislocation and GND densities are analyzed separately via etch-pit and HR-EBSD, respectively. The 3D dislocation etch-pit structure is analyzed using a sequential polishing and etching technique (SPET). The HR-EBSD and etch-pit analysis conducted on SPET sections facilitates the analysis of complete sets of dislocation patterns and GNDs distributions.

2. Experimental

Single crystalline STO with <001> orientation supplied by Alineason Materials Technology GmbH (Frankfurt am Main, Germany) was used in the present work. In order to differentiate between pre-existing dislocations and the dislocations from residual impressions, the polished specimen (4 × 4 × 8 mm^3) was etched for 20 s (10 ml 65% HNO_3 with few drops of 40% HF). The dislocation structure around the indentations was revealed by re-etching the samples for 10–20 s using the same etchant. The three-dimensional plastic zone evolution was studied via sequential polishing and etching technique (SPET), which allows removing a desired amount of material from the surface of the specimen by vibration polishing using a 40 nm silica suspension. The detail SPET experimental protocol is given in Ref. [33]. Dislocation etch-pits were analyzed by using confocal laser scanning microscopy (LEXT 4000, Olympus, Tokyo, Japan) and scanning electron microscopy (MIRA 3XMH, TESCAN, Brno, Czech Republic).

Nanoindentation experiments were performed with a diamond Berkovich indenter tip using a nanoindenter (iNano, Nanomechanics Inc., Oak Ridge, Tennessee, USA) equipped with load controlled (LC) and continuous stiffness measurement (CSM) units. A tip radius R = 130 nm was measured via the Hertzian Fit method, in which the elastic part of the curve (before the first pop-in event, see Fig. 1) is fitted using $P = \frac{4}{3}E^* \sqrt{R} h^{1.5}$, where P is the load, E^* is the reduced modulus, R is the tip radius and h is the depth [35]. A Poisson's ratio (υ) of 0.237 [14] and Young's modulus (E) of 264 GPa [15] was used in this analysis, which results in $E^* = 225$ GPa. For R = 130 nm, the critical transition depth from spherical to conical geometry is < 10 nm. Hence, the measurements >10 nm indentation depth are already in the self-similar regime of indents. Fused silica was used for calibrating the tip area function. A range of loads up to 45 mN was used in these experiments. The hardness was measured based on the Oliver-Pharr method [36]. The LC and CSM methods were used to study the ISE behavior and the effect of a change in hardness during multiple pop-in events, respectively.

The HR-EBSD measurements on non-etched STO were made using a TESCAN MIRA3 SEM equipped with an EDAX TSL DigiView EBSD system (EDAX, Mahwah, NJ, USA). The system was operated at 15 keV with a pattern resolution of 1 MP. A very thin layer of carbon was deposited on the surface of the specimen to avoid drift and charging effects. A step size of 100 nm was used for all measurements and EBSD patterns were analyzed using the commercial software Crosscourt V4 (CC4) from BLG Vantage Software Inc. (Bristol, UK). The software CC4 involved the cross-correlation analysis based on the detection of small shifts with respect to a reference pattern, representing a strain free region. The details of GND density measurements and elastic strain calculations can be found in Ref. [32]. The $<110>\{1\bar{1}0\}$ type slip systems were used for the calculation of the GND distribution maps [12–16,18–20]. The HR-EBSD measurements were conducted on 5 mN (residual indentation depth = 40 nm) and 10 mN (residual indentation depth = 90 nm) indentations, after removing 80 nm and 180 nm of material from the surface of specimen, respectively. At these particular polishing depths, both indentations have a self-similar