Functional Materials

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Line defects in TiO_2 single crystals and their influence on ionic and electronic transport

M. Kelsch[1]

[1]Max-Planck-Institut for Intelligent Systems, Stuttgarter Center for Electron Microscopie, Stuttgart, Germany

kelsch@is.mpg.de
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Point defects play a critical role in ionic solids. In fact, many physical properties are influenced by these zero dimensional defects. Therefore, studies on point defects have a paramount importance in the field of solid state ionics. By the advent of nano-ionics, it was found that the interplay of point defects and interfaces (such as grain boundaries and hetero-interfaces) could result in different properties compared to the bulk properties [1]. Thus, it is important to study also the interplay of point defects with other extended defects. The energetically least costly extended defects are line defects (dislocations), which take an intermediate place between point defects and frozen interfaces as far as thermodynamics and kinetics are concerned. TiO_2 was chosen as the model material not only for its versatile technological applications but also owing to its mobile cation and anion defects which are essential for dislocation generation.

Dislocations were created in TiO_2 single crystals by compressing at 1200 ^oC with 40 MPa for 5 min. TEM revealed that dislocations preferably lie on {110} which is one of the commonly observed slip systems for TiO_2 [3], as shown in Fig.1-3. The plan view specimens in Figs. 1 and 3 were cut out from a TiO_2 single crystal using a Well diamond wire saw to 2 mm square. These specimens were mechanically ground from the back side to a thickness of 70 µm and then further thinned and polished to less than 20 µm thickness in the dimpled area with a Gatan dimple grinder. The specimens were then mounted on a clamp type DuoPost and put it in a Precision Ion Polishing System (PIPS™691). Finally the specimens were thinned with Ar^+ to electron transparency.
The cross sections of the specimen as shown in Fig. 2 were prepared using an Allied Multiprep™ System. A wedge of material is prepared using a specially designed tripod specimen holder for polishing. Finally the specimens were thinned with Ar+ to electron transparency. TEM investigations were performed with a Philips CM200 microscope operated at 200 kV and large tilting angles. The point-resolution was 2.7 Á.

To understand the effect of dislocations on the electronic and ionic transport, electrical properties were studied parallel and perpendicular to the slip planes i.e., in [001] and [110] directions, respectively. For the [001] direction, the dislocations enhance the conductivity at high oxygen partial pressures (pO_2) from 1 – 10^5 bar, cf. Fig. 4. Wagner-Hebb type polarization measurements (green symbols in Fig. 2) on these samples revealed an increase in the hole conductivity by half an order of magnitude, and an increase by 3 orders of magnitude in ionic conductivity (oxygen vacancies and/or Ti interstitials) compared to the pristine crystals without dislocations. The sample measured along [110] did not show any conductivity change despite the presence of dislocations. Under reducing conditions, i.e. pO_2 below 10^{-12} bar there is no change in the n-type electronic conductivity, irrespective of the measurement axis. Furthermore, oxygen tracer experiments and SIMS analysis indicate that Ti interstitials make larger contributions to the increased ionic conductivity than oxygen vacancies.

The enhanced ionic and hole conductivities of [001] crystals at high pO_2 and unchanged n-type conductivity at low pO_2 can be well explained in the framework of negatively charged dislocation cores and space charge accumulated layers for positive carriers. This model can also explain the unchanged conductivity along [110], as the space charge zones do not overlap in this direction.

The present observations on TiO_2 single crystals demonstrate an alternative way to modify the ionic and electronic conductivities of ionic solids. A potential advantage of such a technique could be a spatial variation of ionic and electronic conductivity by locally generating dislocations, e.g. by nano indentation.

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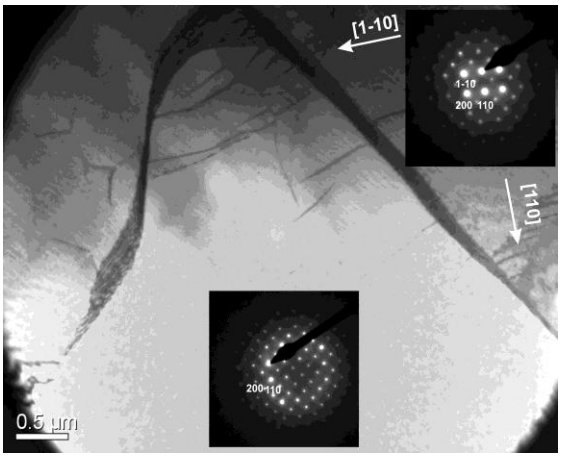

Figure 1. TEM bright field image of a plan view [001] sample with electron beam parallel to [001], from ref. [2].

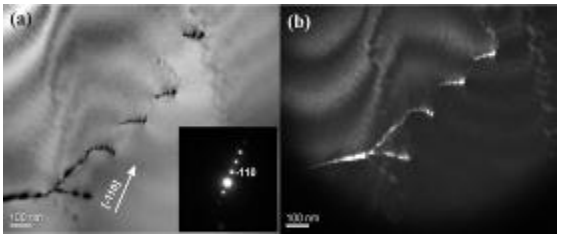

Figure 2. a) TEM-BF image of the T_{001} sample prepared from cross-section, two beam condition with -110 diffraction spot excited (electron beam parallel to [110]). b) DF image using -110 diffracted beam.

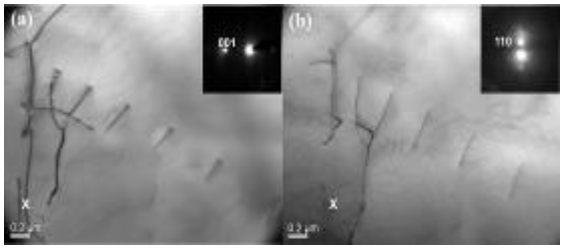

Figure 3. TEM-BF images of the T_{110} plan view sample with electron beam parallel to [110]:
a) two beam condition with 001 and b) 110 diffraction spots excited.

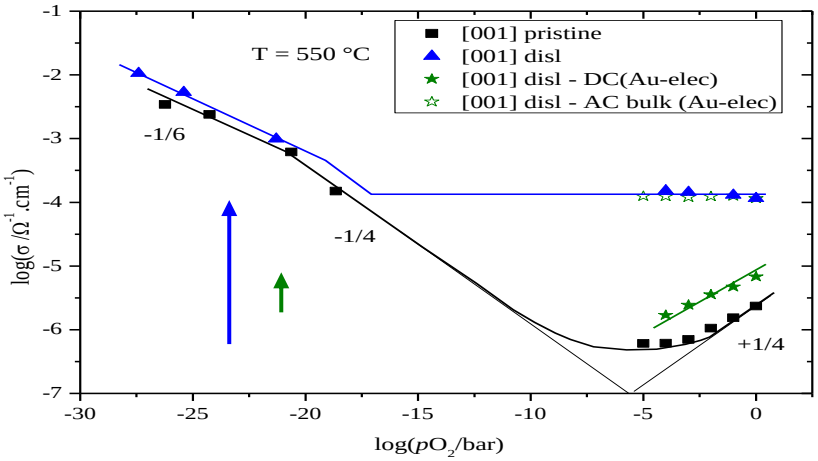

Figure 4. Conductivity of untreated (pristine) TiO_2 compared to a crystal with high dislocation density [2].