Altering electrical properties by "one-dimensional doping": Case study of TiO_2

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Defects are an essential ingredient for charge and mass transport in (ionic) solids. In addition they are sites with locally increased free energy so that often they become the catalytically active centers for heterogeneous reactions. When one wants to tune the materials properties by adjusting its defect chemistry, typically the first choice is to modify the point defect concentrations, e.g. by aliovalent doping or by equilibration with different component activities. Another alternative approach to tune the materials (electrical) properties is by introducing higher dimensional charged defects such as boundaries (two-dimensional doping). By this method, the total conductivity is not only governed by the bulk point defect chemistry but rather under the influence of space charge zones [1]. Such effects were shown for various solid-solid interfaces, heterolayers, nanocrystalline materials etc. So far, defect chemical studies focused on the influence of two dimensional boundaries or interfaces on the transport of point defects and very little is known about one-dimensional doping by deliberately introducing dislocations. A key advantage of "one-dimensional doping" is that with respect to kinetics dislocations take an intermediate position between point defects which are easily equilibrated with external conditions, and grain boundaries which are essentially frozen after sample preparation. Dislocations can be generated at intermediate temperatures (typically about 3/4 of the melting temperature) by mechanical deformation of the sample. Dislocations are formed only in specific directions and hence it is possible to modify the properties directionally. In addition, applying the deformation only locally would enable one to create spatially varying defect concentrations. To demonstrate these effects of mechanical action on defect chemistry, we chose TiO_2 single crystals as the model material. It is particularly suited because of its mobile anion and cation defects at elevated temperatures which is essential for the generation of dislocations.

Dislocations were generated in TiO_2 (rutile) single crystals by hot uniaxial pressing at 1200 ^oC with a pressure of 40 MPa. Due to high temperature and pressure, the plastic deformation of the crystal occurs via dislocation creep. According to the literature, the favorable slip system in TiO_2 at these conditions are on {110} <001> [2]. Two orientations, viz. [001] and [110], were studied to understand the effect of dislocations on the electrical measurements; these two orientations correspond to the conductivity parallel and perpendicular to slip planes, respectively. To characterize the dislocations, TEM samples were prepared from the longitudinal and transverse directions of the deformed crystals. Fig. 1a shows the bright field TEM image of [001] crystal with beam axis parallel to [001], dislocations appear in dark contrast and are preferably oriented on {110}. The bright field TEM image of [110] crystal (sample prepared from the cross-section) shows similar features. The distance between the dislocations can be estimated to about 300 nm based on observations from several TEM images.

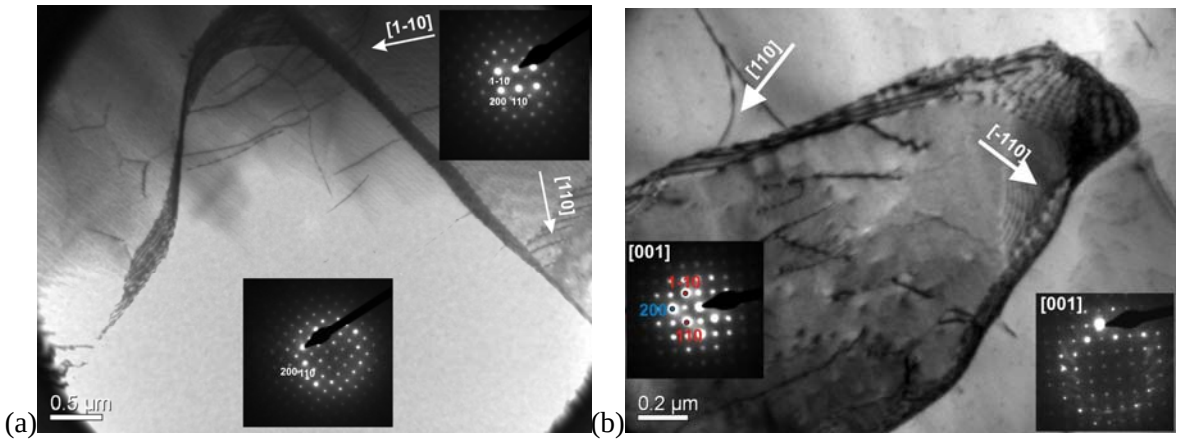

Figure 1. Bright field TEM image of (a) [001] crystal plan view and (b) [110] crystal cross-section view with beam axis parallel to [001]. Reprinted with permission from [3], copyright (2013) Wiley.

Electrical conductivity is measured as a function of oxygen partial pressure (pO_2) for [001] crystals, as shown in Fig. 2a. For comparison, the conductivity of pristine crystals without dislocations is also shown. It is known that in oxidizing conditions and moderate temperature (550 ^{o}C), nominally undoped TiO_2 (which is slightly acceptor doped by impurities) is a p-type conductor. However, with dislocations, [001] crystals show an increased, pO_2-independent ionic conductivity (mobile oxygen vacancies $V_O^{\bullet\bullet}$ and/or titanium interstitials $Ti_i^{\bullet\bullet\bullet\bullet}$) which is not typical even for heavily acceptor doped TiO_2. Since the measured conductivity is the total conductivity, i.e., including the electronic and ionic defects, it is interesting to separate the contributions from electron holes and ions. For extracting partial hole and ionic conductivities, a Wagner-Hebb type polarization cell was constructed by depositing thick Au layers as ionic blocking electrode. The extracted hole and ionic conductivities were increased by approx. ½ an order and 3 orders of magnitude compared to the pristine crystal. Interestingly, in strongly reducing conditions, there is no change in the conductivity by dislocations. In case of [110] crystals, no changes were observed in the electrical conductivity either at high or low pO_2 (see Fig.2.b) despite the presence of a comparable number of dislocations as in [001] crystals.

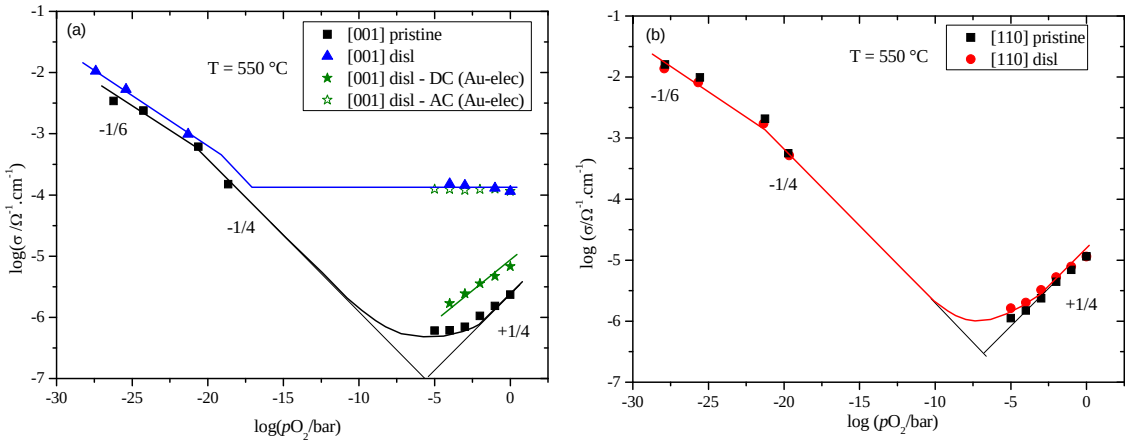

Figure 2. Electrical conductivity as a function of oxygen partial pressure (pO_2) for (a) [001] crystal and (b) [110] crystal. Reprinted with permission from [3], copyright (2013) Wiley.

The systematic enhancement of positive charge carriers (holes and ionic defects) in the [001] crystal at high pO_2 (½ order and 3 orders in the magnitude respectively) and the absence of change in the negative charge carriers at low pO_2 can be well explained in the framework of negatively charged dislocation cores (due to formation of $V_{Ti}^{////}$) and space charge zones with accumulation of positive electronic and ionic carriers, as shown in Fig.3. The defect accumulation is more pronounced for defects with higher relative charge, i.e. stronger for the ionic defects $Ti_i^{\bullet\bullet\bullet\bullet}$ and $V_O^{\bullet\bullet}$ compared to the electronic defects $h^{\bullet}$. This is exactly what is found in Fig. 2.a with a stronger increase of the ionic conductivity compared to the hole contribution. Independent oxygen tracer diffusion experiments (not discussed here) revealed that the oxygen vacancy concentration $[V_O^{\bullet\bullet}]$ is enhanced by only one order in the magnitude compared to pristine crystals. This analysis shows that the major contribution to the enhanced ionic conductivity is due to increased $[Ti_i^{\bullet\bullet\bullet\bullet}]$ rather than $[V_O^{\bullet\bullet}]$, in perfect agreement with the accumulation space charge model. In order to actually measure the increased conductivity in the space charge zones, it is necessary that the dislocations (or at least the surrounding space charge zones) form a continuous percolating network. This condition is fulfilled for measurements parallel to the slip direction.

At very low pO_2, the concentration of electrons is higher in the undisturbed bulk compared to the space charge zones (as shown in Fig.3). Hence, conduction via the undisturbed bulk (without dislocations) is the preferred conduction path independent of the presence of dislocations or space charge zones (due to the lower mobility of $V_O^{\bullet\bullet}$ compared to $e^{/}$, the contribution of the accumulated

$V_O^{\bullet\bullet}$ is negligible), leaving the total electrical conductivity unchanged. In case of the [110] crystals, the slip planes are perpendicular to the electrical measurement axis and no significant changes are expected as long as the space charge zones do not overlap. As mentioned earlier, the distance between the dislocations is about 300 nm whereas the Debye length (the extension of the accumulation zones) for these crystals is approximately 3 nm. Therefore, there is no possibility of space charge overlap in this system, which is the key reason for not observing any changes in the electrical conductivity of [110] crystals.

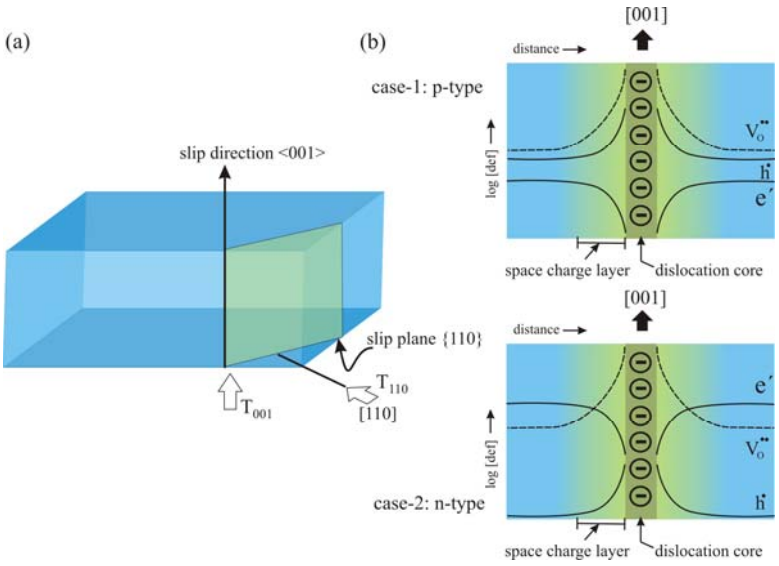

Figure 3 (a) Schematic representation of the slip system and electrical measurement axis (only one plane is shown for better view) and (b) space charge model for p-type and n-type regimes. Reprinted with permission from [3], copyright (2013) Wiley.

The present findings on TiO_2 single crystals show that one-dimensional doping – i.e. formation of charged dislocation cores upon mechanical deformation - offers interesting properties. By one-dimensional doping, slightly acceptor doped TiO_2 single crystals which are typically p-type semiconductors can be transformed into predominant ionic conductors at high pO_2 and moderate temperatures. It is also shown that in TiO_2 the ionic/electronic hole conductivities could be modified locally (in the regions close to dislocation cores) and directionally (only in [001] direction). Similar studies on other ionic solids are promising for tuning properties of functional materials such as ionic/electronic conductivity for a number of electrochemical devices in the future.

References:

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