

## Full length article

## Impact of intrinsic point defect concentration on thermal transport in titanium dioxide



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## ABSTRACT

The thermal conductivity of functional oxide materials can be significantly impacted by variations in point defect concentration, especially at high concentrations where defect interactions can result in extended defects and secondary phase formation. In this work, we systematically study the impact of high point defect concentrations on thermal transport in rutile TiO<sub>2</sub>. Using atmospherically controlled annealing, we vary equilibrium point defect concentrations and measure the resulting thermal conductivity using time domain thermoreflectance. We verify our results with analytical modeling and find that it is not until very high defect concentrations (> 0.5 mol.%) that the phonon thermal conductivity is impacted. We vary the partial pressure of oxygen to low enough levels that sub-stoichiometric Magnéli phases form and find that these highly defective phases severely reduce the thermal conductivity and anisotropy from intrinsic levels.

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## 1. Introduction

Dielectric degradation and breakdown are major reliability issues in microelectronics devices [1,2]. Since increases in temperature can significantly accelerate dielectric breakdown, understanding the evolution of the intrinsic thermal properties of dielectric materials under prolonged electric fields is of critical importance to addressing this failure mechanism [3,4]. The local point defect concentration is a material property that is subject to evolution during exposure to electric fields [5–9] and can have a significant impact on thermal transport.

With increased concentration of point defects, thermal carrier propagation will be disrupted and local hotspots may lead to increased probability of device failure [10–12]. In the region of the electrodes of a dielectric material under prolonged electric fields, point defect concentrations can increase well beyond initial, homogeneous concentrations and lead to highly defective layers that can even move into entirely new phases from the severe non-stoichiometry [8,13].

The impact of this defect buildup on thermal transport can be assessed in a systematic way by analyzing systems with similar levels of homogenous defect concentrations. The literature clearly outlines the general trend of reduced phonon transport with high point defect concentrations in a crystal [14,15]. The analytical form of this increase in phonon scattering with point defects has been previously determined not only for elemental crystals, but for oxides as well [16,17]. In oxides, not only are substitutional (alloying or doping) defects important, but non-stoichiometric point defects due to equilibration with the external oxygen activity ( $p_{O_2}$ ) must be considered as well.

Previous studies have investigated the impact of these intrinsic defects, such as oxygen vacancies, on bulk thermal transport at dilute concentrations [18,19]. Recently, Brooks et al. [20] have conducted a similar study using thin films, relying on molecular beam epitaxy to control the stoichiometry of constituent atomic species incident to the sample during growth, fabricating severely non-stoichiometric samples with secondary phases. However, there has yet to be a systematic experimental study that takes into account the thermal impact of the environmentally driven interaction of various intrinsic point defects in oxide single crystals, pushing defect concentrations beyond known trends in homogeneous concentrations and into the regime of defect ordering and

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secondary phase formation. Studies addressing the change in thermal conductivity of severely non-stoichiometric bulk oxides with secondary phases have concentrated on polycrystalline materials [21]. The strong crystallographic dependence of these non-stoichiometric secondary phases compels the present study of high defect concentrations in single crystalline materials.

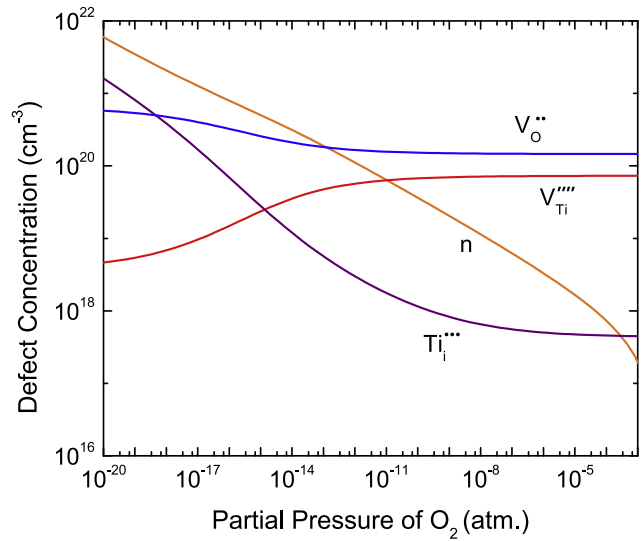
Control over defect profiles in bulk, single crystal oxides can be accomplished by dictating the partial pressure of oxygen during annealing to modify oxygen activity and alter relative equilibrium concentrations of point defects [22]. This technique can be used to produce single crystals with point defect concentrations that span the range of the variable defect concentrations found within a dielectric during degradation and breakdown. The information gleaned from this study can then be used to model the evolution of thermal transport under prolonged electric fields and determine the threshold at which the local thermal conductivity will have an impact on thermal runaway and dielectric breakdown.

This work aims to experimentally elucidate the impact of intrinsic defect concentration on thermal transport by manipulating bulk point defect concentrations in rutile TiO<sub>2</sub>, an important dielectric material. We use analytical models to further understand the trends in thermal transport and identify the threshold of the impact of defectivity on the thermal conductivity as well as the impact of new phase formation at very high defect concentrations.

## 2. Experimental procedure

The rutile single crystals used in this study ([100] and [001] orientation) are purchased from the MTI corporation (10 mm × 10 mm × 0.5 mm). We anneal each crystal at 1100 °C for 36 h at varying partial pressures of oxygen ( $p_{O_2}$ ) in order to control the defect concentrations. In order to precisely control the  $p_{O_2}$ , we vary the flow rate of an Ar/H<sub>2</sub> forming gas mixture in the annealing furnace. We quench the crystals in the forming gas environment to room temperature using a sealed interlock. We vary the  $p_{O_2}$  during the anneal to range from  $1.7 \times 10^{-12}$  to  $8.4 \times 10^{-18}$  atm.

Using the well-established defect reactions and mass action relations, shown in Table 1, we calculate the concentration of various species of point defects during high temperature equilibration [23–26]. The major populations of point defects present in the investigated regime are oxygen vacancies, titanium interstitials, and titanium vacancies. During the quench process, to be consistent with defect models, we assume the population density of ionic defects to be fixed and only the valence of titanium interstitials and the populations of intrinsic electronic carriers are allowed to change. The defect relations controlling the process, derived from high temperature conditions and the previous assumptions, are



**Fig. 1.** Concentration of primary point defects in TiO<sub>2</sub> at room temperature dictated by partial pressure of oxygen in 1100 °C anneal. The defects, shown in Kroger-Vink notation, are oxygen vacancies, V<sub>O</sub><sup>..</sup>, conducting electrons, n, titanium interstitials with 3 + valence, Ti<sub>i</sub><sup>'''</sup>, titanium interstitials with 4 + valence, Ti<sub>i</sub><sup>''''</sup>, and titanium vacancies, V<sub>Ti</sub><sup>'''</sup>.

detailed in Table 1. The calculated concentrations of these defects, along with the concentrations of the electrons and holes can be seen in Fig. 1, calculated at an equilibrium temperature of 1100 °C with an assumed acceptor concentration of  $5 \times 10^{-3}$  mol.% (typical of nominally undoped TiO<sub>2</sub>) which is then quenched to room temperature. The defect concentrations from this calculation are subsequently used in the model for the phonon thermal conductivity to predict the change in phonon scattering by point defects in TiO<sub>2</sub>.

In reduced TiO<sub>2</sub> (TiO<sub>x</sub>), when the level of substoichiometry is in the range of  $1.999 < x < 1.9999$ , the point defects tend to order into crystallographic shear planes termed “Wadsley” defects. Extremely reduced TiO<sub>x</sub>,  $1.67 < x < 1.999$ , can have sufficient driving force to order the shear planes into Magnéli phases [27]. The homologous Magnéli phases have the general formula, Ti<sub>n</sub>O<sub>2n-1</sub> ( $3 \leq n \leq 38$ ), and known shear planes are: {132}, {121} and {011} [28,29].

According to the defect equilibrium calculations featured graphically in Fig. 1, the level of substoichiometry (O/Ti ratio) for heavily reduced samples at a  $p_{O_2}$  of  $4.2 \times 10^{-16}$  atm and  $8.4 \times 10^{-18}$  atm are 1.99 and 1.98, respectively. These values, however, are only estimates considering the uncertainty on temperature,  $p_{O_2}$ , and finite quench rates. Additionally, these calculations assume dilute solutions of defects and do not take into

**Table 1**

Defect relations controlling the population of point defects in the annealed TiO<sub>2</sub> crystals. The subscript  $q$  refers to the quenched state [23–26].

H (kJ mol <sup>-1</sup> ) S (J mol <sup>-1</sup> K <sup>-1</sup> )	Annealing equations	Quench relations
H <sub>1</sub> = 493.1 S <sub>1</sub> = 106.5	$[V_O^{..}] = K_1 n^{-2} p_{O_2}^{-1/2}$	$[V_O^{..}]_q = [V_O^{..}]$
H <sub>2</sub> = 879.2 S <sub>2</sub> = 190.8	$[Ti_i^{'''}] = K_2 n^{-3} p_{O_2}^{-1}$	$\frac{[Ti_i^{'''}]_q}{[Ti_i^{''''}]_q} = \frac{K_2 n_q}{K_3}$
H <sub>3</sub> = 1025.8 S <sub>3</sub> = 238.3	$[Ti_i^{''''}] = K_3 n^{-4} p_{O_2}^{-1}$	$[Ti_i^{''''}]_q + [Ti_i^{''''}]_q = [Ti_i^{''''}] + [Ti_i^{''''}]$
H <sub>4</sub> = 354.5 S <sub>4</sub> = -202.1	$[V_{Ti}^{'''}] = K_4 h^{-4} p_{O_2}$	$[V_{Ti}^{'''}]_q = [V_{Ti}^{'''}]$
H <sub>i</sub> = 222.1 S <sub>i</sub> = -44.6	$h = K_i n^{-1}$	$h_q = K_{iq} n_q^{-1}$
$K = \exp[(TS - H)/k_B T]$ $x[A^x] + n + [V_{Ti}^{'''}] = p + 2[V_O^{..}] + 3[Ti_i^{''''}] + 4[Ti_i^{''''}] + y[D^y]$		

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