CHARACTERIZATION OF DISCONNECTIONS AT GENERAL GRAIN BOUNDARIES IN $SrTiO_3$ AND THEIR ROLE IN GRAIN BOUNDARY MOTION

Hadas Sternlicht[1], Wolfgang Rheinheimer[2], Alex Mehlmann[1], Avner Rothchild[1], Michael J. Hoffmann[2] and Wayne D. Kaplan[1]

[1] Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel.
[2] Karlsruhe Institute of Technology, Institute of Applied Materials, Karlsruhe, Germany.

The kinetics of grain boundary (GB) motion can be determined experimentally by measuring the average grain size in samples annealed at different temperatures for different durations. In $SrTiO_3$ annealed under an oxidizing atmosphere, the GB mobility was previously found to decrease with an increase in temperature (in the temperature range of 1350-1425°C), deviating from the expected Arrhenius behavior [1]. In samples annealed under reducing atmosphere the change in mobility is shifted (in the temperature range of 1350-1490°C and 1460-1500°C), and a second phase wets some of the boundaries at certain temperatures [2]. While this complex behavior of $SrTiO_3$ is unique among ceramics, several other perovskites are known to show some of these grain growth effects as well (e.g. lithium lanthanum titanate and $BaTiO_3$ [3]).

While GB mobility can be measured, the mechanism by which a general GB moves has not yet been determined at the atomistic level in general polycrystalline systems. Following the terrace ledge kink (TLK) model [4], GBs were described as stepped planes which move by step-motion along the boundary plane during grain growth. The concept of steps at GBs includes line defects; such that steps can have both a step and a dislocation character (so called disconnections [5]). The role of disconnections at GBs in GB motion is an extension to the previously described concept of surface steps which play a role in crystal growth [6].

The present work focuses on the atomistic mechanism by which GBs migrate, using high resolution transmission electron microscopy (HRTEM) and $SrTiO_3$ as a model system (due to the existence of multiple grain growth effects). In this work, general GBs in $SrTiO_3$ are studied *ex-situ*, and compared to the surface of $SrTiO_3$ grains which are studied *in-situ* under vacuum. The existence of steps and ledges in both in-situ and ex-situ experiments indicate their role in the GB motion process.

In order to examine the role of disconnections at GBs, general GBs in polycrystalline $SrTiO_3$ and GBs between a single crystal diffusion bonded to polycrystalline $SrTiO_3$ were characterized using aberration corrected HRTEM. Steps were identified and correlated to the grain growth mechanism, following the TLK model and disconnection theory. Electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) were used to characterize the chemistry of these boundaries. In addition, step motion on the surfaces of thin $SrTiO_3$ films were characterized in-situ using HRTEM. When orienting general GBs in $SrTiO_3$ to the “edge-on” condition (in which both the grain boundary and step planes are parallel to the electron beam direction), both the step and dislocation components of the disconnection were visible. In samples annealed under an oxidizing atmosphere the steps were found to be aligned mainly parallel to {001} and {110} type planes, regardless of the annealing temperature, annealing duration, cooling rate and orientations of the grains creating the boundary (see Figure 1) [7].

Motion of the steps parallel to {001} and {110} type planes was recorded during in-situ HRTEM experiments along surfaces of grains in polycrystalline $SrTiO_3$ annealed in vacuum. The steps consistently appeared along {100} and {110} planes regardless of the annealing temperature, indicating their significance in the grain growth mechanism, in agreement to the ex-situ results. In samples annealed under a reducing atmosphere, a similar step behavior appeared, indicating that the mechanism is defined by thermodynamics.

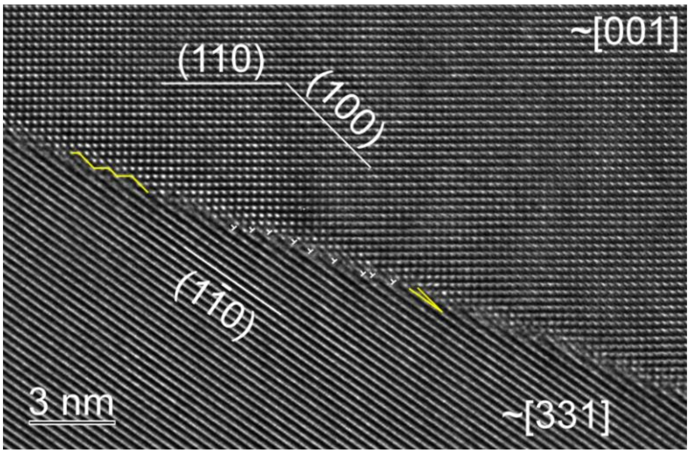

Figure 1: HRTEM micrograph of an edge-on general grain boundary in polycrystalline $SrTiO_3$ annealed at 1350˚C for 10hr oxygen and furnace cooled. Nanometer length-scale steps and dislocations are visible along the boundary. The micrograph was acquired using a Cs of -5.7 μm, and Wiener filtered to remove noise.

References:

1. W. Rheinheimer, M.J. Hoffmann. Non-Arrhenius behavior of grain growth in strontium titanate: New evidence for a structural transition of grain boundaries, Scr. Mater. 101 (2015) 68-71.
2. W. Rheinheimer, M. Bäurer, M.J. Hoffmann. A reversible wetting transition in strontium titanate and its influence on grain growth and the grain boundary mobility, Acta Mater. 101 (2015) 80-89.
3. W. Rheinheimer, M.J. Hoffmann. Grain growth in perovskites: What is the impact of boundary transitions?, Current Opinion in Solid State and Materials Science, 2016, 20, 286–298.
4. H. Gleiter. Mechanism of Grain Boundary Migration, Acta Metallurgica 17 (1969) 565-573.
5. J.P. Hirth, R.C. Pond. Steps, dislocations and disconnections as interface defects relating to structure and phase transformations, Acta Mater. 44 (1996) 4749-4763.
6. W.K. Burton, N. Cabrera, F.C. Frank. The Growth of Crystals and the Equilibrium Structure of their Surfaces, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 243 (1951) 299-358.
7. H. Sternlicht, W. Rheinheimer, M. J. Hoffmann, W. D. Kaplan. The mechanism of grain boundary motion in $SrTiO_3$, J. Mater. Sci. 51 (2016) 467-475.