# Comments

## Comment on "Origin of Giant Dielectric Response in Nonferroelectric $CaCu_3Ti_4O_{12}$: Inhomogeneous Conduction Nature Probed by Atomic Force Microscopy"

Recently, Fu et al.[1] reported local current variations on polycrystalline $CaCu_3Ti_4O_{12}$ (CCTO) samples using current-sensing atomic force microscopy (AFM). Many previous investigations have experimentally demonstrated the electrically inhomogeneous microstructure of CCTO.[2−9] In particular, the presence of electrostatic potential at grain boundaries of polycrystalline CCTO has been directly verified by scanning Kelvin probe microscopy under a lateral bias[3,4] as well as via the microcontact current−voltage measurement.[3,5,7,9] In addition, thermopower measurements have clearly revealed that the charge carrier in the bulk is *n*-type by electrons.[3] As a result, the electron energy band structure across a grain boundary in CCTO has been suggested to be equivalent to "*n-i-n*" with acceptor-like interface traps for electrons within the band gap at the boundary regions.[3] However, a recent report by Fu et al.[1] includes remarks that are contradictory to previous results.[3−9] While ref 1 has shown a possibility of inhomogeneous conductance in the bulk grains, there are seriously misleading interpretations and inaccurate statements that should be pointed out.

**1**. It appears that the authors have misunderstood the geometry of the grain boundaries in polycrystals. The width of the grain boundaries in polycrystalline oxides including a variety of perovskite-type titanates is known to be in a range of a few nanometers.[10] Figure 1 shows a typical grain boundary of a polycrystalline CCTO sample sintered at 1100 °C, directly demonstrating subnanometer-scale geometry in width. In contrast, the high-current regions in the current-sensing AFM images, as shown in Figures 1(a) and 3(b) of ref 1, are more than a few hundred nanometers in width, and furthermore, some are even more than 1 $\mu$m (Figure 1(a) of ref 1). Even if the space charge regions adjacent to a grain boundary are taken into account, such thick grain boundaries of several tens of nanometers in width are, on a physical basis, unreasonable. During the visualization of the conductance variation in contact-mode AFM, the grain boundaries cannot be precisely resolved from the bulk in a micrometer-level image with commercially available diamond-coated cantilever tips, most of which are too blunt (20−100 nm in tip radius) to clearly detect the current change in nanoscale regions. In particular, when the relative conductance of the grain boundaries is lower than that of the interior grains (which is the case in CCTO), obtaining current images that show the variation of conductance between grains and grain boundaries in AFM presents a considerable challenge. Because of this critical limitation, the measurement of surface potential across a grain boundary under a lateral bias has been utilized in ZnO[11,12] as well as CCTO[3,4] instead of direct current sensing to visualize the electrical inhomogeneity. Consequently, it is significantly misleading to claim that the "grain boundaries" were conductive, based solely on AFM images that only show the existence of regions with relatively different conductance.

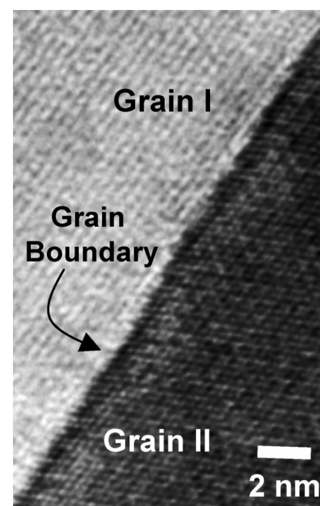


**Figure 1.** High-resolution transmission electron micrograph showing a typical grain boundary in a polycrystalline CCTO sample sintered at 1100 °C.

**2**. It should be noted that Sample B shown in Figures 2 and 3 of ref 1 is not in a thermodynamically equilibrium state. As noted in the paper, the sintered sample has been annealed again at a higher temperature (close to the melting point) for a very short time (several minutes), to prepare Sample B. Such a short heat-treatment at high temperature

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10.1021/cm801275k CCC: $40.75 © 2008 American Chemical Society
Published on Web 09/03/2008

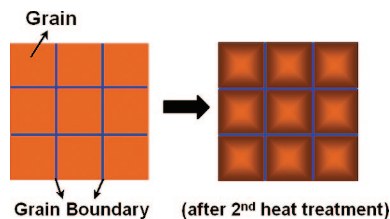


**Figure 2.** Schematic diagrams illustrating the nonequilibrium state with a higher concentration of charge carriers near the surface regions (dark brown) of grains as a result of the second heat treatment.

may remarkably increase the concentration of point defects (including ionic vacancies and free charge carriers) near the surfaces of each grain, resulting in higher conductance in the grain shells, as schematically illustrated in Figure 2. Compared to the considerably narrow current variation (0−0.2 nA) for Figure 1(a) of ref 1, the one-order higher current values up to a few nA observed in Figures 1(d) and 3 of ref 1 strongly support the existence of a nonequilibrium state of the surface shell regions with higher conductance. Therefore, the current-sensing AFM images in Figures 2 and 3 of ref 1 do not justify the nanometer-wide grain boundaries of different conductivity but rather merely show the high-conductance surface regions.

**3**. Based on the current image shown in Figure 1(a) of ref 1 the volume fraction of the insulating regions with low conductance appears to dominate. Even in Figures 3 (c) and 3(d) of ref 1 the fraction of the low-conductance regions is comparable to that of the high-conductance regions. It is very difficult to derive such a low volume fraction (∼0.001) of the insulating regions from the current images. Thus, the AFM observation and the model described by eq 1 are not consistent with each other. Unless the low volume fraction of the insulating regions is verified, the model shown in Figure 4 and eq 1 of ref 1 cannot be used to explain the high dielectric response.

**4**. As already well documented in a number of reports,[13−17] in most gas sensors made of semiconducting oxides, the basic principle for the gas sensing is based on the resistance measurement induced from variation of the electrical property change at grain surfaces and interfaces between grains by absorbed gas molecules. Therefore, in contrast to the statement of the authors in the last paragraph of ref 1, controlling the defect density and electrostatic potential at the grain boundaries and grain surfaces rather than at the interior grains is much more critical. A recent report regarding a sensor application using porous CCTO films,[18] which has been mentioned in ref 1, clearly proves the significance of the change in the potential barrier at grain boundaries or surfaces by the absorption of reducing gases, again supporting a "*n*-*i*-*n*"-type structure in the electronic energy band across a grain boundary in CCTO[3,7] rather than conductive grain boundaries.

Finally, previous reports[3,6,19−23] have already shown that there are various lattice defects including twins and structural domains and resulting misfit dislocations inside CCTO crystals. In addition, recent investigations have also suggested possible disordering between the cations.[24,25] In this respect, it is likely that nanoscale regions with different conductances are present within the CCTO crystals, as shown in Figure 3(c) of ref 1, as might be expected. More accurate measurements of dimensions of the regions as well as investigation of the difference in conductance between the regions in a single grain may be thus proposed for future study.

**Acknowledgment.** This work was financially supported by the Korea Science and Engineering Foundation, Grant no. R01-2006-000-10765-0.

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