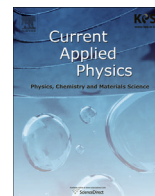




Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Donor–acceptor bifunctionality of dysprosium in perovskite calcium copper titanate polycrystals



Gi-Young Jo ^a, Hee-Suk Chung ^b, Suk-Joong L. Kang ^{a, c, *}, Sung-Yoon Chung ^{d, **}

^a Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 34141, Republic of Korea

^b Jeonju Center, Korea Basic Science Institute, Jeonju, 54907, Republic of Korea

^c Korea Institute of Ceramic Engineering and Technology, Jinju, 52851, Republic of Korea

^d Graduate School of EEWs, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 34141, Republic of Korea

ARTICLE INFO

Article history:

Received 27 March 2017

Received in revised form

2 May 2017

Accepted 19 May 2017

Available online 24 May 2017

Keywords:

I-*V* curve

Impedance complex plane

Scanning transmission electron microscopy (STEM)

CaCu₃Ti₄O₁₂

Rare-earth doping

Schottky barrier

ABSTRACT

Systematic control of electrical properties is a challenging task in polycrystalline materials having significant electrical heterogeneity. In particular, as most aliovalent dopants in oxides usually play a single role of either a donor or an acceptor, controlling the respective electronic conductance of grains and grain boundaries in a separate manner by simple doping is not easily achieved. Using the polycrystalline perovskite Ca_{1/4}Cu_{3/4}TiO₃, the grains of which have relatively high conductance and the grain boundaries reveal much lower conductance, we demonstrate the donor–acceptor bifunctionality of dysprosium (Dy) and its impact on the variation of electrostatic potential barriers at grain boundaries. DC current–voltage measurements and impedance spectroscopy analyses consistently show that Dy selectively affects the grain-boundary conductance without a substantial change of conductance in the grains. Atomic-scale scanning transmission electron microscopy also visualizes the distinct site occupancy of Dy at the Ti columns in the grain-boundary region in contrast to the Dy occupation at the Ca columns in the bulk grains, directly showing that Dy is a donor in the bulk and simultaneously an acceptor in the grain-boundary region. In addition to providing an efficient way of tuning the electrostatic potential barriers, this bifunctional effect of Dy emphasizes the significance of understanding the correlation between the atomic-level site occupancy of dopants and the overall electrical properties.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The perovskite-derivative Ca_{1/4}Cu_{3/4}TiO₃, (equivalently CaCu₃Ti₄O₁₂; CCTO for brevity) has garnered notable attention since 2000 due to its exceptionally high permittivity with a dielectric constant of up to ~100,000 for a single crystal and ~10,000 for a polycrystal at room temperature [1–4]. In addition, it was found that CCTO maintained a high dielectric permittivity without any phase transition over a wide range of temperature from 100 to 400 K in contrast to other ferroelectric perovskites. Numerous theoretical and experimental studies thus have been conducted to reveal the origin of the peculiar dielectric response of CCTO [5–10]. It is now generally accepted that in polycrystalline CCTO that, analogous to

the internal boundary-layer capacitor (IBLC) model, the extrinsic mechanism [4,6,9,10] is responsible for its apparent high permittivity rather than the intrinsic mechanism related to the local dipole moments induced by the Ti displacement, based on the electrically heterogeneous microstructure consisting of semiconducting grains and insulating grain boundaries [4,11].

By using Kelvin probe force microscopy and microcontact current–voltage (*I*–*V*) measurements, a previous study in 2004 first identified the remarkable nonlinearity in *I*–*V* behavior resulting from the electrostatic potential barrier at grain boundaries [11]. Considering the nonlinear *I*–*V* characteristics, a new application employing CCTO ceramics as a surge protector has been suggested. The electrostatic potential barrier at grain boundaries and the band bending in the electron energy band diagram stem from the difference in the Fermi energy level within the electrically inhomogeneous microstructure consisting of the *n*-type semiconducting grains and insulating boundaries [12,13]. Therefore, tuning the band structure between grains and grain boundaries may have a strong influence on the electrical features of polycrystalline CCTO.

* Corresponding author. Korea Institute of Ceramic Engineering and Technology, Jinju, 52851, Republic of Korea.

** Corresponding author.

E-mail addresses: sjkang@kaist.ac.kr (S.-J.L. Kang), sychung@kaist.ac.kr, nalphates@gmail.com (S.-Y. Chung).

In this regard, many previous groups have carried out doping experiments with various aliovalent transition metal and rare-earth metal cations to elucidate the role of dopants and their correlation with dielectric and electrostatic properties [14–22]. While diverse cation dopants have been investigated over the last decade, few in-depth analytical works directly linking the effect of dopants to the electrical property of grain boundaries have been reported.

In this study, by doping a small amount of rare-earth dysprosium (Dy), we demonstrate that the threshold voltage in the nonlinear I – V relationship and the subsequent Schottky barrier at grain boundaries drastically vary with the Dy addition. In particular, the threshold voltage and the grain-boundary resistivity were identified to systematically increase with the Dy addition when the concentration of added Dy exceeded a certain level, whereas they became substantially lower than those of pristine CCTO in cases of doping with very small amounts. We utilized high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) to directly observe the dopant ions incorporated into the CCTO lattice at an atomic scale. This direct visualization successfully demonstrates the unexpected and distinct site occupation of Dy near grain boundaries. A correlation between the atomic site occupied by the dopant and the electrostatic potential barrier at grain boundaries is also suggested on the basis of direct visualization by STEM, impedance spectroscopy, and I – V measurements along with the well-established electron energy band theory.

2. Experimental methods

2.1. Sample preparation

Pristine and doped CCTO powders were first synthesized by the conventional solid state reaction method using CaCO_3 (99.995%, Aldrich), CuO (99.9%, Kojundo Lab.), and TiO_2 (99.8%, Aldrich) as the starting materials. Various amounts of Dy_2O_3 (99.99%, Aldrich) were used as a dopant from 0.02 to 1 at.% to obtain a stoichiometric composition of $\text{Ca}_{1/4-x}\text{Dy}_x\text{Cu}_{3/4}\text{TiO}_3$. Each of the powder mixtures was ball milled in ethyl alcohol for 24 h with zirconia balls and then the dried slurry was calcined at 950 °C for 10 h in air. The pristine and Dy-doped powders were both slightly pressed into discs and then cold isostatically compressed at 200 MPa to prepare dense pellets. These pellets were sintered at 1100 °C for 72 h in air.

2.2. Electrical property measurements

To measure the electrical properties, silver paste was painted on the polished surface of sintered pellets as electrode material. The sintered pellets were used for the current density–electric field (J – E) measurement (4200-SCS, Keithley) and also for the impedance spectroscopy (VSP-300, Biologic) over a frequency range from 0.1 Hz to 5 MHz with an oscillation voltage of 500 mV.

2.3. STEM analysis

The 1 at.% Dy-doped sample for STEM observation was grinded mechanically to a thickness of 60 μm and dimpled to a thickness of less than 5 μm , and finally ion milling thinning was performed. By using scanning transmission electron microscopy (JEM-ARM200F, JEOL) with spherical-aberration correction, Z-contrast STEM images in HAADF mode were obtained to directly observe the site occupation of the dopant in the 1 at.% Dy-doped sample. The size of an electron probe in STEM mode was ~ 1.0 Å with a convergence semiangle of 22 mrad. The collection semiangles of the HAADF detector were adjusted from 67 to 170 mrad in order to use incoherently scattered electrons at large angles for clear Z-sensitive images. The obtained raw images were band-pass filtered by using

Radial Wiener Filter (HREM Research Inc.) to reduce background noise. To statistically estimate the number of Ti columns substituted with dopants, ~ 700 columns near the grain boundaries and inside the bulk, respectively, were investigated to compare relative intensities for brightness.

3. Results and discussion

3.1. DC current-voltage measurement

Fig. 1 shows a set of the J – E measurements of polycrystalline samples including pristine CCTO. As already reported for many other polycrystalline CCTO specimens [11,15–17,20], the samples in this work consistently exhibit nonlinear J – E behavior, which is attributed to the presence of an electrostatic potential barrier at grain boundaries [11]. In particular, very systematic variation of the threshold electric field (E_T), above which the current density abruptly rises, with the addition of Dy is the most notable feature, with a negligible E_T observed for the 0.05-at.% Dy-doped sample and an exceptionally high value of E_T up to ~ 1182 V/cm for the 1-at.% Dy-doped sample. In addition to this controllable E_T by a different amount of Dy, other noteworthy characteristics are identified in Fig. 1. First, the E_T value decreases with increasing Dy doping content as down to 0.05 at.%. As a result, the sample containing 0.05-at.% Dy shows negligible nonlinearity, as observed in its J – E plot in blue color. This J – E behavior appears to be nearly identical with that of donor-doped CCTO samples, as previously reported [15,16]. In contrast, when Dy dopant with concentrations from 0.1 to 1 at. % is added, the E_T considerably increases with a doping concentration, as observed in acceptor-doped CCTO samples [17]. In fact, based on the ionic radius of Dy^{3+} ($r = 1.253$ Å) being similar to that of Ca^{2+} ($r = 1.34$ Å) in the interstitial site coordinated with 12 oxygens in oxides [23], such as the A site in ABO_3 -type perovskites, we anticipated that Dy^{3+} was substituted for Ca^{2+} as a typical donor. However, this set of measurements strongly implies that Dy plays two distinct roles at grain boundaries as a donor at a low concentration and as an acceptor at a relatively high concentration (>0.1 at. %).

3.2. AC impedance spectroscopy

Impedance spectroscopy is a suitable electrical analysis tool to

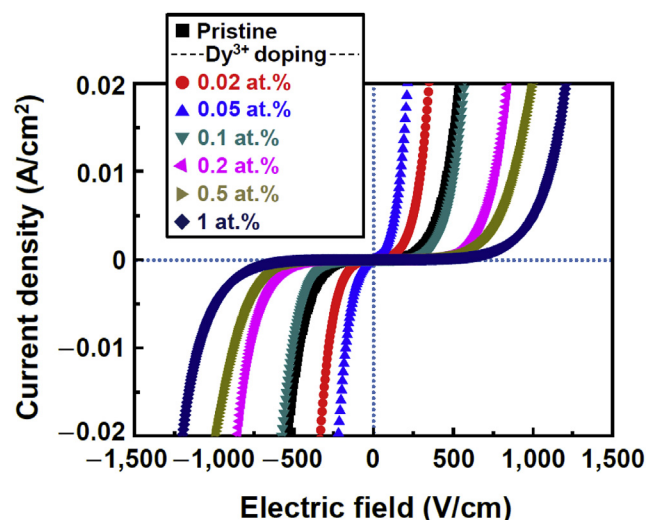


Fig. 1. Current density vs. electric field (J – E) characteristics of pristine and Dy-doped samples. Variable threshold voltage by Dy doping is noted.

Download English Version:

<https://daneshyari.com/en/article/5488744>

Download Persian Version:

<https://daneshyari.com/article/5488744>

[Daneshyari.com](https://daneshyari.com)