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Acceptor segregation and nonlinear current-voltage characteristics in H_2-sintered $SrTiO_3$

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The current-voltage characteristics with acceptor segregation at grain boundaries have been investigated in H_2-sintered $SrTiO_3$. Al-added $SrTiO_3$ was sintered in H_2 and then annealed in air for selective oxidation of grain boundaries. The samples showed nonlinear current-voltage characteristics, and both the breakdown voltage and nonlinearity coefficient increased with Al concentration. An energy dispersive spectroscopy analysis revealed that Al ions were segregated at the grain boundary, suggesting the formation of Schottky barriers at the boundary. The present results thus point toward the possibility of modifying the grain boundary composition in $SrTiO_3$ as well as fabricating effective switching devices by H_2 sintering. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2236212]

Nonlinear electrical properties of electroceramics have been widely utilized for such devices as varistors, thermistors, boundary layer capacitors (BLCs), sensors, and switching devices.[1–4] The origin of the nonlinear properties is well known to be related to the electrically active grain boundaries in polycrystals.[2,3,5–7] A number of investigations using high resolution transmission electron microscopy (HRTEM) and nanometer scale analysis have shown that the nonlinear properties vary considerably with the chemical composition and structure of the grain boundaries—specifically the height of the potential barrier, the density of defects, and the impurities at the grain boundaries.[8–13] One of the key processing parameters that control these grain boundary properties is the doping of impurity elements. It is therefore critical to control the impurity doping for preparation of nonlinear devices with optimal properties.

Many investigations have been made on the segregation of dopants and related electrical properties in ABO_3-type perovskite titanates.[9–17] When utilized as a multifunctional component of varistors and BLCs, $SrTiO_3$ is sintered in a reducing atmosphere and heat treated in air.[1] Nevertheless, little research has been reported on the specific technical process in polycrystalline $SrTiO_3$. To optimize the utilization of this material, it is necessary to understand the correlation between the dopant segregation and electrical properties. The present investigation systematically studies the control of nonlinear electrical properties with acceptor addition in H_2-sintered $SrTiO_3$ using energy dispersive spectroscopy with a nanometer size probe.

$SrTiO_3$ samples were prepared by the conventional powder processing technique from commercial $SrTiO_3$ (Ferro Corp., Penn Yan, USA), Nb_2O_5 (Hermann C. Starck, Berlin, Germany) and Al_2O_3 (Sumitomo Chem., Tokyo, Japan) powders. Niobium (0.4 mol %), a donor dopant, and aluminum (0, 0.2, 0.5, 1, and 1.5 mol %), an acceptor dopant, were added to $SrTiO_3$ powder, and the powder mixtures were ball milled in ethyl alcohol for 24 h with a polyethylene bottle and zirconia balls. The addition of Nb is simply to make the grains conductive after sintering in H_2.[2] The mixed powders were lightly pressed into ~1 mm thick disks of 9 mm in diameter and then isostatically pressed at 200 MPa. The powder compacts were sintered at 1350 °C for 12 h in a hydrogen atmosphere and quenched to room temperature. After being sintered in H_2, the samples were annealed at 1100 °C for 1 h in air to selectively oxidize the grain boundary regions and thus form an electrical potential barrier at these regions. For *I-V* measurements, gold was sputtered on both sides of the dense pellets as electrodes.

For TEM observation and chemical composition analysis in the grain boundary regions, the sintered samples were ultrasonically cut into 3 mm disks, mechanically ground to a thickness of 100 μm, dimpled to a thickness of less than 10 μm, and finally ion milled until perforation for electron transparency. HRTEM observations were performed using a field-emission-type TEM (TECNAI, model F30, Philips, Eindhoven, Netherlands) operated at 300 kV. Chemical analyses of the grain boundary regions were carried out with an energy dispersive spectrometer (EDS) attached to the TEM with a probe size of less than 1 nm.

After sintering at 1350 °C in H_2, all of the samples consisted of grains of similar sizes, ~2 μm on average. The preparation of such a fine and uniform microstructure without large abnormal grains was possible only in a very low oxygen partial pressure, H_2. The benefit of the fine microstructure is, of course, the maximization of grain boundary properties. The small grain size, however, remained unchanged during subsequent air annealing at 1100 °C.

Figure 1(a) shows current-density against electric-field (*J-E*) curves of Al-doped $SrTiO_3$ samples. This figure reveals that all samples have a nonlinear current-voltage characteristic, which indicates the presence of active states trapped at the grain boundaries. When Al concentration increases from undoped to 1 mol %, the breakdown voltage and nonlinearity coefficient increase, respectively, from 18.2 to 41.5 V/cm^2 and from 4.5 to 21.2 [Fig. 1(b)]. In the case of 1.5 mol %, however, these properties are slightly reduced. According to previous investigations, nonlinear electrical properties, including breakdown voltage and nonlinearity coefficient, can be affected by grain size (number of grain boundaries), the electrical conductivity of the grain interior, and the height of

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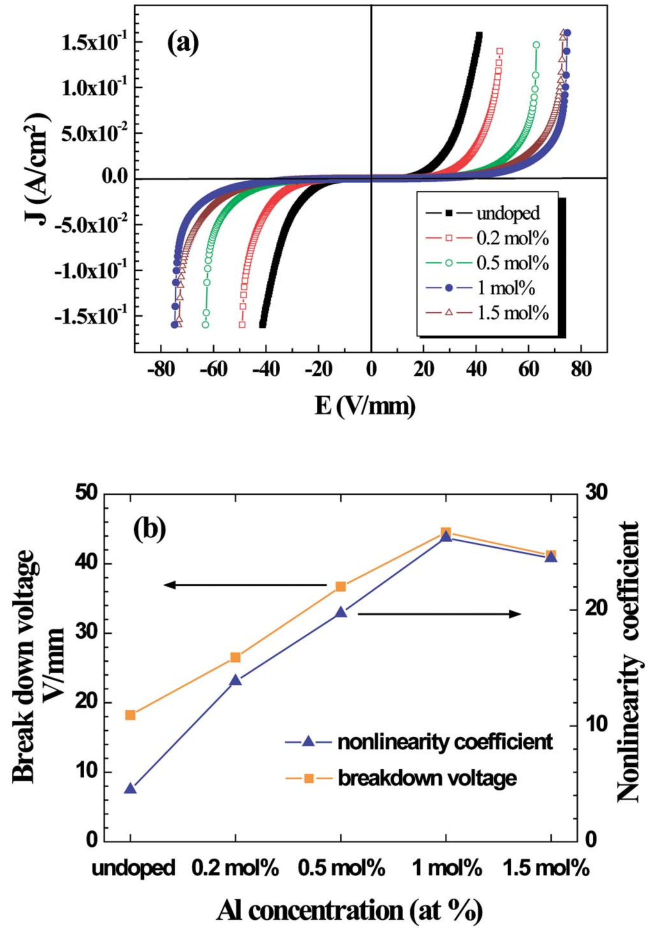

FIG. 1. (Color online) (a) Current-voltage characteristics of 0.4 mol % Nb-excess $SrTiO_3$ samples doped with Al. (b) Variation of breakdown voltage and nonlinearity coefficient with Al concentration. (The samples were sintered at 1350 °C for 12 h in H_2 and annealed at 1100 °C for 1 h in air. Breakdown voltage and nonlinearity coefficient were measured at 5 and 100–150 mA/cm^2, respectively.)

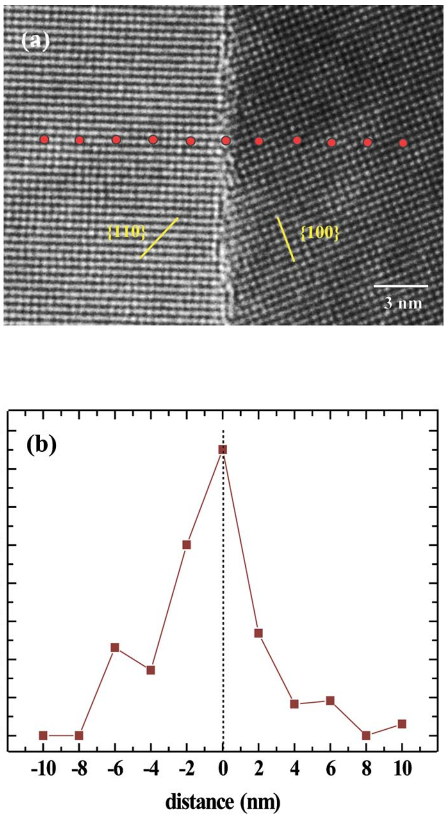

FIG. 2. (Color online) (a) HRTEM image of 0.4 mol % Nb-excess $SrTiO_3$ doped with 1 mol % Al sample sintered at 1350 °C for 12 h in H_2. (b) EDS analysis across the boundary in (a). The dots in (a) represent the spots of analysis.

the electrical potential barrier at grain boundaries.[2,8,18] In the present case, the grain size is constant for different samples. The conductivity of reduced grains must also be similar because the solubility of the acceptor dopant in $SrTiO_3$ is negligible in a reducing atmosphere.[19] Concerning the effect of the oxidation and reduction on the electrical potential barrier, the barrier height is known to be influenced by the oxygen vacancy concentration and chemisorption of O^- and O^{2-} at the grain boundary.[14] In our case, however, this effect should not be dominant, because the nonlinear properties of the undoped sample are much lower than those of the Al-doped samples. Consequently, it can be postulated that the electrical potential barrier formed at the grain boundaries increases as the Al concentration increases up to 1 mol %.

Chemical analyses of the grain boundary were performed with an EDS attached to TEM in order to confirm the formation of an electrical potential barrier formed at the grain boundaries. Figure 2(a) shows a typical HRTEM image of a 1 mol % Al-doped $SrTiO_3$ sample sintered in H_2. At most of the grain boundaries, no second phase was observed, as shown in Fig. 2(a). Figure 2(b) displays the result of an EDS analysis across the boundary shown in Fig. 2(a) with an interval of ~2 nm. It is seen from the figure that a considerable amount of Al ions is segregated $[Al/(Al+Ti)\approx 0.04]$ at the grain boundary core, whereas Al ions are rarely detected $[Al/(Al+Ti)\approx 0.00]$ in the region ~10 nm away from the boundary core. It is thus evident that, in H_2, the solubility of Al acceptor in Nb-containing $SrTiO_3$ is negligible and Al ions segregate at grain boundaries, similar to the case of pure $SrTiO_3$ or $BaTiO_3$.[17,19] On the other hand, Nb donors up to 2.4 at. % are known to be soluble in $SrTiO_3$ irrespective of oxygen partial pressure.[17] It appears therefore that the distribution of Nb donors in $SrTiO_3$ grains induces high electrical conductivity in the grain interior. In addition, the segregation of Al acceptors at the grain boundary cores results in the formation of electrical potential barriers at the boundary, causing nonlinear electrical properties.

Figures 3(a) and 3(b) show TEM images with 0.5 and 1 mol % Al-doped samples, respectively, sintered at 1350 °C for 12 h in H_2. No second phase is observed in the sample with 0.5 mol % Al doping, but a second phase with a plate shape is found in the sample with 1 mol % Al doping. The second phase is rich in Al and its crystal structure differs from that of the grains, as revealed in the HRTEM image and diffraction patterns shown in Fig. 3(c). A chemical composition analysis revealed that the second phase was $Sr_3Al_{32}O_{51}$. The presence of a small amount (~1 vol %) of the second phase with a plate shape suggests that the Al concentration at the grain boundaries is saturated at around 1 mol % Al doping. The segregation of solutes at grain boundaries is generally intensified towards the saturation with a gradual increase of solute concentration in the bulk.[20] In addition, in a recent segregation study,[21] when solutes were added above a critical bulk concentration, precipitates were detected at triple or multiple junctions. Since a second phase appears in the 1 mol % Al-doped sample, the saturation of grain boundary

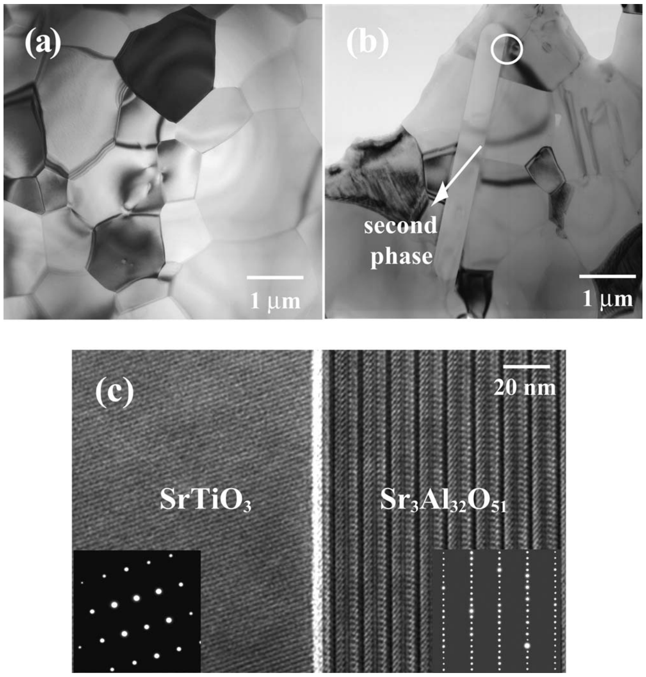

FIG. 3. TEM micrographs of 0.4 mol % Nb-excess $SrTiO_3$ doped with (a) 0.5 and (b) 1 mol % Al sample sintered at 1350 °C for 12 h in H_2. (c) High resolution images of $SrTiO_3$ and a second phase with plate shape near the interface shown in (b) (circle).

segregation occurs at ~1 mol % Al doping. This result suggests that the Al concentration and the height of the Schottky barrier at the grain boundaries increase gradually from undoping to 1 mol % Al doping. As a result, both the breakdown voltage and the nonlinearity coefficient must increase, as observed in Fig. 1. Above 1 mol % doping, the volume increase of the second phase appears to deteriorate the boundary properties, as shown in Fig. 1(b), with the formation of the boundaries between $SrTiO_3$ and the second phase.

In summary, we reported a new approach to control the nonlinear current-voltage characteristics in H_2-sintered $SrTiO_3$. As the Al concentration increased up to 1 mol %, both the breakdown voltage and nonlinearity coefficient increased. These increases are attributed to increased acceptor segregation and increased potential barrier at the boundary. The formation of a second phase at grain boundaries caused a slight deterioration of the nonlinear properties. The present results suggest the possibility of the development of acceptor-doped $SrTiO_3$-based switching devices with high nonlinear properties via H_2 sintering and selective oxidation of grain boundaries.

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