Non-linear current–voltage characteristics related to native defects in SrTiO$_3$ and ZnO bicrystals

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Abstract

SrTiO$_3$ and ZnO bicrystals with various types of boundaries were fabricated in order to examine their current–voltage characteristics across single grain boundaries. Their grain boundary structures were also investigated by high-resolution transmission electron microscopy. In Nb-doped SrTiO$_3$, electron transport behaviors depend on the type of boundaries. Random type boundaries exhibit highly non-linear current–voltage characteristics, while low angle boundaries show a slight non-linearity. On the contrary, undoped ZnO does not exhibit non-linear current–voltage characteristics in any type of boundaries including random ones. It is suggested that the differences observed in current–voltage properties between the two systems are mainly due to the difference in the accumulation behavior of acceptor-like native defects at grain boundaries. A clear non-linearity is obtained by means of Co-doping even for the highly coherent $\Sigma 1$ boundary in a ZnO bicrystal. This is considered to result from the production of acceptor-like native defects by Co-doping.

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1. Introduction

Semiconducting SrTiO$_3$ and ZnO polycrystals are widely used as varistors [1–5]. Varistors are electric devices to protect electronic circuits, power lines and so on from surges or noises using an abrupt decrease of the resistivity at a critical voltage. The resistivity change is given by unique electrical properties of double Schottky barriers (DSB) formed at grain boundaries [6]. The current–voltage ($I$–$V$) characteristic across DSB exhibits non-linearity. In the lower voltage region, current is proportional to applied voltage (Ohmic relation). However, the current remarkably increases over a critical voltage, which means abrupt decrease of resistivity. This is due to a band bending of DSB caused by the applied voltage. From a viewpoint of practical use, it is very important to increase a rate of the resistivity change as much as possible, i.e. a discrete change is favorable. So far, many investigations have been performed for this purpose, and now the devices with $\alpha > 50$, where $\alpha$ is a non-linearity coefficient defined as $\delta \log I/\delta \log V$, have been developed in commercial products.

Generally, $n$-type DSB is generated when majority carriers (i.e. electrons) are trapped at interface states that are formed at grain boundaries. In order to know the formation mechanism of DSB, it is necessary to clarify the nature of the interface states. As known in a field of semiconducting devices such as Si, the formation of interface states is closely related to grain boundary structure [7]. In the case of Si, atomic disarrangement such as dangling bonds often gives interface states. Dangling bonds tend to give extra energy levels in the band gap, and they trap electrons effective to form DSB [8]. On the contrary, it has been reported that the charged point defects play an important role in SrTiO$_3$ and ZnO [9–12]. In the case of ionic materials such as SrTiO$_3$ and ZnO, when charged point defects segregate, they possibly give some effects to electrical properties. To clarify and confirm these points more precisely, systematic investigations of electrical properties are necessary.
properties in combination with the grain boundary structure and the behavior of point defects should be needed.

The objective of the present study is to investigate electrical properties across single grain boundaries in SrTiO$_3$ and ZnO. In order to control grain boundary misorientation and dopant systematically, SrTiO$_3$ and ZnO bicrystals were prepared, including highly coherent and incoherent random boundaries. Their atomic structures were investigated by high-resolution transmission electron microscopy (HRTEM), and $I$–$V$ characteristics across the boundaries were measured. In addition, the dependence of the $I$–$V$ characteristics on the cooling rate was also measured to examine the effect of native defects.

2. Experimental procedure

Commercial 0.2 at% Nb-doped SrTiO$_3$ and undoped ZnO single crystals (Earth Chemical Co. Ltd.) were used for the preparation of bicrystals. The sizes of the respective single crystals are $10 \times 10 \times 5 \text{ mm}^3$ in SrTiO$_3$, and $5 \times 5 \times 0.5 \text{ mm}^3$ in ZnO. Here, Nb dopants are necessary to increase the donor concentrations in SrTiO$_3$. Bicrystals were prepared by hot-joining technique. The contact planes were ground and polished with diamond slurry finally using $0.25 \mu\text{m}$, and further mechano-chemically finished with silica sol. After then, two single crystals were joined by hot-pressing method at 1400 $^\circ\text{C}$ for SrTiO$_3$ and 1100 $^\circ\text{C}$ for ZnO in air. Detailed sample preparation methods are described elsewhere [13]. Boundaries prepared in the present study are summarized in Table 1. It includes highly coherent and random boundaries from a viewpoint of coincident site lattice (CSL) theory [14]. A part of the boundaries was prepared with a cooling rate of $200 \text{ C/h}$ in SrTiO$_3$ bicrystal as shown in Table 1. As for Co doped ZnO bicrystals, Co metals were deposited onto one of the contact planes at room temperature by thermal evaporation before the hot-pressing.

After joining, thin plates with dimensions of $10 \times 10 \times 1 \text{ mm}^3$ for SrTiO$_3$ and $1 \times 3 \times 1 \text{ mm}^3$ for ZnO were machined from respective as-joint bicrystals, and used for measurement of $I$–$V$ characteristics and the observations of grain boundary structures as schematically shown in Fig. 1.

$I$–$V$ characteristics of the bicrystals were investigated by a four-probe method at room temperature in air by a current source (Model 220, Keithley Instruments, Inc.) and a voltage meter (Model 2010, Keithley Instruments, Inc.). Ag-based paste was used as electrodes, which was confirmed to provide Ohmic contact.

Grain boundary structures were investigated by HRTEM (JEM-4010 JEOL Co., Ltd, H-9000NAR Hitachi Co., Ltd, EM-002BF, Topcon Co., Ltd operated at 400, 300, and 200 kV, respectively). Specimens for HRTEM observation were prepared by a conventional ion-milling technique using Ar ion beam (Duomill, model 600 Gatan Co., Ltd).

3. Results

3.1. SrTiO$_3$ bicrystals

Fig. 2 shows $I$–$V$ characteristics of random type boundaries in Nb-doped SrTiO$_3$ bicrystals. In the figure, the characteristic taken from the $\Sigma 1$ boundary is also shown for comparison. The $\Sigma 1$ boundary, whose tilt angle is $0.43^\circ$, clearly exhibits Ohmic relation over the whole voltage range, i.e. $\alpha = 1$. The behavior of the $\Sigma 1$ boundary is confirmed to be similar to that of a single crystal. Compared with $I$–$V$ relation of the $\Sigma 1$ boundary, $I$–$V$ behaviors in both random type boundaries show clear non-linear characteristics, which indicates that the formation of DSB along the boundaries. A height of DSB is slightly larger in a symmetric random boundary because the current is smaller in Ohmic region below an applied voltage of 0.1 V as in Fig. 2. On the other hand, these two boundaries do not exhibit sub-Ohmic region of $\alpha < 1$, which is often observed in $I$–$V$ characteristics across simple DSB.
Fig. 2 shows $I$–$V$ characteristics in low angle boundaries, which were prepared with different cooling rates after joining. A slight non-linear characteristic appears in a slowly cooled boundary as in (b), while the relation similar to Ohmic behavior is obtained in a rapidly cooled boundary as in (a). Non-linear properties become observed by a decrease in cooling rate after joining.

Fig. 3 shows $I$–$V$ characteristics in low angle boundaries in 0.2 at% Nb-doped SrTiO$_3$ bicrystals. A slight non-linear characteristic appears in a slowly cooled boundary as in (b), while the relation similar to Ohmic behavior is obtained in a rapidly cooled boundary as in (a). Non-linear properties become observed by a decrease in cooling rate after joining.

Fig. 4 shows HRTEM images in random type boundaries as presented in Fig. 2. The insets are selected area diffraction patterns including both adjacent crystals in respective boundaries. The crystals in the respective boundaries are oriented to the [001] electron beam direction. From the diffraction patterns, the tilt angles in the respective boundaries are confirmed to be [001] 22.3$^\circ$ asymmetric tilt type in (a) and [001] 45$^\circ$ symmetric tilt type in (b). It can be seen that both the crystals were perfectly joined without any secondary phases even at an atomic scale, although faceted structures are formed along the respective boundaries. The traces of the habit planes tend to be parallel to low index planes as shown in the images. In general, random type boundaries tend to have higher boundary energy compared with CSL boundaries [15]. The faceted boundary is, therefore, considered to be formed due to the boundary migration to reduce the boundary energy during annealing.

Fig. 5(a) shows HRTEM images of a low angle boundary. The boundary is also free from any secondary type in (a) and [001] 45$^\circ$ symmetric tilt type in (b). It can be seen that both the crystals were perfectly joined without any secondary phases even at an atomic scale, although faceted structures are formed along the respective boundaries. The traces of the habit planes tend to be parallel to low index planes as shown in the images. In general, random type boundaries tend to have higher boundary energy compared with CSL boundaries [15]. The faceted boundary is, therefore, considered to be formed due to the boundary migration to reduce the boundary energy during annealing.

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phases, and the two single crystals contact each other at an atomic scale. The contrasts appear periodically along the boundary as indicated by the arrows in the figure. These contrasts are due to the presence of grain boundary dislocations. Fig. 5(b) shows a magnified HRTEM image around two grain boundary dislocations. In the image, Burgers circuits are schematically shown around each dislocation core. In the circuit, clear discontinuity can be seen, which is a projection of a Burgers vector onto (001) plane. Furthermore, one extra plane can be seen at the dislocation core as indicated with a white line in the image. This means that the Burgers vector is dissociated as follows

$$a[001] \rightarrow 1/2a[001] + 1/2a[001],$$

where $a$ is a lattice constant of SrTiO$_3$. This type of the core structure is firstly observed by Zhang et al. in the SrTiO$_3$ low angle boundary with a tilt angle of 5.4° [16]. The boundary shown in Fig. 5 can be considered to have a similar structure, although it has a smaller tilt angle.

3.2. ZnO bicrystals

Fig. 6 shows $I$–$V$ characteristics of undoped ZnO bicrystals. For comparison, those along the [0001] and the [1120] of ZnO single crystals are also shown. The left and the center graphs show the $I$–$V$ characteristics across [0001] twist boundaries, and the right one shows that across [1120] twist boundary. These results indicate that the boundaries are well joined and higher resistive layer such as DSB are not formed.

Fig. 7 shows a typical example of HRTEM image of undoped [0001] 19° twist boundary in ZnO bicrystal. In the image, the [1120] of the lower crystal is parallel to the incident electron beam direction, while that of the upper crystal is inclined by 19° with respect to that of the lower crystal and incident electron beam direction. The boundary is perfectly joined even at an atomic scale by the hot-pressing condition used in the present study. No intergranular phase such as an amorphous phase was observed at the boundary. Similar joining conditions could be obtained also in other ZnO bicrystals.

4. Discussion

Non-linear I-V characteristics observed in SrTiO$_3$ and ZnO are often discussed in terms of DSB formed at their grain boundaries [6]. The barriers are considered to be generated by electrons trapped at interface states formed at grain boundaries. In general, simple DSB exhibits three regions in $I$–$V$ characteristics, i.e. Ohmic($\alpha = 1$), sub-Ohmic($\alpha < 1$) and exponential regions($\alpha > 1$) with an increase in the voltage [5,18]. This can be considered to
depend on the density and the energy position of acceptor-like interface states in the band gap.

So far, two candidates have been considered as the origin of such acceptor-like states, i.e. atomic disarrangements such as dangling bonds, and accumulation of negatively charged-up point defects. In the case of SrTiO$_3$, the point defects mechanism is presumably accepted [9], and it has been reported that the effect of atomic disarrangement can be negligible [19].

This is also confirmed in the present study using low angle boundaries. The low angle boundary comprises an array of grain boundary dislocations as shown in HRTEM image of Fig. 5. The dislocation structure such as their interval and Burgers vector is determined by a tilt angle. In other words, the boundary atomic structure does not change without any change of a tilt angle. As shown in the $I$–$V$ characteristics, the non-linearity is confirmed to change with cooling rates. This result strongly suggests that the change of non-linearity is not due to a change of grain boundary structure because a variation of cooling rate does not change a tilt angle, i.e. dislocation structure, and therefore gives a piece of evidence that the formation mechanism of DSB is due to the accumulation of negatively charged point defects. This will be described in the following discussion.

The defect species in Nb-doped SrTiO$_3$ mainly consist of $V_{Sr}$ and Nb$_{Ti}$ [20] besides smaller amount of Schottky type defects such as \( \text{NULL} \rightarrow V^+_{Sr} + V^0_{Ti} + 3V^0_O \). These types of defects are counterbalanced each other at the equilibrium state, and tend to generate or vanish at distorted area, such as surfaces, grain boundaries, and dislocations.

In the present study, $V_{Sr}$, $V_O$, and $V_{Ti}$ are generated at grain boundary during annealing, and flow into grain interiors until their concentrations reach equilibrium condition. After that, during cooling from annealing temperature, these defects concentrations start decreasing so as to achieve the equilibrium condition at lower temperature.

In the case of rapidly cooled boundary, the concentration of vacancies cannot decrease and remains at the equilibrium of annealing temperature, because diffusivities of all ion species are not large enough to achieve the equilibrium condition in all over the specimen at lower temperature. On the contrary, in the case of slowly cooled boundary, oxygen vacancies preferentially decrease in concentration near the grain boundary because of larger diffusivity of oxygen ion than the other ions. As a result, negatively charged ($V^0_{Sr}$ and/or $V^0_{Ti}$ relatively accumulated) zone as shown in Fig. 8 is formed along the grain boundary. This accumulated zone operates as a trapping area of electrons and DSB are formed.

As for random type boundaries, such accumulating effects should become more remarkable because of their low coherencies, which is also confirmed by large $\alpha$. Namely, wider trapping areas are formed along the boundary. These areas give $I$–$V$ curves like space charge limited current property as reported by Hayashi et al. [21].

On the other hand, all the boundaries, which include random type boundaries with large disordered atomic arrangements, showed Ohmic relations in ZnO as shown in Fig. 6 [22]. This means that no effective acceptor states are formed in any type of boundaries in undoped ZnO. This is also supported by the other experiment [23] and theoretical calculations using first-principles methods [24, 25]. On the other hand, the dominant point defect species in ZnO are considered to be oxygen vacancy ($V_O$) [26] or zinc interstitial (Zn$_i$) [27]. Even if oxygen vacancies preferentially decrease like in SrTiO$_3$, it is all $V_O$ or $Zn_i$ slightly decrease near the grain boundary. Therefore, negatively charged zone and DSB are not formed, because these defects have positive/neutral charges. This should be the important point why DSB are not formed in undoped ZnO bicrystals.

In order to generate the non-linear $I$–$V$ characteristics in ZnO, it will be necessary to produce acceptor-type point defect such as O$_i$ and $V_{Zn}$. Doping other elements can be considered as one of the effective methods to stabilize these defects. For ZnO based varistor materials, Co dopant is known as one of the key additives to obtain/improve non-linear $I$–$V$ characteristics in ZnO varistor [1,2]. Although Co dopant itself cannot be an acceptor [24,28,29], it has been proposed that Co dopant generate DSB by the stabilization of O$_{Zn}^i$ [30,31] or $V_{Zn}^0$ [29] in ZnO.

Finally, $I$–$V$ characteristic for Co-doped $\Sigma 1$ boundary in ZnO bicrystal is shown in Fig. 9 [32]. This boundary has Co dopant without any atomic disarrangement because the boundary is set at the $\Sigma 1$ misorientation. As clearly shown in the figure, non-linear property appears by Co-doping. This indicates that Co dopant can stabilize acceptor-like defects in ZnO.
5. Conclusion

SrTiO$_3$ and ZnO bicrystals with various types of boundaries were fabricated by hot-joining technique. $I$–$V$ characteristics across their boundaries and their grain boundary structures were investigated.

In Nb-doped SrTiO$_3$, electron transport behaviors depended on a type of boundaries. Random type boundaries exhibited clear and large non-linear current–voltage characteristics, while low angle boundaries showed a slight non-linearity. It was found that such dependencies of the non-linearity observed in $I$–$V$ characteristics are due to a change of accumulating behavior of negatively charged point defects.

On the contrary, undoped ZnO did not exhibit non-linear $I$–$V$ characteristics in any type of boundaries including random ones. These differences between SrTiO$_3$ and ZnO are considered to be due to the difference in the accumulation behavior of acceptor-like native defects at the grain boundaries. In the case of Co-doped ZnO bicrystal, non-linear $I$–$V$ characteristics were obtained. It is concluded that Co-doping can stabilize acceptor-like defects such as O$_i$ or V$_{Zn}$ in ZnO.

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