Oxide Ceramics with High Density Dislocations and Their Properties

Yuichi Ikuhara\textsuperscript{1,2,3,*}

\textsuperscript{1}Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan
\textsuperscript{2}Nanostructures Research Laboratory, Japan Fine Ceramic Center, Nagoya 456-8575, Japan
\textsuperscript{3}WPI, Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Dislocations are of scientific and technological interest due to their unusual physical properties, which are quite different from those in the bulk. It is, therefore, expected to use dislocations as nanowires which provide functional properties in a crystal. In this study, high densities of dislocations were introduced in oxide single crystals by high-temperature plastic deformation. Insulating sapphire and YSZ single crystal were used as model systems. The electron and ion conductivities were measured for the dislocation introduced crystals respectively. It was found that the dislocations with Ti segregation in sapphire crystal showed excellent electrical conductivity and dislocations themselves in YSZ crystal improved the ionic conductivity. This technique has a potential to be applied for any crystals because of its simplicity, and will be expected to give special and unprecedented properties to common materials. [doi:10.2320/materttrans.MF200928]

(Received March 12, 2009; Accepted April 10, 2009; Published June 3, 2009)

Keywords: dislocation, nanowire, oxide, ceramics, plastic deformation, transmission electron microscopy

1. Introduction

Dislocation is a line defect, with which the atomic bond on the lattice plane is cut, and there is a bonding defect line in its core region; thus, a large elastic strain field is formed around it and the dislocation itself has a different electronic state from the one in the crystal, having potential to express peculiar physical properties. Shockley has pointed out that a bonding defect line aligned with the edge dislocation bring about 1-dimensional electron conduction for diamond. After that, the electrical conduction characteristics of the samples, to which dislocation was introduced by plastic deformation at various conditions, were reported for various semiconductors such as CdS, Si, Ge, and SmS.

In this review paper, the method to form high density of nanowires by introducing high density of aligned dislocations will be described. Oxide crystals were used in the present experiments, and the electric conductivity and ionic conductivity were measured. As model systems, we selected insulating sapphire and Y\textsubscript{2}O\textsubscript{3} Stabilized Zirconia (YSZ) single crystal, expected as an ion conductor, respectively to introduce dislocations by high temperature plastic deformation.

2. High Temperature Plastic Deformation

High temperature compression test is one of the effective methods to introduce dislocation into the crystalline solid. In this study, since we intend to arrange linear dislocation with high density, experiments using single crystals are performed to activate the primary slip. In this case, consideration regarding the slip system is required; for example, it is recommended to select the compression direction, which make the Schmidt factor of the target primary slip system the maximum. Figure 1 shows a schematic view of the dislocation introduction method by the compression test. On the other hand, in case that the application as a device is considered, although the introduction of high density of dislocations is effective for the device, attention should be taken because if the strain amount is too much, it makes the secondary slip system active, making the dislocations are clasped intricately. Accordingly, for the crystals with high symmetry like cubic structure, even if the Schmidt factor of the primary slip system is the maximum, some ideas like the shift of the compression axis slightly to make the particular primary slip system active is required since many equivalent slip systems are present in the cubic system. Furthermore, the density and the substructure of the dislocations introduced by the mechanical test strongly depend on the deformation conditions such as temperature and a strain rate as well. For example, to obtain a high density of dislocation, deformation at low temperature and with the high strain rate is required. However, in case that the target crystals are ionic or covalent bonded, the crystals are easily fractured under such conditions. It is therefore needed to find the optimum deformation conditions, under which fracture does not occur, by systematic deformation tests. As described above, in order to obtain the 1-dimensionally arranged, high density dislocations, the optimum control of the high temperature deformation conditions, the compression direction, and the strain amount is required.

\*Corresponding author, E-mail: ikuhara@sigma.t.u-tokyo.ac.jp

\*Received March 12, 2009; Accepted April 10, 2009; Published June 3, 2009

Keywords: dislocation, nanowire, oxide, ceramics, plastic deformation, transmission electron microscopy

1. Introduction

Dislocation is a line defect, with which the atomic bond on the lattice plane is cut, and there is a bonding defect line in its core region; thus, a large elastic strain field is formed around it and the dislocation itself has a different electronic state from the one in the crystal, having potential to express peculiar physical properties. Shockley has pointed out that a bonding defect line aligned with the edge dislocation bring about 1-dimensional electron conduction for diamond. After that, the electrical conduction characteristics of the samples, to which dislocation was introduced by plastic deformation at various conditions, were reported for various semiconductors such as CdS, Si, Ge, and SmS.

In this review paper, the method to form high density of nanowires by introducing high density of aligned dislocations will be described. Oxide crystals were used in the present experiments, and the electric conductivity and ionic conductivity were measured. As model systems, we selected insulating sapphire and Y\textsubscript{2}O\textsubscript{3} Stabilized Zirconia (YSZ) single crystal, expected as an ion conductor, respectively to introduce dislocations by high temperature plastic deformation.

2. High Temperature Plastic Deformation

High temperature compression test is one of the effective methods to introduce dislocation into the crystalline solid. In this study, since we intend to arrange linear dislocation with high density, experiments using single crystals are performed to activate the primary slip. In this case, consideration regarding the slip system is required; for example, it is recommended to select the compression direction, which make the Schmidt factor of the target primary slip system the maximum. Figure 1 shows a schematic view of the dislocation introduction method by the compression test. On the other hand, in case that the application as a device is considered, although the introduction of high density of dislocations is effective for the device, attention should be taken because if the strain amount is too much, it makes the secondary slip system active, making the dislocations are clasped intricately. Accordingly, for the crystals with high symmetry like cubic structure, even if the Schmidt factor of the primary slip system is the maximum, some ideas like the shift of the compression axis slightly to make the particular primary slip system active is required since many equivalent slip systems are present in the cubic system. Furthermore, the density and the substructure of the dislocations introduced by the mechanical test strongly depend on the deformation conditions such as temperature and a strain rate as well. For example, to obtain a high density of dislocation, deformation at low temperature and with the high strain rate is required. However, in case that the target crystals are ionic or covalent bonded, the crystals are easily fractured under such conditions. It is therefore needed to find the optimum deformation conditions, under which fracture does not occur, by systematic deformation tests. As described above, in order to obtain the 1-dimensionally arranged, high density dislocations, the optimum control of the high temperature deformation conditions, the compression direction, and the strain amount is required.

\*Corresponding author, E-mail: ikuhara@sigma.t.u-tokyo.ac.jp
3. Dislocation Control in Sapphire and Fabrication of Conductible Nanowire

3.1 High temperature compression method

Here, the method to introduce high density dislocations into sapphire is described. As the primary slip systems of sapphire, the basal slip ((0001), \( b = 1/3(1120) \)) and the prismatic plane slip ((1120), \( b = (1100) \)) are known, but the basal slip system is dominantly activated at high temperature above 700°C. In order to form the dislocations by introducing only the basal slip, deformation was performed along the compression axis with the 45° tilted direction to both the basal plane and the slip direction so that the Schmidt factor is 0.5. This is the condition where other slip systems do not occur easily from the fact that sapphire has a rhombohedral structure.

To introduce dislocations into the crystal with high density, in general, deformation at low temperature with the high strain rate is recommended. However, in case of the compression deformation to the above described direction, for example, with 10% deformation under the conditions of the temperature of 1200°C and the strain rate of \( 1.0 \times 10^{-5} \text{s}^{-1} \), many R (rhombohedral) twins are formed to partially fracture the sample. However, if it is deformed at 1400°C with the strain rate of the same \( 1.0 \times 10^{-5} \text{s}^{-1} \), although only the basal slip is activated and it shows the uniform plastic deformation even with 10% deformation, the dislocation density of this case will be about \( 10^{8} / \text{cm}^2 \). In case that after deformation at 1400°C to introduce many mobile dislocations into the crystal, if it is deformed again at 1200°C, it plastically deforms uniformly without the formation of twin crystals even with the 10% deformation. In this case, the dislocation density increases about more than 10 times compared with that of the deformation only at 1400°C. By the high temperature deformation with 2 steps like this, it becomes possible to introduce about \( 10^9 / \text{cm}^2 \) to \( 10^{10} / \text{cm}^2 \) of the dislocation density into sapphire. Figure 2(a) shows the TEM bright field image of the dislocation, which was introduced in this way, viewed from the [0001] direction (the direction perpendicular to the slip plane). It is recognized in the figure that although the introduced dislocations are about aligned to the constant direction (parallel to the [1100] axis), it still shows rather wavy shape. As a result of the \( g \cdot b \) analyses, it is confirmed that almost all of these dislocations are provided with the Burgers vector of \( b = 1/3[1120] \). However, to form 1-dimensional nanowires, these dislocations are required to be arranged linearly.

In this study, heat treatment, with which the surface effect is utilized, was performed to linearize the wavy dislocations in the crystal. At first, the sample, to which high density dislocations were introduced by the 2 step compression test, was sliced in the direction perpendicular (parallel to the [1100] plane) to the basal plane to about 10μm in thickness to make it plates and both surfaces were mirror polished. Next, this plate shape sample was filled in the high purity alumina crucible and 30 minutes of heat treatment was performed at 1400°C in air. Figure 2(b) is a TEM bright field image of the sample, to which heat treatment like this was performed, viewed from the [1100] direction perpendicular to the (1100) plane. In this image, a lot of dot contrasts are observed; they correspond to the dislocations arranged perpendicular to the paper plane. Figure 2(c) is a TEM bright field image of the sample viewed from the direction ([4401] direction) slightly tilted around the [1120] rotation axis in the same area in (b). It is recognized that the contrast, observed as dots in (b), is the linearly arranged dislocations. Linearization of dislocations by this heat treatment is believed to be caused by the strong image force due to the surface effect.
3.2 High resolution TEM characterization of the dislocation core structure

As for the basal slip, Kronberg first predicted\textsuperscript{23} that a basal dislocation with \( b = 1/3(1120) \) would dissociate into two half partial dislocations by glide as the following reaction:

\[
\frac{1}{3}(1120) \rightarrow \frac{1}{3}(10\bar{1}0) + \frac{1}{3}(01\bar{1}0) . \tag{1}
\]

But the dissociation on the (0001) basal plane caused by glide has not been observed yet. As pointed out by Phillips et al.,\textsuperscript{24,25} the separation distance by the glide dissociation is considered to be too narrow to distinguish by the conventional electron microscopy techniques. On the other hand, Lagerlöf et al.\textsuperscript{25} confirmed the dissociation of a basal dislocation by self-climb using the weak-beam dark field technique. According to their results, a basal dislocation dissociated into the two partials with \( b_1 = 1/3(10\bar{1}0) \) and \( b_2 = 1/3(01\bar{1}0) \) perpendicularly to the (0001) slip plane. But it remains unclear whether the glide dissociation takes place or not since the separation distance between the two partials is seemingly very narrow. Thus, it is needed to reveal the core structure of a basal dislocation in order to clarify this point. Meanwhile, high-resolution transmission electron microscopy (HRTEM) is one of the most powerful techniques to analyze microstructure at atomistic level. Here, a basal dislocation was directly observed by HRTEM from the direction parallel to the dislocation line in order to clarify the atomic structure of the basal dislocation in sapphire.

Figure 3(a) shows a typical HRTEM image around the basal dislocation observed along the [\( 1\bar{1}00 \)] parallel to the dislocation line.\textsuperscript{22} It is noted that the two disconnected contrasts clearly appeared on the HRTEM image, which implies that the dislocation dissociated into two partial dislocations. Burgers circuits are schematically described around each partial and also two partials. Figure 3(b) shows a schematic of the atomic arrangement projected along the [0001] direction of \( \alpha\)-Al\(_2\)O\(_3\), in which large open circles, small fill circles and small open circles represent oxygen atoms, Al atoms and Al vacancies, respectively. The HRTEM image in (a) is observed along the heavy arrow in (b). The size of the perfect dislocation thus corresponds to the fine black arrow perpendicular to the [\( 11\bar{0}0 \)] observation direction ([\( 1\bar{1}20 \)] direction), and the size of partials correspond to the two gray arrows tilted by 30° from the [\( 1\bar{1}20 \)] direction. In the figure (a), the two circuits have clear lattice discontinuity in their centers, and the edge segment on the (1100) plane is estimated to be 1/6[\( 1\bar{1}20 \)]. Here, the \( b_1 \) and \( b_2 \) of the two half partials, which were produced from a basal dislocation according to the reaction (1), also have the edge segment of 1/6[\( 1\bar{1}20 \)] on the (1100) plane. Thus, it was reconfirmed that the basal dislocation dissociate into two half partials, as reported in the past.\textsuperscript{24,25} The two partials separate with a distance of 4.7 nm along the [0001] in the Fig. 3(a).\textsuperscript{22} Defining ‘the dissociation by self-climb’ as the dissociation perpendicular to the (0001) slip plane, which can be caused by the climbing with diffusion, it can be said that the basal dislocation dissociated by self-climb as suggested in the past. On the other hand, in general, ‘the dissociation by glide’ means the dissociation on the slip plane by dislocation glide. Here, the two partials were located at the nearest neighbor position along the [\( 1\bar{1}20 \)] direction, which is parallel to the (0001) slip plane. That is, the dissociation by glide isn’t developed in the basal dislocation. Thus, it can be concluded that the dissociation by self-climb is developed but the dissociation by glide is not in a basal dislocation, on the relaxed condition where compressive stresses are removed and the motion of the dislocation is ceased. In addition, they were located adjacent each other along the [\( 1\bar{1}20 \)]. Here, the spacing between (\( 1\bar{1}20 \)) layers is 0.235 nm, which corresponds to the projected spacing of cation or anion sublattice along the [\( 1\bar{1}20 \)] direction. Thus, the two half partials are located at the nearest neighbor position along the [\( 1\bar{1}20 \)], and in addition no stacking fault is formed if the two partials exists on the same (0001) plane.
3.3 Fabrication of metal nanowire and its electric properties

By above described two step deformation and heat treatment, it was become possible to arrange straight dislocations with high density into sapphire. Since it is expected that the dislocation itself shows different properties from the ones of the bulk, the dislocation can be regarded as nanowire already as well. Here, moreover, for example, by diffusing heterogeneous metals along the dislocation, nanowires composed of the doped metal elements are possible to be obtained. Around the dislocation, a strain field exists; under its influence, it is known that the phenomena such as Cottrell effect which induces segregation of solute elements, and the pipe diffusion,26,27) with which the diffusion rate becomes faster than the one in the bulk, occurs. Utilizing the characteristics of dislocation like these, it is possible to diffuse various metals along the dislocation. We have tried diffusion of various metal elements; here, the results of the metal Ti diffusion are introduced. In the meantime, it is reported that the pipe diffusion of Ti along the dislocation in sapphire is $10^6$ to $10^7$ times faster than the one in the bulk.27)

Figure 4 shows a schematic of the method to diffuse Ti element along the dislocations.9) At first, as shown in Fig. 4(a), a film of metal Ti was deposited by the vacuum deposition method on the plane (in this case, the (1100) plane), into which dislocation lines are penetrated. Next, in order to form the Ti rich nanowire like the one in Fig. 4(b) by diffusing Ti along the dislocation, 2 hours of heat treatment was performed at 1400°C in an Ar atmosphere to the sample with which the metal film was deposited. After the heat treatment, remained Ti on the surface was removed by such as mechanical polishing and the sapphire substructure was observed with the TEM. The result was that it showed almost the same dislocation substructure to the ones in Fig. 2(b), (c) and there were no drastic change in the distribution or the arrangement of dislocations by this heat treatment.

Figure 5(a)(b) show EDS spectra obtained from a basal dislocation and an area 20 nm off the dislocation in the plate, respectively, after the infiltration process.9) It should be noteworthy that the Ti Kα-peak was clearly observed in Fig. 5(a), whereas that was not found in Fig. 5(b). Figure 5(c) also shows distribution of elements taken across the dislocation by line EDS analyses. It can be seen that Ti atoms were localized in a region of about 5 nanometers around the dislocation. Moreover, the amount of Al decreased in that region in an opposite way of Ti. This indicates that Ti atoms infiltrated along the dislocations from the plate surface, and that Ti atoms intensely segregated throughout the dislocation lines. That is, nanometer-sized wires enriched by Ti, namely, “Ti-enriched nano-wires”, were formed along high density of unidirectional dislocations in the sapphire plate. The striking infiltration behavior of Ti atoms along the dislocations would be attributed to the rapid pipe-diffusion in sapphire, which was found to be faster by $10^6$~$10^7$ times than bulk-diffusion.27) In addition, ionic radii of Ti ions (such as Ti$^{3+}$ or Ti$^{4+}$) are by 30%~50% larger than that of Al$^{3+}$ ions, depending on the charge states of Ti.28) This difference in
ionic size likely gives rise to an attractive interaction between Ti and the dislocation due to Cottrell effect. In this case, it is expected that Ti ions are present as substitutional solutes for Al, not as interstitial solutes, because Ti ions with the larger ionic size are more favourably located at the Al sites. As a result, Ti infiltrates into a crystal along the dislocation and remains in the vicinity of it. To investigate electronic states of Ti in the nano-wires, electron-energy loss near edge structures (ELNES) of Ti L_{2,3}-edge were also measured as shown in Fig. 5(d). As a reference, near-edge X-ray absorption fine structure (NEXAFS) of Ti L_{2,3}-edge in TiO_{2} and TiO_{2}^{29} are displayed in Fig. 5(e). The ELNES spectrum is comparable with those of NEXAFS because both spectra reflect local atomic structures and partial density of states for Ti in respective materials. As seen in the figures, spectrum from the Ti-enriched nano-wire shows four separated peaks, which was similar to that of TiO_{2} rather than Ti_{2}O_{3}. This means that valence state of Ti in the nano-wire is closely similar to Ti^{4+} in TiO_{2}. Here, TiO_{2} itself is an insulator (< 10^{-10} \Omega^{-1} \text{cm}^{-1}). However, Ti in the nano-wires should be slightly reduced to form TiO_{2-\delta} like bonding state since the heat-treatment for infiltration of Ti was conducted in a reduced atmosphere (1400°C in Ar).\textsuperscript{30} Accordingly, the nano-wires are considered to include both Ti^{4+} and a small amount of Ti^{3+}. In addition, TiO_{2-\delta} containing Ti^{3+} ion is known to exhibit electronic conduction, which can be classified into semiconductors. Thus, the present Ti-enriched nano-wires could exhibit unusual electric conduction even inside sapphire insulator.

In order to evaluate the electric characteristics of the above described nanowire, evaluation of conductivity was performed using the contact current mode of the AFM. During probe scanning, the measurement was performed applying the voltage of 1 to 10 V. Figure 6 shows the current image of the scanning in the case of applied voltage of 10 V and the measurement region of 5 \mu m × 5 \mu m. From this image, it is recognized that the current value rapidly increases discretely at the particular site only. Since this distribution and density are almost equal to the introduced dislocation distribution, it is suggested that current is flowing along these nanowires. Furthermore, by rough estimate of current, it has been revealed that the current flowing along the nanowires reached as much as 10^{13} times or more of the one in sapphire. In this way, it has become possible to form conductive nanowires with high density arranged linearly in sapphire, an insulator. Despite that innumerable nanowires are introduced in this sample, it is still provided with perfect transparency equivalent to the one of sapphire as well. Applications as a new functional device is therefore expected in the future.

4. Dislocation Control in YSZ and Ionic Conductivity

Cubic zirconia has a fluorite type structure, and has the [001]\{110\} slip system and the [111]\{110\} slip system, in which the multiple slip can easily occur.\textsuperscript{31} For introducing the straightly aligned dislocations, it is required to make only the single slip active and suppress the secondary slip. The main slip system of the cubic YSZ used in this study is the [001]\{110\} system. There is a possibility that the multiple slip becomes active if it is compressed in the direction with the Schmidt factor of 0.5. Therefore, the compression axis was slightly tilted to be the (112) direction, and it was selected as a compression axis.\textsuperscript{14,15} In this case, although the compression axis is tilted by 55° against the [001] plane and its Schmidt factor is 0.47, the single slip is expected in the beginnings of deformation. In this study, the dislocation density and its arrangement were controlled by compression deformation tests systematically at various temperatures and at different strain rates. Figure 7 shows the microstructure with strain amount of (a) 1% and (b) 10% in the case where deformation was made at the temperature of 1300°C at the strain rate of 8 × 10^{-6} s^{-1}, respectively.\textsuperscript{14,15} The observations were made along the [110] direction, in which the
electron was transmitted from the direction parallel to the slip plane. If the direction of the incident beam and the dislocation line are parallel, dislocation should be observed as like black dots in the figure. As shown in (a), it is recognized that almost all dislocations are arranged upright in case of the strain amount of 1%. On the other hand, in case of applying 10% deformation, the dislocations themselves intertwine each other because of the activity of the secondary slip system. Here, the dislocation densities of the samples with the strain amount of 1% and 10% were $8 \times 10^{12}$/$\text{cm}^2$ and $1.2 \times 10^{13}$/$\text{cm}^2$, respectively. In addition, as a result of the $g \cdot b$ analysis, it has been confirmed that all the dislocation of the present samples with the strain amount of 1% has the Burgers vector of $b = a/2[110]$.

Recently, the YSZ is paid attention as a conductor of oxygen ions. If the fast pipe diffusion along the dislocations occurs, the ion conductance should be increased along the dislocation line in the sample, in which high density dislocations were introduced. Then, the ionic conductance in the parallel direction (the $[1\bar{1}0]$ direction) to the introduced dislocation was measured at various temperatures using an impedance analyzer. Figure 8 is a diagram of the ionic conductance plotted against the deformation strain amount. In this way, it was revealed that the ionic conductance of the deformed sample actually increases with the increase in the strain amount at every temperature. For example, the ionic conductance of the sample with the strain amount of 1% at $600^\circ\text{C}$ increases about 10% compared with the one of the nondeformed sample. This result suggests that the ionic conductance is possible to be improved if the high density dislocations can be introduced.

We examine how highly the improvement in ionic conductance can be expected based on these experimental results. Since the dislocation is aligned almost straight with the sample with the strain amount of 1%, we take this sample as a model for the present evaluation. In case where the dislocations are straight and they penetrate the sample, the diffusion path of oxygen ions can be evaluated by dividing it into the dislocation part and the bulk part as shown in the inset of Fig. 9. Accordingly, the total resistance $R_{\text{total}}$ of the sample is regarded as a parallel circuit of the resistance $R_{\text{bulk}}$ of the bulk and the resistance $R_{\text{dis}}$ of the dislocation. On the assumption of the parallel circuit, by substituting the result obtained by the experiment, $\frac{\sigma_{\text{dis}}}{\sigma_{\text{bulk}}}$, the ratio of the ionic conductance of the one of the dislocation to the one of the bulk, can be calculated as a function of $r$, an effective radius of the dislocation core. Figure 9 shows the result of the calculation. It is recognized that as $r$ decreases, $\frac{\sigma_{\text{dis}}}{\sigma_{\text{bulk}}}$ increases. From the result, although the ionic conductance along the dislocation line depends on $r$, it can be estimated to be as large as $10^2$ to $10^4$ times compared with the bulk one. Using these results, a trial calculation was made regarding the relationship between the dislocation density and ionic conductance. With the dislocation density of about $10^2$ indicated this time, it only improved ionic conductance of the bulk by about 10%. However, it is suggested that there is a possibility that if the dislocation density of about $10^3$ can be introduced for example, 10 to 20 times, and if with the dislocation density of about $10^4$, 100 times or more of the ionic conductance of the bulk one can be achieved.

5. Summary

In this review paper, the method to introduce high density dislocations in oxide crystals were shown. Sapphire and YSZ single crystal were uses as model systems, and high density dislocations were introduced by high-temperature plastic deformation. These dislocations were modified with and without secondary elements to form nanowires in the respective single crystals. It was found that thus fabricated nanowires enhanced electron and ion conductivities in sapphire and YSZ crystal, respectively. If it becomes possible to form a low-dimensional structure inside any crystals with high density, since the handling also becomes easy, there is a potential for various applications as functional devices. Although the techniques introduced here are in the incunabula of the study, they are one of the effective methods, which can introduce high density of aligned nanowires into the crystal.
Acknowledgements

The author would like to acknowledge the collaboration with Drs. A. Nakamura, K. Otsuka, A. Kuwabara, T. Nakagawa, N. Shibata, T. Mizoguchi, K. Matsunaga and T. Yamamoto. A part of this work was supported by the Grants-in-Aid for Scientific Research on Priority Areas “Nano Materials Science for Atomic-scale Modification” (No. 19053001) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

REFERENCES