RAPID PUBLICATION

Hall Effects of Rutile Crystals Grown by the Floating Zone Method

Shin Tsunekawa*, Hiroshi Machida*[†], Masashi Suezawa*
and Tsuguo Fukuda*

Temperature dependence and anisotropy of Hall effects of as-grown TiO_x ($x \sim 2$) crystals grown by the floating zone method are measured by conventional method in the temperature range of 20–330 K. The results reveal that these crystals have better crystallinity and homogeneity than TiO_x ($x \sim 2$) crystals grown by the flame fusion method which were annealed for a long time at high and lower temperatures to reduce subboundaries and oxygen vacancy, respectively.

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I. Introduction

There have existed many studies^{(1)–(7)} on semiconducting properties of slightly reduced rutile crystals. However, the research has not been completed yet, because the difference of the results among researchers remarkably depends on the difference of heat treatments after the growth with the flame fusion (FF) method, usually called Verneuil method. The crystals grown by FF method should be first well-annealed in air above 2000 K followed by furnace cool to room temperature in order to diminish the distortion and the number of grains which are induced due to large growing temperature gradients, and then well-oxidized for a week near 1100 K in order to cancel the heavy reduction. These have been slightly reduced again in order to measure Hall effects.

Recently, high quality single crystals have been grown by the floating zone (FZ) method⁽⁸⁾⁽⁹⁾. The crystals have density of etch pit due to grain boundaries, about $7 \times 10^2 \text{ mm}^{-2}$, and spatial fluctuation of refractive index due to compositional dispersion, about 3×10^{-6} in an as-grown state⁽⁹⁾. Both figures are lower than those of crystals grown by FF method, well-annealed and well-oxidized. Moreover, they have suitable electric conductivity to measure Hall effects. Therefore, semiconducting properties due to interstitial and/or defect levels of these crystals are investigated even without heat treatments. For usual use such as a polarizer and a prism in optical devices, where the interstitials and/or defects are harmful, these crystals do not need anneals above 2000 K which are necessary for Verneuil crystals, but require only oxidation for two or three days near 1100 K and

cooled down to room temperature in 40 h in order to change the color from blue to achromatic. It is expected that new optical usage of moderately reduced crystals might be created, if the mechanism of semiconductivity in TiO_x ($x \sim 2$) becomes entirely clear.

In this report, the temperature dependences and the anisotropies of Hall coefficient and electrical resistivity of the crystals grown by FZ method are shown, as a first step for clarification of the mechanism.

II. Experimental

Rutile crystals grown by FZ method were obtained by the same method previously reported^{(8)–(10)}: Fine powder of TiO_2 (99.98%) was hydrostatically pressed at 10^2 MPa and then fired in air at 1673 K. The sintered rods were melted in a bi-ellipsoidal halogen-lamp image furnace and grown up single crystals in the size of about 10 mm in diameter and 100 mm in length. The growth rate was 5 mm/h and a gas mixture of 97% argon and 3% oxygen

Fig. 1 Bridge-shaped sample of 1 mm thick. Measurements are performed under the current along the direction of the largest dimensions and the magnetic field along the direction of the thickness.

* Institute for Materials Research, Tohoku University, Katahira, Sendai 980, Japan.

[†] Present address: Chichibu Cement Co., 5310 Mikajiri, Kumagaya, Saitama 360, Japan.

was continually passed through the growth chamber at a rate of $1.2 \times 10^{-1} \text{ m}^3/\text{h}$. It has been found that there appear subgrains under the growth condition with a mixed gas of more concentrated oxygen.

Measurements of Hall coefficient and electrical resistivity were made for these as-grown crystals along the a and c directions in the range of 20 to 330 K. The samples were cut from the periphery and center of the crystal rods, and formed in a bridge shape (see Fig. 1) by ultrasonic machining. Ohmic contacts were attained by "cerasolzer #246" (Asahi Glass Co.) electrodes using an ultrasonic soldering iron (Model USM-III, Kuroda Electric Co.). Measurements were carried out under constant currents of 4 mA near room temperature and 1 mA at lower temperatures. The magnitude of the applied magnetic field was varied between 0 and 0.73 T.

III. Results and Discussion

Temperature dependences of Hall coefficient, R_H , for as-grown crystals with the largest dimensions along the a and c directions are shown in Fig. 2, where the coefficients were negative in all the temperature range. A maximum of the coefficient and its anisotropy with a factor of 3.5 are clearly represented only around 100 K. Becker and Hosler⁽³⁾ reported that the ratio of $R_{H//c}/R_{H//a}$ (=the factor of anisotropy) is the largest value=2 at 110 K. The change of the factor from 2 to 3.5 represents a clear improvement in single-crystallinity, because speaking generally, anisotropy is diminished when crystal orientation is confused. However, it is difficult to understand the observed maximum and anisotropy of R_H by one-band model, because in that case the values of R_H should be a function of only the carrier density, and the

Fig. 2 Temperature dependence of Hall coefficients of as-grown crystals by FZ method obtained from the center ($\circ$) and periphery ($+$) with the magnetic field $H//c$ and the current $J//a$, and from the center ($\bullet$) and periphery ($\times$) with $H//a$ and $J//c$.

Fig. 3 Temperature dependence of electrical resistivities of as-grown crystals by FZ method obtained from the center ($\circ$) and periphery ($+$) with the current $J//a$, and from the center ($\bullet$) and periphery ($\times$) with $J//c$.

factor of anisotropy depend only on the effective mass ratios corresponding to the curvatures of the band. This problem will be clarified through further analyses for rutile crystals oxidized or more reduced after the growth with FZ method in the near future.

Temperature dependences of electrical resistivity, ρ , for the same samples are shown in Fig. 3, where the anisotropy with a factor of 3 to 4 is exhibited in the whole temperature range. This is easily understood to be due to the anisotropy of electron mobilities. From Figs. 2 and 3, it is found that there exists only a little difference in the electrical properties between the center and periphery of the present as-grown crystals. This fact assures the homogeneity of composition in the crystals.

As shown in Fig. 4, the temperature dependences of the Hall coefficient and electrical resistivity obtained by the present authors are similar to those by Hasinguti *et al.*,⁽⁷⁾ except for about one order higher magnitude in the values of R_H and ρ than theirs. This suggests that the carrier density of the present sample is about one order of magnitude lower than that of Hasinguti *et al.*'s. Their samples were obtained from the crystals grown by FF method, annealed in air at the rate of 40 K/h from 2123 K to room temperature, oxidized for a week at 1123 K, cooled down to room temperature in 10 h, and reduced in a vacuum of about 3×10^{-3} Pa for 300 h in many cases between 1173 and 1573 K. Their measurement was performed under the current only along the c direction. For comparison, temperature dependences of another representative data⁽²⁾ are also illustrated. It is thought from

Fig. 4 Temperature dependences of Hall coefficient with $H//a$ and electrical resistivity with $J//c$ obtained by Hasiguti *et al.*⁽⁷⁾ for the reduced crystals after the growth with FF method: Oxygen deficient densities of 3.7×10^{24} (○), 4.5×10^{24} (Δ), 5.0×10^{24} (□), 7.9×10^{24} (●), 8.5×10^{24} (▽), 1.0×10^{25} (⊖), and 1.3×10^{25} (⊕) in the unit of m^{-3} . Those with $H//c$ and/or $J//a$ obtained by Frederikse⁽²⁾ are illustrated: Heat treatments of 1 h at 1323 K (—) and of 8 h at 1273 K (---) in a vacuum of about 1×10^{-1} Pa after the growth with FF method. Our results with $H//a$ and/or $J//c$, and $H//c$ and/or $J//a$ are represented by thick lines and thin lines, respectively.

these comparison that the large difference in the temperature dependences is due to the different reduction time and/or temperature. It is concluded that the present as-grown crystals show better quality than the crystals suffered long duration anneals and oxidations in air, and reduced in a vacuum for a long time after the growth with FF method, because the present Hall coefficients and their anisotropy are larger than the other in almost all the temperature range, and above all, such long time and high temperature anneals and oxidations several times cause a fatal contamination and produce the samples which include various degree of oxidation.

IV. Conclusion

It was shown that the temperature dependences of Hall coefficient and resistivity in as-grown rutile crystals produced by FZ method are superior to Hasiguti *et al.*'s results which have been so far most reliable data of the crystals grown by FF method, annealed at high temperature, oxidized and reduced for a very long time. The present crystals are expected to contribute much to the basic knowledge on unsolved semiconducting mechanism in oxygen deficient materials, because they show good crystallinity in large anisotropy and homogeneity in small dispersion of Hall coefficient and resistivity even in an as-grown state.

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