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研究課題名（和文）電子線誘起電流法によってSrTiO3結晶中の転位の電気特性評価

研究課題名（英文）EBIC study of dislocations in SrTiO3

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研究成果の概要（和文）：電子材料の開発では、新規材料の導入で、従来素子の高性能化や新たな動作特性の探求がなされている。抵抗変化型メモリの材料として、チタン酸ストロンチウム（STO）が注目され。STOは、シリコンに比べて欠陥が多く、期待していた物性値が得られていないのが現状である。一方で、結晶欠陥が機能に大きく関与しているという報告がある。本研究では、STO中の拡張欠陥が、どのように電気的性質に関与しているかを研究する。電子線誘起電流（EBIC）法によって試料内の転位密度と電気特性を調べ、メモリ作用との関連を明らかにする。更に、電子顕微鏡観察によって転位の性格を決定する。

研究成果の概要（英文）：Material innovation on new devices is indispensable for the advancement of semiconductor technology. With the rising interests in resistance switchable oxides as promising candidates for next generation resistance random access memory, much attention has been paid to investigate the resistance switching in strontium titanate (STO). Compared with silicon, a higher density of dislocations is introduced in STO. Crystallographic defects such as dislocations may play an important role in the resistance switching phenomenon. In this work, the electrical activities of dislocations have been studied by electron-beam-induced current technique. The nature of dislocations has been studied by using transmission electron microscopy. These data suggested that not all the dislocations contribute to the switching phenomenon. The active dislocations for resistance switching were discussed.

研究分野：半導体材料・電子顕微鏡

キーワード：SrTiO3　Resistive switching　Dislocation　EBIC　TEM

１．研究開始当初の背景

Resistive switchable oxides are promising candidates for nonvolatile resistive random access memory. Several models have been brought forward to explain the switching mechanism, including the interface model concerning the electron charging/discharging of trapping states and the filament model describing oxygen transport along conduction paths.

It has been considered that crystallographic defects such as dislocations may play an important role in the resistance switching phenomenon. While some suggested that dislocation is not a limiting factor for resistive switching devices.

On the other hand, the ratio between high and low resistance states was sensitive to Nb concentration, which in turn may cause the difference in defect density and electrical property. Hence, the effect of doping level should also be taken into account.

２．研究の目的

Until now there is no extensive study on the electrical activities of dislocations in $SrTiO_3$.The first target is to clarify the role of dislocation on resistive switching in $SrTiO_3$. For this purpose, electron-beam-induced current (EBIC) technique has been used for imaging electrically active dislocations.

Since either oxygen vacancies or dislocations may act for the switching, it is necessary to separate these impacts with respect to the variation of Nb doping concentrations.

３．研究の方法

Nb-doped $SrTiO_3$ single crystals grown by Verneuil process were used in this study. For the electrical test, Schottky contacts on as-prepared and air-annealed $SrTiO_3$ wafers have been fabricated by e-beam deposition of Pt.

Note for EBIC measurement, annealed samples showed better surface condition. And for most EBIC observation, the samples were annealed at 1000 °C in air for 2h to obtain an atomically flat surface before the electrodes were deposited. EBIC observation was performed by a JEOL 7600F field-emission scanning electron microscope at an accelerating voltage of 7 kV. Current-voltage (*I-V*) testing was performed by a Keithley S4200 semiconductor characterization system attached to the microscope. A kleindiek micromanipulator installed inside the chamber was used for the electrical connections of *I-V* and EBIC measurements.

The characters of dislocations were explored based on chemical etching and transmission electron microscope (TEM). Dislocations were delineated by chemical etching with aqua regia. The dislocation etch pits were imaged by the same scanning electron microscope. For TEM observation, foil specimens were prepared by ion thinning method. The specimens were observed using a Topcon EM-002BF microscope at an accelerating voltage of 200 kV. The character of dislocations was determined by $g \cdot b$ analysis.

４．研究成果

Part-I　The role of dislocations

Figure 1 showed the EBIC images of dislocations in a $Pt/SrTiO_3$ Schottky taken at zero bias and -2 V. The $SrTiO_3$ wafer was <111> oriented with Nb of 0.01wt%. Crystal orientations were indicated by the Thompson tetrahedron in Fig. 1(a).

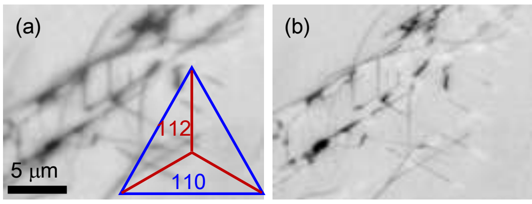

Fig.1. EBIC images of dislocations in $SrTiO_3$ at zero bias (a) and at -2 V (b). All the dislocations exhibited dark EBIC contrast at zero bias. When applying bias, bright contrast appeared in the vicinity of some straight lines with the directions along <112>.

Dark lines (either straight or curved) and individual dark spots were observed. These lines and spots are attributed to dislocations. The dislocations exhibited dark EBIC contrast at zero bias, indicating that they acted as recombination centers for minority carriers. The straight lines along <112> showed weak contrasts of about 10-20% while the curved lines and spots showed medium contrasts of about 20-30%. The tangled dislocations had strong contrasts of up to 50%. When applying bias, bright contrast (indicated by the arrow) appeared around the straight lines along <112>. While there was no bright contrast near the curved lines, spots and tangles. The narrowing of line contrast under the negative bias indicated that the carriers drift motion suppressed the carrier diffusion and recombination.

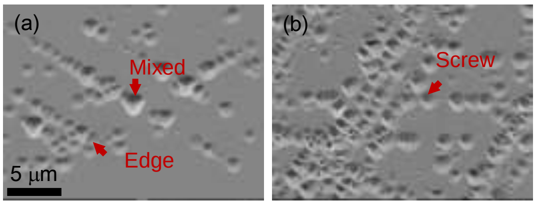

Fig. 2. SE images of dislocation etch pits in $SrTiO_3$ etched with aqua regia. (a) The dislocations array along <112> and (b) The dislocations array along <110>. Edge, screw and mixed types co-existed.

Figure 2 showed the secondary electron images of dislocation etch pits in $(111)SrTiO_3$. There were regular etch pits arrayed along either <112> or close to <110> directions. These dislocation arrays were categorized as the slip systems of

{110}<110>. The regular arrays of dislocation etch pits along <112> corresponded well with the straight lines along <112> in the EBIC images.
The shape of etch pits can give hints of the dislocation type. There existed three kinds of dislocation pits. The first kind was a shallow pit with a wide flat bottom, indicating the edge dislocation. The second was a spiral triangular pit with a small flat bottom, indicating the mixed type. The third was an inclined spiral pit with a sharp bottom, indicating the screw type. Most of the etch pits arrayed along <112> were the mixed and edge types. Considering the symmetry of the etch pits, the mixed type was equilateral triangle, suggesting that the dislocations were perpendicular to the surface and the line direction is parallel to [111]. Further TEM observation has confirmed it.

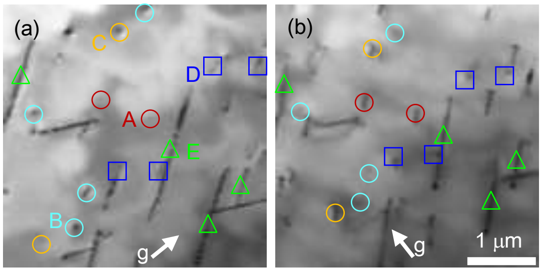

Fig. 3 Bright-field TEM images of dislocations in $SrTiO_3$ under two-beam conditions with zone axes of [111] (a) and [110] (b). Diffraction vector is indicated by *g*.

Figure 3 showed the bright-field TEM images of dislocations in $SrTiO_3$ taken under two-beam conditions. Diffraction vector *g* was also indicated. Typical dislocations (denoted as A to E) were selected for the analysis. It was found that almost all the dislocations have Burgers vectors of the <110> type.
According to trace analysis, the dislocation lines of A, B, and C were parallel to [111], D parallel to [110], and E parallel to [001]. Dislocations D and E were of screw and edge type, respectively. Although dislocations A, B, and C have the same line directions, A and B belonged to the mixed type, while C was the edge type. This finding corresponded with the etching results shown in Fig. 3, in which etch pits of the mixed and edge types co-existed.

In summary, the EBIC, etching and TEM results suggested that dislocations in $SrTiO_3$ are associated with different defect levels depending on their characters. There Dislocations with line vector of [111] tend to have shallow levels and relate to the resistance switching. This first finding has been published in Appl. Phys. Lett. in 2015.

Part-II The effect of Nb-doping
On the other hand, we noticed that there existed significant difference in the switching behaviors in differently Nb-doped $SrTiO_3$ samples undergone oxidation process or not. Three kinds of doping levels were compared, i.e., low (0.01wt% Nb), medium (0.05wt% Nb), and high (0.5wt% Nb). It was found that air-annealing could greatly suppress the switching in the samples of low and medium doping, but not work for high doping. It is considered that there exist different key factors for switching depends on the doping level.
It is speculated that both oxygen vacancies and dislocations have important influences on the switching. Oxygen vacancies are dominated for the switching in the low and medium doping samples. While for the high doping, there existed more important factor.
It should be noted that the number and interaction of dislocations increased rapidly under high doping concentration such as 0.5wt%. And EBIC observation suggested that the dislocations in heavily Nb-doped $SrTiO_3$ were quite electrically active and much deeper defect levels were introduced. The presence of high density dislocations and high concentration of Nb atoms, may affect the motion of oxygen vacancies, and thus result in different response to the oxidation process. This work has recently been accepted for the publication in Superlattices and Microstructures. Supplementary study will be carried on to support this hypothesis.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）
〔雑誌論文〕（計 2 件）

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６．研究組織

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